The latest process and challenges of microwave dielectric ceramics based on pseudo phase diagrams

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Abstract: The explosive process of 5G communication evokes the urgent demand of miniaturized and integrated dielectric ceramics filter. It is a pressing need to advance the development of dielectric ceramics utilization of emerging technology to design new materials and understand the polarization mechanism. This review provides the summary of the study of microwave dielectric ceramics (MWDCs) sintered higher than 1000 ℃ from 2010 up to now, with the purpose of taking a broad and historical view of these ceramics and illustrating research directions. To date, researchers endeavor to explain the structure–property relationship of ceramics with multitude of approaches and design a new formula or strategy to obtain excellent microwave dielectric properties. There are variety of factors that impact the permittivity, dielectric loss, and temperature stability of dielectric materials, covering intrinsic and extrinsic factors. Many of these factors are often intertwined, which can complicate new dielectric material discovery and the mechanism investigation. Because of the various ceramics systems, pseudo phase diagram was used to classify the dielectric materials based on the composition. In this review, the ceramics were firstly divided into ternary systems, and then brief description of the experimental probes and complementary theoretical methods that have been used to discern the intrinsic polarization mechanisms and the origin of intrinsic loss was mentioned. Finally, some perspectives on the future outlook for high-temperature MWDCs were offered based on the synthesis method, characterization techniques, and significant theory developments.

Keywords: high-temperature microwave dielectric ceramics (MWDCs); pseudo phase diagram; developments and challenges; composition–structure–property relationship

1 Introduction

Over the past half century, semiconductor integration...
the huge amount and a wide variety of components with different functions are passive devices. The core materials of these components are various types of functional ceramic materials. Microwave dielectric ceramics (MWDCs) are the pivotal component of a passive device, which are mainly used as filters, resonators, RF antennae, frequency discriminators in electronic countermeasures, navigation, radar, home satellite live television receivers, and hand-held mobile phones. The applications of MWDCs in different frequency are directly plotted in Fig. 1. However, the development of microwave ceramics had gone through a sluggish procession because of the lack of suitable materials for dielectric resonator. The discovery of rutile (also known as titanium dioxide ceramics) in the 1970s makes it possible to synthesis dielectric resonator [1]. Various literature has been reported to explore the potential candidates of MWDCs after that, from single oxide, binary oxide, to ternary oxide. According to the data in the Web of Science, over 1000 papers were published about MWDCs around the world after 2000. Figure 2 presents the trend of published papers where more than 30% of investigations belong to China.

To evaluate the dielectric properties of ceramics, the relative permittivity ($\varepsilon_r$), dielectric loss (loss tangent or quality factor ($Q\times f$ value)), and temperature coefficient of resonant frequency ($\tau_f$) are the three pivotal characteristics. As early as in 2006, the direction of development of microwave dielectric materials has been highlighted by Ohsato et al. [2], including high $Q$ and low $\varepsilon_r$ ceramics for millimeter-wave application, high $Q$ and high $\varepsilon_r$ ceramics for base station, and high $\varepsilon_r$ ceramics for miniaturization of mobile phone. Up to now, researchers have explored hundreds of ceramics to enrich the database of MWDCs, but only a dozen of those ceramics with unique properties have been commercially used to fabricate relevant devices because most of the ceramics lack stability or generate large loss in the electronic components. Booming development of millimeter technology and 5G communication have rendered a new round of requirement of MWDCs of low permittivity with a stable dielectric loss in the scope
of frequency up to 100 GHz. Especially, the emergency of COVID-19 makes video conferencing and telecommuting as a daily part in our lives. Consequently, the unprecedented growth of global data volume and huge demand for high data rates urge researchers to search more alternative materials for commercial electronic market. It is also a very significant issue for the industry to yield ceramics with ultra-low permittivity which are suitable for 5G and 6G communication system. However, it is still a “try and error” state in our experiments for discovering materials or optimizing the properties of the reported ceramics. The main difficulty in the development of MWDCs is to understand the fundamental relationship of composition–structure–property and draw general trends throughout the field, after normalizing and comparing the various results. Despite long-term sustained attempts, there is no systematic or comprehensive theory which can provide common guidance in the experiments and drive currently reported ceramics toward commercialization applications.

With the exploration of MWDCs clusters and the development of modern experiment techniques, investigations about MWDCs have been largely scoped by the designs and search for new systems and reoptimizing their properties. It is paramount that an MWDCs candidate has an appropriate dielectric constant, low dielectric loss, and near-zero temperature coefficient of resonant frequency for applications. Generally, to tune the microwave dielectric properties, there are two parts that should be taken into consideration (extrinsic and intrinsic parts). Extrinsic part is usually regarded as the influence originated from the synthesis method and raw materials. MWDCs usually prepare by solid state reaction method, and the sintering conditions directly influence the microstructure and compactness of ceramics, which subsequently affect the microwave dielectric properties. Meanwhile, the selectivity of size distribution, purity, non-stoichiometric ratio, species of different compounds, and pretreatment of raw materials based on their physical and chemical properties are crucial for reaching optimal microwave dielectric properties. For example, the procedures to reduce pores are designed for ceramics containing the volatile element, evolving non-stoichiometric ratio in the chemical formula, and providing the compensation atmosphere of volatile element. The relevant attempts are mostly discussed for the rock salt structure ceramics such as Li2Mg3TiO6. Besides, various synthesis methods, namely sol–gel method, sink plasma sintering method, and high energy ball-milling method are gradually used for preparing the MWDCs, and numbers of studies analyze the discrepancy of microwave dielectric properties obtained with different methods. The intrinsic part stems from anharmonic lattice vibration, which primarily generates large dielectric loss. As yet, there is no technology or theory that could feasibly adjust the anharmonic lattice vibration to reduce dielectric loss. In the experiment, after carefully controlling the sintering conditions and selecting raw materials, the most pragmatic approach to optimize the properties is cation substitution with the consideration of the radii and the electronegativity of cations, contributing to reducing the dielectric loss or modifying the temperature coefficient of resonant frequency. Near-zero temperature coefficient of resonant frequency is also obtained by designing co-exited phase system with introduction of two ceramics with opposite τr values, but the composite ceramics may lead to a poor Q×f value. More recently, the strategy of tri-layer structures of Zn1.01Nb2O6/TiO2/Zn1.01Nb2O6 [3], MgTiO3/TiO2/MgTiO3 [4], and Zn3Nb2O6/TiO2/Zn3Nb2O8 [5] were verified as a method to obtain the temperature-stable ceramics with low dielectric loss.

Currently, the database of MWDCs is enriched by insightful information about the structure and properties, and the growing number of literature converts from description of phenomena to explanation of the theoretical mechanism of the dielectric materials. Thorough and comprehensive investigation of ceramics is gradually presented to estimate the extrinsic and intrinsic influence on the microwave dielectric properties. For instance, the common discussion of polarization mechanism is usually based on the ionic polarization, where the Clausius–Mossotti (C–M) equation is applied to evaluate the discrepancy of theoretical εr and measured εr. The popularization of Rietveld-refinement in the literature supports the analysis of lattice parameters, packing fraction, and chemical bond characteristic obtained by the complex chemical bond theory (P–V–L) theory. Especially, disassembling the crystal into the sum of sample binary compound based on the crystal parameters and coordinate numbers of each ions [6], the investigations about application of P–V–L theory into multi-type structure emerge in abundance. The origin of dielectric loss is quantified by lattice vibrational spectroscopy, and the contribution of each chemical bond to the microwave dielectric
properties is verified by P–V–L theory. For some unique ceramics, researchers bend themselves to exploring the underlying mechanism for the observed phenomenon. The influence of long-range movement of charged defects in the grain and grain boundary was estimated by the impedance analysis, terahertz (THz) time-domain spectroscopy analysis, and the electron paramagnetic resonance spectra, which can explain the defect generation mechanism in doped Li2ZnTi3O8 ceramics. The analysis of disordered–ordered crystal structure evolution and super-lattice in rock salt ceramics and complex perovskite ceramics gives evidence to explain the ultra-low dielectric loss. Both the development of experimental and theoretical method allows us to summarize the relevant experimental probes of different systems and propose the challenges and prospects of MWDCs.

While many great review and perspective articles have been published about MWDCs, they have finished the review by classified MWDCs based on the criteria of sintering temperature, dielectric constant, and crystal structure [1,7–9]. Furthermore, the early works before 2010 are mainly concentrated on the description of phase composition, micrographic images, and variation of microwave dielectric properties. The topic about the MWDCs sintered lower than 950 °C is especially focused owing to the advantages of low-temperature co-fired ceramics (LTCC) technology where this approach guarantees the integration of electronic components. Considering either the timespan or topic covered, the mentioned ceramics, in this review, are all sintered higher than 1000 °C. The LTCC system including ceramics with a few sintering aids, glass–ceramics system, or glass-free system is not referred. To follow the development of new analysis methods, MWDCs, beginning with the first reported properties and upgrading the relevant references after 2010, were included. Additionally, because of so various structures and properties of MWDCs, pseudo phase diagram was used to classify the ceramics according to the composition, which will serve as the basis and link for each pseudo phase diagram of diversity composition. The organization of this review consists of a brief section detailing the phase evolution or structure transformation of oxide ceramics in the designed pseudo phase diagram, and then the chronological experimental probes for a unique system are summarized.

2 Phase diagram

The phase diagram is a visual representation of the phase equilibrium, which defines the composition of multiphase system. It is an efficient and convenient technique to analyze the composition and their proportion, which plays a significant role in guiding the research and exploration of materials to reduce the manpower and material resources effectively. This section provides a broad context by summarizing the ceramics system based on pseudo phase diagram, and all the composition in the following pseudo phase diagram is in molar ratio. The endpoint of each pseudo phase diagram contains more than one component, and the labelled ceramics are the primary system reported by researchers. The summary of investigations in the same general form is listed in detail.

2.1 Silicate and germanate

There is a low εr (< 10) for silicates, owing to the low ionic polarizability of Si4+ and half covalent bond in Si–O. In the binary silicate, the CaSiO3, Mg2SiO4, Zn2SiO4, and Re2SiO5 are the main representatives, where CaSiO3 usually appeared as the crystalized phase in CaO–B2O3–SiO2 glass. Ternary silicate such as diopside-type CaMgSi2O6, melitile-type A2BC2O7 and AB2C2O7 (A = Sr, Ca, Ba; B = Mg, Zn, Co, Mn, Cu), and cuspidine-type Ca3SnSi2O9 were highlighted by researchers, due to the diverse crystal structures in those systems. With the wake of exploration of new ceramics, the germanate gradually occurred as a candidate material with low dielectric loss despite of the expensive cost of GeO2 as raw material. The pseudo phase diagram of the silicate and germanate is presented in Fig. 3, where the primary phases of binary and ternary silicate and germanate are listed in the phase diagram.

2.1.1 Binary silicate ceramics

Synthesis of dense SiO2 ceramic is challengeable because of its complexity in polymorphs and phase transitions. Until 2012, microwave dielectric properties of SiO2 ceramic were reported as εr ≈ 3.81, Q×f value ≈ 80,400 GHz, and τf ≈ −16.1 ppm/℃, sintered at 1650 °C for 3 h [10]. After that, Li et al. [11] illustrated that 0.84SiO2–0.16TiO2 composite ceramics possessed satisfied properties of εr ≈ 5.91, Q×f value ≈ 39,680 GHz, and τf ≈ −4.5 ppm/℃, sintered at 1275 °C for 3 h.
Comparing to the difficulty of preparing compact SiO\textsubscript{2} ceramic, the restriction of preparing dense CaSiO\textsubscript{3} ceramic stemmed from the narrow sintering temperature range of pure CaSiO\textsubscript{3} and the porous microstructure [12]. Commonly, CaSiO\textsubscript{3} was reported as a main phase in the CaO–B\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} glass–ceramic system, which primarily determined the properties. There are two main phases of CaSiO\textsubscript{3}, containing low-temperature wollastonite (\(\alpha\)-CaSiO\textsubscript{3}) and high-temperature pseudo-wollastonite (\(\beta\)-CaSiO\textsubscript{3}). Through a sol–gel method, the microwave dielectric properties of \(\alpha\)-CaSiO\textsubscript{3} are: \(\varepsilon_r \approx 6.69, Q\times f\) value \(\approx 25,398\) GHz, sintered at 1320 °C [13]. In order to improve the microwave dielectric properties, (\(\text{Ca}_{1-x}\text{Mg}_x\text{Si}_2\text{O}_6\)) ceramics with \(x = 0.1, 0.5, 0.9\) were verified as single phases, and properties of \(\varepsilon_r \approx 6.49, Q\times f\) value \(\approx 62,420\) GHz, and \(\tau_f \approx -43.3\) ppm/\textdegree Celsius were obtained when sintered at 1320 °C with \(x = 0.1\) [14]. Besides, the investigation of CaSiO\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3} ceramics revealed that the secondary phases of CaAl\textsubscript{2}SiO\textsubscript{4} and CaAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{6} would deteriorate the microwave dielectric properties with excessive Al\textsubscript{2}O\textsubscript{3} [15,16]. According to Hu et al. [17], the phase transformation of CaSiO\textsubscript{3} was inhibited with the increase of SiO\textsubscript{2} content, and \(\alpha\)-CaSiO\textsubscript{3}–2 wt% Al\textsubscript{2}O\textsubscript{3}–2.5 wt% TiO\textsubscript{2} shows excellent properties of \(\varepsilon_r \approx 7.88, Q\times f\) value \(\approx 24,412\) GHz, and \(\tau_f \approx -0.52\) ppm/\textdegree Celsius [18]. To obtain compact ceramics, SnO\textsubscript{2}-doped \(\alpha\)-CaSiO\textsubscript{3} ceramics with \(\varepsilon_r \approx 9.27, Q\times f\) value \(\approx 53,000\) GHz, and \(\tau_f \approx -52\) ppm/\textdegree Celsius sintered at 1450 °C were reported in a relative density higher than 97% [19].

With a \(Q\times f\) value larger than 100,000 GHz, another class of binary silicate can be written as A\textsubscript{2}SiO\textsubscript{4} (A = Ba, Sr, Ca, Mg, Zn) [20–23]. Forsterite Mg\textsubscript{2}SiO\textsubscript{4} is extensively explored because of its superior microwave dielectric properties (\(\varepsilon_r \approx 7.8, Q\times f\) value \(\approx 240,000\) GHz, and \(\tau_f \approx -67\) ppm/\textdegree Celsius, sintered at 1450–1500 °C) [2,24,25]. Nevertheless, the high sintering temperature and large \(\tau_f\) value inhibit its application. To adjust \(\tau_f\) value, both co-existed phase of Mg\textsubscript{2}SiO\textsubscript{4}–Ca\textsubscript{0.9}Sr\textsubscript{0.1}TiO\textsubscript{3} [26] and Zn\textsubscript{2}SiO\textsubscript{4}–TiO\textsubscript{2} [27] contributed to a near-zero \(\tau_f\) value. Melting CuO could enhance the sintering procession of Zn\textsubscript{2}SiO\textsubscript{4} and the quality factor reached 105,500 GHz when sintered at 1150 °C [28]. Zn-deficient formula was verified valid to suppress the formation of secondary phase in Zn\textsubscript{2}SiO\textsubscript{4} ceramics, and Zn\textsubscript{1.8}SiO\textsubscript{3.8} was estimated with properties of \(\varepsilon_r \approx 6.451, Q\times f\) value \(\approx 102,807\) GHz, and \(\tau_f \approx -32\) ppm/\textdegree Celsius, sintered at 1300 °C [29].

After predicting the permittivity of ZrO\textsubscript{2}–SiO\textsubscript{2}, HfO\textsubscript{2}–SiO\textsubscript{2}, La\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}, and Y\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}, those systems were clarified as an alternative of dynamic random access memory capacitor dielectric materials [30]. The exploration of properties of Sm\textsubscript{2}SiO\textsubscript{5} and Nd\textsubscript{2}SiO\textsubscript{5} ceramics compensated the absence of study on microwave dielectric properties of Re\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}, where the microwave dielectric properties were listed as \(\varepsilon_r \approx 8.44, Q\times f\) value \(\approx 64,000\) GHz, and \(\tau_f \approx -37\) ppm/\textdegree Celsius and \(\varepsilon_r \approx 7.94, Q\times f\) value \(\approx 38,800\) GHz, and \(\tau_f \approx -53\) ppm/\textdegree Celsius with the molar ratio of Re\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} = 1:1.05, respectively [31,32].

2.1.2 Ternary silicate and germanate ceramics

Clinopyroxene-type ABC\textsubscript{2}O\textsubscript{6} (A = Ca; B = Co, Mg, Zn, Fe; C = Si, Ge) materials, akermanite-type A\textsubscript{2}BC\textsubscript{2}O\textsubscript{7} (A = Sr, Ca; B = Mg, Zn, Co, Mn; C = Si, Ge), and meilitite-type A\textsubscript{2}BSi\textsubscript{2}O\textsubscript{7} (A = Sr, Ca; B = Mg, Zn, Co, Mn, Cu) occupied the primary family of ternary silicate ceramics. Increasing attention has been paid for CaMgSi\textsubscript{2}O\textsubscript{6} owing to its low permittivity \(\approx 7.5\), which is suitable to be substrate [14,33–35]. Both the substitution of Zn\textsuperscript{2+}, Co\textsuperscript{2+}, Cu\textsuperscript{2+}, Mn\textsuperscript{2+} for Mg\textsuperscript{2+} and introduction of Sr\textsuperscript{2+} into Ca\textsuperscript{2+} of CaMgSi\textsubscript{2}O\textsubscript{6} were benefit for reducing the dielectric loss. Microstructure with many pores of CaMnSi\textsubscript{2}O\textsubscript{6} was observed by Chen et al. [36], and the effect of porosity on the properties was investigated by spherical-pore model. Akermanite-type A\textsubscript{2}BC\textsubscript{2}O\textsubscript{7} (A = Sr, Ca; B = Mg, Zn, Co, Mn; C = Si, Ge) systems belong to the structure group of \(P4\text{\textsuperscript{2}}\text{\textsuperscript{1}}m\) (113) in tetragonal, while meilitite-type A\textsubscript{2}BC\textsubscript{2}O\textsubscript{7} (A = Ba; B = Co, Zn, Cu, Mg; C = Si, Ge) and AB\textsubscript{2}C\textsubscript{2}O\textsubscript{7} (A = Ba; B = Co, Zn; C = Si, Ge) systems were clarified in monoclinic structure [37–44]. The literature about the effect of structure evolution and chemical bond parameters in A\textsubscript{2}BSi\textsubscript{2}O\textsubscript{7} and AB\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} represented that
the Si–O bond played the significant role in structural stability and dielectric polarization.

The monoclinic Ca₃SnSi₅O₁₃ and Ca₃MgSi₅O₁₃ with space group P2₁/c were investigated to supplement the compound of ternary silicate oxides. Ca₃SnSi₅O₁₃ ceramics were obtained in a wide sintering temperature region from 1400 to 1525 °C, with non-stoichiometric composition (molar ratio of Ca:Si:Sn = 1:2:1) as raw materials [45]. Single phase Ca₃MgSi₅O₁₃ possessed near 99% of the theoretical density after sintered at 1375 °C, with εᵣ ≈ 13.8, Qᵣ/f value ≈ 27,000 GHz, and τᵣ ≈ –62 ppm/°C [46]. Sintering behavior and phase composition of gillespite-structured MCuSi₄O₁₀ (M = Ba, Sr, Ca) ceramics were established by Song et al. [47], and SrCuSi₄O₁₀ possessed microwave dielectric properties of εᵣ ≈ 5.59, Qᵣ/f value ≈ 82,252 GHz, and τᵣ ≈ –41.34 ppm/°C. The first-principles calculation was applied to determine where Ni²⁺ and Li⁺ would occupy in BaAl₁ₓSi₂O₈ ceramics, and the change of bond strength and bond valence were analyzed [48,49].

The unpresented ternary silicate and germanate phase in pseudo phase diagrams are summarized as well in this section. The rare earth-based ternary silicate oxides, such as apatite with general formula Aₓ(MO₄)₆O₂ (A = alkaline earth, rare earth, Pb; M = Si, Ge, P, V), have received much attention since the first application to determine where Ni²⁺ and Li⁺ would occupy in BaAl₁ₓSi₂O₈ ceramics, and the change of bond strength and bond valence were analyzed [48,49].

To improve the densification of lithium apatite LiRe₆(SiO₄)₂O ceramics (Re = La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Tm, Yb, and Y), relative density was higher than 90% for all samples after doping 1 wt% LiF [51]. The microwave dielectric properties of SrRE₂Si₃O₁₃ (RE = La, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, and Y) were in the range of 9–16 for permittivity with the maximum of Qᵣ/f value ≈ 26,000 GHz [52], while the optimal microwave dielectric properties of CaRE₂Si₃O₁₃ (RE = La, Nd, Sm, and Er) were εᵣ ≈ 13.37, Qᵣ/f value ≈ 18,600 GHz, and τᵣ ≈ –17.8 ppm/°C at Re = Er [53].

To obtain new dielectric materials, some researchers pursued materials with the composition containing GeO₂ and Ga₂O₃ and reported microwave dielectric properties of those materials firstly. With inverse spinel structure, Li₅Ga₆O₁₃ was verified as a cubic structure where Li⁺ and Ga³⁺ distributed in the octahedral B site with 1:3 ordering [54]. The large deviation between εᵣ and εᵣnth in Ba₂MGe₁₁O₃₀ (M = Bi, La) was ascribed to the “rattling” effect of cations and the existence of lone pair ions of Bi⁺³ [55]. The different τᵣ values of AĜ₂O₆ (A = Ba, Sr) were ascribed to the distortion of [GeO₄] octahedron where τᵣ values were –44.2 ppm/°C for the former and –11.7 ppm/°C for the later [56]. Normal garnet A₃Y₂Ge₃O₁₂ (A = Ca, Mg) ceramics possessed τᵣ ≈ 120.5 ppm/°C for A = Ca and –40.6 ppm/°C for A = Mg [57]. As doped ions, (Li₀.₃Ga₀.₇)₃⁺ in Mg₂Al₁ₓSi₁₀O₁₈ would obtain the highest Qᵣ/f value of 50,560 GHz [58]. Ca₃Mg₃Si₁₀O₃₂ (M = Yb, Y) ceramics were consistent with the general formula of garnet structure, and those ceramics crystallized as silico-carnotite structure with high-energy ball milling method [59]. The microwave dielectric properties were recorded as εᵣ ≈ 9.2, Qᵣ/f value ≈ 56,400 GHz, and τᵣ ≈ –77.5 ppm/°C and εᵣ ≈ 8.7, Qᵣ/f value ≈ 29,094 GHz, and τᵣ ≈ –76.8 ppm/°C for Ca₃Y₂Si₁₀O₃₂ and Ca₃Y₂Si₁₀O₁₂, respectively. A serial of Ca₃MzGe₃O₁₂ (M = Co, Zn), Ca₃ZrGe₃O₁₂, and Ca₃B₂Ge₆O₁₇ (B = Al, Ga) ceramics were successfully prepared, and the quality factors were higher than that of Ca₃Mg₃Si₁₀O₃₂ [60–62]. Similarly, Sr₁₋ₓBₓGe₂O₁₂ (B = Yb, Ho) were investigated by Li et al. [63] using vibration spectroscopy, and the τᵣ was tuned to near zero with CaTiO₃ ceramics. 0.8YₓMgₓAl₁₂O₃₋ₓTi₂O₅ ceramic sintered at 1475 °C showed a τᵣ = +5.2 ppm/°C, where the co-exsisted phase contained Y₂Ti₂O₇ and TiO₂ along with Y₃MgAl₁₂O₃₋ₓTi₂O₅ phase [64]. Dense MgₓGa₂Ge₆O₁₇ ceramics presented microwave dielectric properties of εᵣ ≈ 9.41, Qᵣ/f value ≈ 133,113 GHz, and τᵣ ≈ –63.54 ppm/°C [65]. Single phase LiₓYSi₄O₁₄ ceramics could be obtained in 1100–1140 °C, and a near-zero τᵣ of (+4.52)–(+8.03) ppm/°C was observed [66]. Furthermore, phase transition from A₂/a to P2₁/a was observed in new silicate in the formula of CaSn₁₋ₓTiₓSiO₅, where the variation of τᵣ values was ascribed to the Sn/TiO₆ octahedral distortion [67]. Secondary phase of SnO₂ and SrSiO₃ appeared at 0.2 ≤ x ≤ 0.45 in Ca₁₋ₓSrₓSn₃O₈ ceramics, which could adjust the positive τᵣ of CaSnSiO₃ to –1.2 ppm/°C [68]. CaSiO₃ and CaSnSiO₃ phases would improve the τᵣ to –7.2 ppm/°C in Caₓ(Hf₁₋ₓSnₓ)SiO₃₁₂ when x = 0.4 [69].

2.2 Niobate and tantalate based on ZnO–Nb₂O₅–TiO₂

There is a large body of niobate and tantalate dielectric ceramics, and the relevant researches highlight the phase evolution, structure transformation, and chemical
bond characteristics. In order to elucidate the influence of undercoordinated sites on the dielectric properties, analysis according to P–V–L theory and vibration spectra is verified as valid approach to understand the relationship of the state of chemical bond with polarization and stability of lattice. Indeed, it seems that researchers could identify the contribution of each chemical bond to dielectric properties by P–V–L theory and infrared reflectivity spectrum. However, reaching general conclusions about the effect of a unique chemical bond or Wycoff site on different properties may be difficult, since the P–V–L theory is just predictable theoretically. The actual dielectric properties of ceramics are still evaluated based on experiments, and thorough, quantitative, and multi-perspective analysis is required. Figure 4 is the phase diagram of the mainly reported niobate and tantalite dielectric ceramics, where the rutile-type, ixiolite-type, and columbite-type structures were obtained after (Zn1/3Nb2/3)4+ was doped into TiO2. The detailed phase division of A0.5B0.5CO4 and the relevant investigations of this binary system are summarized in the following.

2.2.1 Rutile–trirutile/ixiolite/wolframite–columbite type ceramics

Rutile, brookite, and anatase are the three types of TiO2 in nature. TiO2 itself possesses a high permittivity ≈ 100, a low dielectric loss tangent (tan δ) value (6×10−5 at a frequency of 3 GHz), and a high τf value of 450 ppm/℃ [70]. It is valid that TiO2 phase is used to target the aim of near zero τf value as a secondary phase in the system with a negative τf value. Meanwhile, long-term focus has been paid on the structure transformation and property optimization of TiO2 with substitution ions of different physicochemical properties. The cation substitution for Ti4+ can reduce the dielectric loss or tune the τf value, evolving monovalent, divalent, trivalent, tetravalent, or pentavalent cations, and their groups of two cations. Especially, the extensive elaboration of dependence of microwave dielectric properties on the crystal structure of (Zn1/3B2/3)4+Ta1−xO2 (B2+ = Nb, Ta) ceramics was reported by Kim and Kang [71]. The phase relation of ternary system of ZnO–TiO2–Nb2O5 was first discussed in 1992 [72]. It summarized that the solid solution of rutile phase appeared in the range of molar content of (Zn1/3Nb2/3)4+ lower than 58%, ixiolite ZnTiNb2O8 exited in the range of 69%–85%, while columbite solid solution of ZnNb2O6 formed when the content was higher than 93% [73], and the solid solution area of different types was marked with shadow in the pseudo phase diagram in Fig. 4.

Compared with the ongoing report of ZnTiNb2O4, the study of Zn0.15Nb0.3Ti0.55O2 is still rare. Generally, Zn0.15Nb0.3Ti0.55O2 appeared as the secondary phase which would control the dielectric properties of composite ceramics [74–76]. It possessed properties of εr ≈ 94.35, Q×f value ≈ 10,889 GHz, and τf ≈ 353.43 ppm/℃, sintered at 1050 ℃ [71], which was potential to be τf compensator as TiO2. Yang et al. [77] directly added the Zn0.15Nb0.3Ti0.55O2 into Zn0.5Ti0.5NbO4 ceramics, and the structure evolution and chemical bond parameters have been calculated. Zr4+ with the larger radius than Ti4+ was used to dope into Zn0.15Nb0.3Ti1−xZrxO2 [78], where the expansion of bond length and cell volume renders the decline of covalency of all bonds. The decline of bond ionicity was obtained since the shrinking of cell volume and bond length in Zn0.15Nb0.3–xTa1−xZryO2 [79].

The structure of formula A0.5B0.5CO4 can be categorized into four types: wolframite-type A2ZrB2O8 (A = Mn, Zn, Mg, Co, Ni; B = Nb, Ta), rutile-type A0.5Ti0.5NbO4 (A = Ni, Co, Cu), tetragonal trirutile-type A0.5TiSn0.5TaO4 structure (A = Co, Ni, Zn, Mg), and ixiolite-type ZnTiNb2O4. The schematic of those classifications is shown in Fig. 5, and the related investigations of each structure are illustrated in this section. The effects of different cations (Mn, Zn, Mg, Ni, and Co) at A-site of A2ZrB2O8 illustrated that dielectric constant, quality factor, and τf values relied on the ionic polarizability, packing fraction, and B-site octahedral distortions, respectively [80–85]. Among them, MgZrTa2O6 shows the optimal quality factor

![Fig. 4](image-url)
were much different. Ni0.5Ti0.5NbO4 and Cu0.5Ti0.5NbO4 stoichiometric MgZrNb2+

where the microwave dielectric properties were determined via combining the far-infrared and terahertz spectroscopy with P–V–L theory [87–91]. Partial replace of A-site (such as Mg0.5Zn0.5ZrNb2O8 [92], Zn1–xCo0.33ZrNb2O8 [93–95]), Zr-site substitution of Zn(Ti1–xZr)xTa2O4 [96], ZnZr1–xSnxNb2O8 [97,98], doped Nb-site of MgZr(Nb1–xTi1–xZr)xO8 [104] and ZnZr1–xTa2O8 [99,100], ZnZrNb2TaO8 [101], MgZrNb2–x(Sn1/2W1/2)1–xO8 [102], and non-stoichiometric MgZrNb2+xAxO8 [103] provided evidence that relative density, packing fraction, bond valence, and chemical bond characteristics majored the variation of microwave dielectric properties. To adjust the negative $\tau_f$ values, the study about the relationship of TiO2 on MgZrNb2O8 [104] and ZnZrNb2O8 [105] presented that co-exited ceramics would reach near zero $\tau_f$ values. The microwave dielectric properties were $e_{\infty} \approx 43$, $Q\times f$ value $\approx 46,110$ GHz, and $\tau_f \approx –2.5$ ppm/$^\circ$C for 0.63MgZrNb2O8–0.37TiO2 ceramics; $e_{\infty} \approx 44$, $Q\times f$ value $\approx 38,500$ GHz, and $\tau_f \approx –2.4$ ppm/$^\circ$C for 0.3ZnZrNb2O8–0.7TiO2 ceramics. Additionally, literature demonstrated that H3BO3 or B2O3 addictive aids could contribute to densification and improvement of the sintering behavior for ZnZrNb2O8 and MgZrNb2O8 [106–108].

The dielectric properties of A0.5B0.5NbO4 ceramics are much different. Ni0.5Ti0.33NbO4 and Cu0.5Ti0.5NbO4 crystalized in rutile structure presented with positive $\tau_f$ values of 79.1 and 49.2 ppm/$^\circ$C, respectively [109,110]. The characteristic of rutile Co0.5Ti1–xNb2O4 was sought by solid state reaction and sol–gel method [111,112], where the microwave dielectric properties were $e_{\infty} \approx 64$, $Q\times f$ value $\approx 65,300$ GHz, $\tau_f \approx –223.2$ ppm/$^\circ$C and $\epsilon_i \approx 64.19$, $Q\times f$ value $\approx 16,800$ GHz, $\tau_f \approx –66.17$ ppm/$^\circ$C, respectively. In the solid solution of Ni0.5Zn0.5Ti0.5NbO4, the dielectric constant was enhanced from 56.8 to 62.54 [113]. Introduction of CoNb2O6 and Zn0.01NbO6 into CoTiNb2O8 rendered the $Q\times f$ increasing considerably due to the enhanced densification and obtained the $\tau_f$ values of 0.5 and 0 ppm/$^\circ$C, respectively [114,115]. Zhang et al. [116] and Li et al. [117] reported that $\tau_f$ value would shift from positive to negative after Zr substitution in CoTi1–xZr,xNb2O8, where the $\tau_f$ value was correlated with oxygen octahedral distortion and B-site bond valence. Superlattice diffraction peak which is relevant with cation ordering was observed in Co0.5Ti0.5Sn0.5Nb2O4 ceramics, contributing to the augment of $Q\times f$ value [118].

The trirutile-type structure was observed in some tantalates, antimonates, and bismuthates. This crystal structure was built by ordering octahedral cations along c-axis, which possessed three times c-axis of rutile-type one [119,120]. Currently, Co0.5Ti0.5TaO4 [121], NiTiTa2O6 [122], Co0.5Zr0.5TaO4 [90], NiSnTa2O8 [123] were reported as trirutile-type structure. Among them, NiSnTa2O8 showed a near zero $\tau_f$ value ($\epsilon_i \approx 21.04$, $Q\times f$ value $\approx 31,328$ GHz, and $\tau_f \approx –2.63$ ppm/$^\circ$C).

Ixiolite phase ZnTiNb2O8 is a fully disordered α-PbO2 structure, where Zn/Ti/Nb ions statistically occupied the octahedral cation sites [124]. Up to now, numbers of substitution on ZnTiNb2O8 have been reported, such as Co [125], Mg [74], Ca [126], Sn [127], Zr [128], and Ta [129–131]. The crystal structure refinement and Raman spectrum study of ZnTiNb2O8, together with the mode assignment were completed by Liao and Li [132]. In the ZnO–Nb2O5–TiO2 (1 ≤ x ≤ 2) system, ceramics were composed of Zn0.17Ti0.33Nb0.5O2 and ZnTiNb2O8 when x ≥ 1.8 [133]. Using the effective

\[ A_{0.5}B_{0.5}CO_4 \]

**Fig. 5** Schematic of classification of $A_{0.5}B_{0.5}CO_4$. 

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route of sintering reaction for ZnNb$_2$O$_6$ and TiO$_2$ nano powders, a superior property of ZnTiNb$_2$O$_6$ was achieved compared with that prepared by solid-state method [134]. Dielectric constant and dielectric loss were evaluated in microwave and THz range in Al$_{0.5}$Nb$_{0.5}$ doped into ZnTiNb$_2$O$_6$, where the results indicated the negligible shift of dielectric constant in those frequencies, as shown in Fig. 6 [135]. Furthermore, ixiolite MgTiNb$_2$O$_8$ prepared by aqueous sol–gel process and then sintered at 1000 °C showed $\varepsilon_r \approx 33.8$, $Q\times f$ value $\approx$ 26,260 GHz, and $\tau_f \approx$ –19.2 ppm/°C [136].

In the family of AB$_2$O$_6$ (A = Ca, Mg, Mn, Co, Ni, Zn; B = Ta, Nb), the relationship of permittivity with electronegativity was presented by Lee et al. [137]. Two structure classifications have been identified in this system, namely rutile-type (trirutile) and $\alpha$-PbO$_2$-type (tri-$\alpha$-PbO$_2$, columbite) [138,139]. Comprehensive studies of columbite niobates concluded that the $\varepsilon_r$ was in the range of 17–22, $\tau_f$ value varied from –45 to –76, and the $Q\times f$ value was over 95,000 GHz of MgNb$_2$O$_6$ [140,141]. The investigations about property optimization and preparation methods were concentrated on Mg$_2$Nb$_2$O$_6$, Zn$_2$Nb$_2$O$_6$, and ZnTa$_2$O$_6$ due to their potential of application. For sintering behavior, the sintering temperature can be reduced to 1150 °C of MgNb$_2$O$_6$ by sol–gel method [142]. Doped ceramics of (Zn$_{1-x}$Ni$_x$)Ta$_2$O$_6$ [143], Zn(Ta$_{1-x}$Nb$_x$)$_2$O$_6$ [144], Zn(Ta$_{1-x}$Sb$_x$)$_2$O$_6$ [145], and composite ceramics composed of ZnO–Nb$_2$O$_5$–1.75TiO$_2$–5 mol% MgO, (1–$x$)ZnTa$_2$O$_6$–$x$MgNb$_2$O$_6$, (1–$x$)ZrTi$_2$O$_6$–$x$ZnNb$_2$O$_6$, and (1–$x$)ZnTa$_2$O$_6$–$x$NiNb$_2$O$_6$ were designed successfully to reach near-zero $\tau_f$ value [146–149]. Liu and Deng [150] proposed that the grain size of ZnNb$_2$O$_6$ became smaller with the ZnNb$_2$O$_6$ content increasing. The secondary ZnV$_2$O$_6$ was obtained by sol–gel procession and solid reaction sintering by Wu et al. [152]. Liu et al. [153] verified that the unpaired d-electrons contribution to the room temperature loss should be taken into consideration of ZrTiO$_4$–ZnNb$_2$O$_6$. It was interesting that the structure transformation was identified as tri-$\alpha$-PbO$_2$, $\alpha$-PbO$_2$, trirutile, and rutile in (1–$x$)ZnTa$_2$O$_6$–$x$TiO$_2$ along with the increase of $x$ [154]. ZnNb$_2$O$_6$ ceramics prepared by microwave sintering exhibited relative density of 94.3%, and the quality factor was dominated by the distribution of grain size [155]. Recently, the intrinsic dielectric properties were investigated using chemical bond theory and lattice vibrational spectra, which indicated that B$_{1u}$ mode at 168.87 cm$^{-1}$ was highly related to the dielectric properties [156], and the fitted results of infrared-related spectrum are presented in Fig. 7.
2.2.2 ReTiCO$_6$ ceramics

The crystal structure of double tantalates of rare-earth elements with titanium tantalite compounds based on ReTiTaO$_6$ is sorted into two parts: orthorhombic aeschynite symmetry with rare earth atomic number in the range of 55–66 and orthorhombic euxenite symmetry with that of 67–71 [157,158]. Generally, high $\varepsilon_r$ and positive $\tau_f$ were obtained for the former, while relatively low $\varepsilon_r$ and negative $\tau_f$ were observed for the latter. The effect of microstructure on properties of RETiNbO$_6$ (RE = La, Sm, and Y) ceramics was presented by Lei et al. [159]. The dielectric constant of RETiNbO$_6$ system (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, and Yb) and RETiTaO$_6$ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al, and In) increases with the RE ionic radius [157,158]. It was reported that LaTiNbO$_6$ usually stabilized as a monoclinic structure, and Zhang and Zuo [160] proposed that ceramics with coexistence of O and M phases could be achieved after prolonging the annealing time. And then, they [161–164] conducted out the substitutions for La and Nb sites, in which the annealing time. And then, they [161–164] conducted out the substitutions for La and Nb sites, in which the annealing time.

2.2.3 ReCO$_x$/Mg$_x$C$_2$O$_y$/Zn$_3$C$_2$Os ceramics

The ABO$_4$ composition material system of RENbO$_4$ (RE = lanthanoid atoms, being La to Lu as well as Y) was firstly investigated in light of their luminescence, damping, and phase transformation characteristics, and their microwave dielectric properties were firstly proposed in 2006 [166]. The satisfied properties of LaNbO$_4$, NdNbO$_4$, and SmNbO$_4$ attracted much attention recently. For NdNbO$_4$ ceramics, substitution for Nd site by single cations such as Sr, Ca, Mn, Co, Mg, Zn, Y, Al, Bi, Sm, La [167–175], and Nb site by Ta, Sb [176–179] were completed to adjust the microwave dielectric properties. In our recent reports, the groups of different isovalent cations of $(A,B_{1-x})^{3+}$ (A = Mg, Al, Si, Zr; B = W, Mo) have been listed as valid substitution for Nb site to reduce dielectric loss [180–183]. The analysis of combination of P–V–L theory and vibration spectrum suggested that doping into Nb site was beneficial to improving quality factor. Meanwhile, NdNbO$_4$ prepared in sol–gel method or composite ceramics composed of NdNbO$_4$–CaTiO$_3$ [184], NdNbO$_4$–CaF$_2$ [185], and NdNbO$_4$–MgO [186] have also been reported to perfect the properties. Similarly, intrinsic dielectric properties of EuNbO$_4$ were studied by Liu et al. [187]. In the full range of La$_2$O$_3$–Nb$_2$O$_5$–V$_2$O$_5$ system, four typical phase regions were verified, including monoclinic fergusonite, tetragonal scheelite, B-site ordered sheelite, and composite of monoclinic LaVO$_4$ and tetragonal scheelite phases [188]. Likewise, MgO was designed as an addition for LaNbO$_4$ ceramics and the excellent properties were listed as $\varepsilon_r \approx 19.8$, $Q\times f$ value $\approx 94,440$ GHz, and $\tau_f \approx 6.1$ ppm/°C [189]. More recently, structure–property relationship of another $A^3^+B^5^+$O$_4$ binary oxide, zircon-type $A$VO$_4$ ($A$ = Eu, Y) ceramics, was discussed by packing fraction and bond valence [190]. Ferroelastic phase transition from monoclinic fergusonite to tetragonal scheelite was observed by in situ Raman spectroscopy and X-ray diffraction of La(Nb$_{0.9}$V$_{0.1}$)O$_4$, and the schematic of $\varepsilon_r$ typical-ceramics versus temperature was shown by Zhou et al. [191]. NiO/CoO added into LaNbO$_4$ would distinctly optimize the quality factor since the larger and uniform grain was obtained [192]. Although the thermal properties [193–196] and the first-principles calculation of electronic structure and optic properties of RETaO$_4$ (RE = Y, La, Sm, Eu, Dy, Er) [197] have been investigated, the intrinsic dielectric loss has not been summarized in this system. Microwave dielectric properties of ErNbO$_4$ prepared by sol–gel method were reported by Devesa et al. [198], and the grain size varied from 31.27 to 86.65 µm and 40.96 to 78.23 µm by Rietveld refinement and Sherrer’s formula, respectively. ZrTiO$_4$ followed the general formula of ABO$_4$, and the intrinsic dielectric loss of Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ was investigated by THz time domain spectroscopy [199].

The structure of corundum-like phase of Mg$_4$Nb$_2$O$_9$ was verified by Kumada et al. [200], where the cations were ordered by the stack of two layers of a mixture of Mg and Nb and one layer of Mg along the c-axis. Mg$_4$(Nb$_{2-x}$Ta$_x$)$_3$O$_9$ solid solution was synthesized in the sintering temperature range of 1350–1400 °C [201], which possesses a comparable quality factor ($Q\times f$ value $\approx 350,000$ GHz for $x = 2$) to that of Al$_2$O$_3$. To deal with the limitation of high sintering temperature, both Mg$_4$Nb$_2$O$_9$ and Mg$_4$Ta$_3$O$_9$ were generated by sol–gel method and the variation of property with
sintering temperature was analyzed [202–204]. An accompanying minor phase of Mg$_2$Nb$_2$O$_7$ gradually disappeared as the calcined temperature increased to 850 °C. High frequency dielectric properties of A$_2$B$_2$O$_7$ microwave dielectric were evaluated by Kamba et al. [205] using far-infrared reflection, transmission spectroscopy, and time-resolved THz transmission spectroscopy. Considering the negative influence of second phase on properties and sintering behavior of Mg$_4$Nb$_2$O$_9$, excess MgO and Mg(OH)$_2$ were used to adjust the composition of Mg$_4$Nb$_2$O$_9$ [206,207], which presented that the appearance of Mg$_4$Nb$_2$O$_9$ pure phase was more easily with Mg(OH)$_2$ as raw materials. A dramatically improvement of quality factor was achieved by Ni and Ta co-doped into this system, and (Mg$_{0.95}$Co$_{0.05}$)$_2$TiO$_3$ ceramics provided their high quality factor. The primarily reported compositions ceramics, many rock-salt Li-containing compounds emerge as focal points. The general formula of rock-salt ceramics is A$_2$B$_2$O$_7$ (A$^+$ = Li, Na; B$^{5+}$ = Ti, Sn, Zr, B$^{5+}$ = Nb and Ta). Li$_2$TaO$_4$ underwent an order–disorder phase transition at 1213 °C, in which the structure consisted of ordered (Li,Ti) layer, with the property of $\varepsilon_i \approx 12.76$, $Q\times f$ value $\approx 44,200$ GHz, and $\tau_f \approx -54$ ppm/°C [213]. The sintering behavior of excess Li for non-stoichiometry Li$_{2x}$TiO$_3$ ceramics was investigated by Bian and Dong [214] and Hao et al. [215] after the determination of pseudo-binary of Li$_2$O–TiO$_2$ [216,217]. For co-doped substitution, Zn$_{1-x}$Nb$_2$O$_7$, Mg$_{1/3}$Nb$_{2/3}$, and Co$_{1/3}$Nb$_{2/3}$ addition into Li$_2$TaO$_4$ could adjust the $\tau_f$ from positive to negative [218–220]. Cu$_{1/3}$Nb$_{2/3}$ doped ceramics with 3 wt% H$_2$BO$_3$ were designed as a patch antenna and a dielectric resonator antenna [221]. The solid solution of Li$_2$TiO$_3$–MgO [222], Li$_2$TiO$_3$–ZnO [223,224], and Li$_2$TiO$_3$–Li$_2$NbO$_4$ [225] attracted much interest of researcher owing to their high quality factor. The primarily reported ceramics of Li$_2$O–MgO/ZnO/CoO–Ti/Sn/ZrO$_2$ ternary system contain Li$_2$MgNiTi/ZrO$_4$, Li$_2$Zn/Mg/CoTi$_2$O$_4$, Li$_2$Mg/Co/Mg$_3$Ti$_4$O$_12$, Li$_2$Mg/Co/Ti/SnO$_6$, Li$_2$Zn/Co/Ti/SnO$_6$, Li$_2$Mg$_2$Ti$_2$O$_7$, Li$_2$Mg$_2$Ta$_2$O$_7$, Li$_2$Mg$_2$Ti$_2$O$_7$, Li$_2$Mg$_2$Ti$_2$O$_7$, and Li$_2$Mg$_2$Ti$_2$O$_7$, while LiZnNbO$_4$, Li$_3$Mg$_3$NbO$_6$, and Li$_2$Mg$_2$NbO$_6$ occupied the dominated composition of Li$_2$O–MgO/ZnO/CoO–Nb/Ta/Sb$_2$O$_5$. The microwave dielectric properties of the mentioned pure phase ceramics are listed in Table 1 [224,226–246], and the phase diagram of rock-salt structure is plotted in Fig. 8, where the ordered–disordered range was summarized from Zhang et al. [246,247]. Simultaneously, Gu et al. [248] stated the two-phase and thermally stable ceramics of 0.8Li$_2$NbO$_4$–0.2Ca$_{0.8}$Sr$_{0.2}$TiO$_3$, where the $\tau_f$ value was 5.2 ppm/°C.

2.3 Rock-salt structure

Closely followed by the ever-growing explosion of global data volume and the rapid boost of millimeter-wave technology, the requirement of materials with low permittivity ($\varepsilon_i \approx 25$) and high $Q\times f$ value is increasingly urgent. In the exploration of new composition ceramics, many rock-salt Li-containing compounds emerge as focal points. The general formula of rock-salt ceramics is A$_2$B$_2$O$_7$ (A$^+$ = Li, Na; B$^{5+}$ = Ti, Sn, Zr, B$^{5+}$ = Nb and Ta). Li$_2$TiO$_4$ underwent an order–disorder phase transition at 1213 °C, in which the structure consisted of ordered (Li,Ti) layer, with the property of $\varepsilon_i \approx 12.76$, $Q\times f$ value $\approx 44,200$ GHz, and $\tau_f \approx -54$ ppm/°C [213]. The sintering behavior of excess Li for non-stoichiometry Li$_{2x}$TiO$_3$ ceramics was investigated by Bian and Dong [214] and Hao et al. [215] after the determination of pseudo-binary of Li$_2$O–TiO$_2$ [216,217]. For co-doped substitution, Zn$_{1-x}$Nb$_2$O$_7$, Mg$_{1/3}$Nb$_{2/3}$, and Co$_{1/3}$Nb$_{2/3}$ addition into Li$_2$TaO$_4$ could adjust the $\tau_f$ from positive to negative [218–220]. Cu$_{1/3}$Nb$_{2/3}$ doped ceramics with 3 wt% H$_2$BO$_3$ were designed as a patch antenna and a dielectric resonator antenna [221]. The solid solution of Li$_2$TiO$_3$–MgO [222], Li$_2$TiO$_3$–ZnO [223,224], and Li$_2$TiO$_3$–Li$_2$NbO$_4$ [225] attracted much interest of researcher owing to their high quality factor. The primarily reported ceramics of Li$_2$O–MgO/ZnO/CoO–Ti/Sn/ZrO$_2$ ternary system contain Li$_2$MgNiTi/ZrO$_4$, Li$_2$Zn/Mg/CoTi$_2$O$_4$, Li$_2$Mg/Co/Mg$_3$Ti$_4$O$_12$, Li$_2$Mg/Co/Ti/SnO$_6$, Li$_2$Zn/Co/Ti/SnO$_6$, Li$_2$Mg$_2$Ti$_2$O$_7$, Li$_2$Mg$_2$Ta$_2$O$_7$, Li$_2$Mg$_2$Ti$_2$O$_7$, Li$_2$Mg$_2$Ti$_2$O$_7$, Li$_2$Mg$_2$Ti$_2$O$_7$, and Li$_2$Mg$_2$Ti$_2$O$_7$, while LiZnNbO$_4$, Li$_3$Mg$_3$NbO$_6$, and Li$_2$Mg$_2$NbO$_6$ occupied the dominated composition of Li$_2$O–MgO/ZnO/CoO–Nb/Ta/Sb$_2$O$_5$. The microwave dielectric properties of the mentioned pure phase ceramics are listed in Table 1 [224,226–246], and the phase diagram of rock-salt structure is plotted in Fig. 8, where the ordered–disordered range was summarized from Zhang et al. [246,247]. Simultaneously, Gu et al. [248] stated the two-phase and thermally stable ceramics of 0.8Li$_2$NbO$_4$–0.2Ca$_{0.8}$Sr$_{0.2}$TiO$_3$, where the $\tau_f$ value was 5.2 ppm/°C.

2.3.1 Li$_2$O–MgO/ZnO/CoO–Ti/Sn/ZrO$_2$ ternary system

Secondary phases of Mg$_3$TiO$_4$ and Li$_2$Mg$_3$Ti$_4$O$_{12}$ were highly related to the properties when Yao et al. [249] prepared the Li$_2$MgTiO$_4$ after sintered higher than 1250 °C. The variation of di
Both Li$_2$Mg$_4$TiO$_7$ and Li$_4$Mg$_3$Ti$_2$O$_9$ exhibited LiFeO$_2$-like cubic phase with space group $Fm\overline{3}m$. The optimal combination of microwave dielectric properties of Li$_2$(Mg$_{0.8}$Al$_{0.2}$)$_2$TiO$_7$ (A = Co, Ni, Mg, Zn, Ca) was observed for Zn doped ceramics ($\varepsilon_r \approx 14.77$, $Q\times f$ value $\approx 162,200$ GHz, and $\tau_f \approx -4.30$ ppm/°C) and Ca ($\varepsilon_r \approx 15.79$, $Q\times f$ value $\approx 100,300$ GHz, and $\tau_f \approx -1.43$ ppm/°C) [252]. Pure cubic Li$_2$Mg$_3$Ti$_2$O$_9$ phase was formed in the whole range of $0 \leq x \leq 0.4$ with Mg$_{1/3}$Ta$_{2/3}$ occupying Ti site [253].

Except for the sintering temperature, the heating rates and substation will directly influence the grain size, densification, and properties. Lu et al. [254] pointed out that the sintering rate increasing from 3 to 7 °C/min would deteriorate the quality factor of Li$_2$ZnTi$_3$O$_8$ ceramics. If ball milling is applied for the raw materials at first for 4 h, then the sintering temperature of Li$_2$ZnTi$_3$O$_8$ ceramics could reduce from 1075 to 925 °C, and those ceramics were chemically compatible with Ag [255]. Sintering the ceramics in a box type electric furnace and in a microwave furnace would obtain Li$_2$ZnTi$_3$O$_8$ ceramics with the grain size of 38 and 7 μm, respectively [256]. Mg, Co, and Zn substitution for Zn in Li$_2$ZnTi$_3$O$_8$ increased the quality factor because of the more compact microstructure [257–259]. Whereas, the secondary phases were recorded after the introduction of Sr$^{2+}$ or (Sr$_{1-x}$Ca$_x$) into Li$_2$ZnTi$_3$O$_8$ [260–262]. Phase evolution of $(1-x)$Li$_2$ZnTi$_3$O$_8$–xTiO$_2$ system indicated that pure Li$_2$ZnTi$_3$O$_8$ with cubic structure was observed when $x \leq 0.2$ (the lattice parameter is similar to MgFe$_2$O$_4$ with space group of $Fm\overline{3}m$ (227)), solid solution was exited in the range of $0.2 \leq x \leq 0.4$ with cubic structure (the lattice parameters is similar to Zn$_2$Ti$_3$O$_8$ with space group of $P4\overline{3}32$ (212)), and rutile TiO$_2$ phase appeared when $x \geq 0.6$ [263]. The $\tau_f$ value moves from –15 to 102.4 in $(1-x)$Li$_2$ZnTi$_3$O$_8$–xTiO$_2$ ($0 \leq x \leq 0.4$) [264]; meanwhile, near zero $\tau_f$ value was also achieved by Bari et al. [265] in this system. 4 wt% TiO$_2$ was added into Li$_2$ZnTi$_3$O$_8$ with different particle sizes, where the nanoparticles and micron particles all generated a more uniform microstructure and relative density reached to 98.5% [266]. Similar to TiO$_2$-doped Li$_2$ZnTi$_3$O$_8$ ceramics, phase composition and properties of Li$_2$Mg(Ti$_{1-x}$Sn$_x$)$_3$O$_8$ ($x = 0.1–0.25$) were concluded as with 0.10 $\leq x \leq 0.15$, the spinel and rutile co-existed; with 0.20 $\leq x \leq 0.25$, the spinel, rutile, and ilmenite were obtained [267], and the optimal properties of Li$_2$ZnTi$_3$O$_8$–0.2SnO$_2$ composite ceramics exhibited: $\varepsilon_r \approx 20.9$, $Q\times f$ value $\approx 89,500$ GHz, and $\tau_f \approx -24$ ppm/°C [268]. The variation of dielectric properties with density of $(1-x)$Li$_2$(Mg$_{0.8}$Zn$_{0.2}$)$_3$Ti$_3$O$_8$–xLi$_2$TiO$_3$ ($x = 0.727, 0.778, 0.821$, and 0.889) was discussed systematically by Zhang et al. [269]. The concentration of oxygen vacancy, relative density, and decrease in damping behavior would influence the $Q\times f$ value of Li$_2$ZnTi$_3$O$_8$–x wt% Nb$_2$O$_5$ [270]. To trace the dielectric response of lattice vibration, the response process of dielectric loss in Li$_2$ZnTi$_3$–xM$_x$O$_9$ ($M = Al^{3+}$, Nb$^{5+}$, (Al$_{0.5}$Nb$_{0.5}$)$^{4+}$

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**Table 1** Microwave dielectric properties of pure phase with rock-salt structure.

| Formula              | $\varepsilon_r$ | $Q\times f$ (GHz) | $\tau_f$ (ppm/°C) | ST (°C) | Ref. |
|----------------------|-----------------|-------------------|-------------------|--------|------|
| Li$_2$MgTiO$_4$      | 17.25           | 97,300            | -27.2             | 1360   | [226]|
| Li$_2$NiTiO$_4$      | 19.25           | 51,290            | -20.1             | 1275   | [230]|
| Li$_2$Mg$_3$TiO$_4$  | 12.30           | 40,900            | -12.31            | 1175   | [234]|
| Li$_2$Zn$_3$TiO$_4$  | 27.27           | 40,000            | 2.6               | 1000   | [227]|
| Li$_2$Co$_3$TiO$_4$  | 28.96           | 52,600            | 7.4               | 1025   | [228]|
| Li$_2$Zn$_3$TiO$_5$  | 25.63           | 90,000            | -10.8             | 1000   | [229]|
| Li$_2$Co$_3$TiO$_5$  | 21.43           | 35,000            | -22               | 1050   | [233]|
| Li$_2$Mg$_2$Co$_{0.1}$Ti$_{0.9}$O$_4$ | 20.2 | 62,300 | -27.1 | 1125 | [232]|
| Li$_2$Zn$_2$Co$_{0.1}$Ti$_{0.9}$O$_4$ | 20.6 | 106,700 | -48 | 1075 | [231]|
| Li$_2$Co$_2$Ti$_2$O$_5$ | 15.2 | 152,000 | -39 | 1280 | [235]|
| Li$_2$Ni$_2$Ti$_2$O$_5$ | 13.18 | 9800 | 7.3 | 1275 | [238]|
| Li$_2$Mg$_3$Zn$_{0.1}$Ti$_{0.9}$O$_4$ | 13.43 | 233,600 | -7.24 | 1600 | [239]|
| Li$_2$Mg$_2$Co$_{0.1}$Ti$_{0.9}$O$_4$ | 15.27 | 209,400 | -11.31 | 1550 | [240]|
| Li$_2$Zn$_2$Co$_{0.1}$Ti$_{0.9}$O$_4$ | 38.4 | 54,300 | 82.9 | 1260 | [237]|
| Li$_2$Mg$_2$Sn$_{0.1}$Ti$_{0.9}$O$_4$ | 12.4 | 58,754 | 12.1 | 1180 | [241]|
| Li$_2$Ni$_2$Zn$_{0.1}$Ti$_{0.9}$O$_4$ | 12.3 | 20,000 | -23.4 | 1300 | [242]|
| Li$_2$Zn$_2$Ta$_{0.1}$Ti$_{0.9}$O$_4$ | 15.6 | 85,310 | -63.7 | 1070 | [236]|
| Li$_2$Mg$_2$Ta$_{0.1}$Ti$_{0.9}$O$_4$ | 14.94 | 100,965 | -21.96 | 1225 | [243]|
| Li$_2$Mg$_2$Sn$_{0.1}$Ti$_{0.9}$O$_4$ | 10.5 | 84,600 | -9.0 | 1300 | [244]|
| Li$_2$Mg$_2$Nb$_{0.1}$Ti$_{0.9}$O$_4$ | 16.8 | 79,642 | -22 | 1300 | [224]|
| Li$_2$Mg$_2$Nb$_{0.1}$Sn$_{0.9}$Ti$_{0.1}$O$_4$ | 16.2 | 96,796 | -24.8 | 1260 | [245]|

ST: sintering temperature (°C).
(Zn_{1/3}Nb_{2/3})^{4+}$, and $(Li_{1/4}Nb_{3/4})^{4+}$) was discussed systematically containing the conduction loss and lattice vibration loss [271]. The conduction loss which acts at frequency lower than terahertz is neglectful by researchers concentrating on MWDCs, while AC impedance analysis was used to identify the effect of dopants and the mechanism of conduction loss in this system. Combining the fitting THz time domain spectrum and far infrared reflectivity spectrum, the dielectric response was illustrated in depth based on lattice loss and conduction loss.

Ultra-low loss microwave dielectric materials of Li$_2$Mg$_3$TiO$_6$-based ceramics are extensively studied via doping cations into Mg and Ti site. Bivalent cations such as Ca$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ were verified effectively to adjust the microwave dielectric properties for Mg site, and co-doped of Al$_{1/2}$Nb$_{1/2}$ and Zn$_{1/3}$Nb$_{2/3}$ for Ti-site enhanced the $Q\times f$ values to 174,300 GHz [273] and 168,911 GHz [274], respectively. For MWDCs, compactness microstructure guarantees the satisfied microwave dielectric properties. However, porous microstructure caused by the loss of Li element under high temperature is a problem for all compounds containing Li. To cure the volatilization of lithium, Fang et al. [275–277] proposed a reliable method which provided the Li-rich sintering atmosphere, and they obtained serial MWDCs based on Li–Mg–Sn/Ti oxides with excellent properties. The schematic representation of the devices provided with the Li-rich atmosphere is shown in Fig. 9, and this similar method was gradually popularized to other systems with volatilization element to obtain the ceramics with dense microstructure. The negative $\tau_f$ values can be compensated by Ca$_{0.8}$Sr$_{0.2}$TiO$_3$, and the sample with 0.91Li$_2$Mg$_3$TiO$_6$–0.09Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ showed a $\tau_f$ value of $-3.65$ ppm/$^\circ\mathrm{C}$ [278].

The phase evolution of Li$_2$O–3MgO–$m$TiO$_2$ ($1 \leq m \leq 6$) was summarized as the phase diagram shown in Fig. 10 [279], where the phase structures changed as (Li$_3$Mg$_2$TiO$_6$, $m = 1$)→(Li$_3$Mg$_2$Ti$_{12}$O$_{36}$ and Mg$_2$TiO$_4$, $m = 2$)→(Li$_3$Mg$_2$Ti$_{12}$O$_{36}$, $m = 3$)→(Li$_3$Mg$_2$Ti$_{12}$O$_{36}$, Mg$_2$TiO$_4$, and Li$_2$MgTi$_3$O$_7$, $m = 4$)→(Li$_3$Mg$_2$Ti$_{12}$O$_{36}$, Mg$_2$TiO$_4$, Li$_2$MgTi$_3$O$_7$, and MgTi$_2$O$_5$, $m = 5$)→(Li$_3$Mg$_2$Ti$_{12}$O$_{36}$, Mg$_2$TiO$_4$, Li$_2$MgTi$_3$O$_7$, and MgTi$_2$O$_5$, $m = 6$). The application of P–V–L theory to Li$_3$Mg$_2$TiO$_4$ [280], Li$_3$Mg$_3$Ti$_4$O$_{12}$ [281], and Li$_3$Mg$_2$Ti$_6$O$_{18}$ [282] revealed that the bond ionicity ($f_i$) descended as $f_i$(Ti–O) > $f_i$(Mg–O) > $f_i$(Li–O). As analogy with Li$_2$O–3MgO–$m$TiO$_2$ ceramics, Li$_2$ZrO$_3$–MgO ceramics were explored as well [234,283,284]. High quality factor could be obtained in (Mg$_{1/3}$Sb$_{2/3}$)$_4^+$ substitutions for Li$_2$MgZrO$_7$ ceramics, which reached 153,140 GHz [285]. Zirconium deficiency of Li$_2$Mg$_2$Zr$_{1-x}$O$_6$ ceramics was designed and remarkable dielectric properties were presented: $\varepsilon_r \approx 13.13$, $Q\times f$ value $\approx 116,400$ GHz, and $\tau_f \approx -26.30$ ppm/$^\circ\mathrm{C}$ [286].

### 2.3.2 Li$_2$O–MgO/ZnO/CoO–Nb/Ta$_2$O$_5$ ternary system

An intermediate compound of Li$_3$Mg$_2$NbO$_6$ at $x = 1/3$ appeared in the investigation of structure evolution of Li$_3$Mg$_2$Nb$_{1-x}$O$_3$ (M = Mg, Zn), and the results indicated that solid solution could be formed in a wide range between Li$_3$NbO$_4$ and MgO [224]. Considering the existed compounds of Li$_3$TiO$_3$–MgO and Li$_3$NbO$_4$–MgO, Zhang et al. [246] supposed that a three-component solid solution would be formed in Li$_2$TiO$_3$–Li$_3$Nb$_{1-x}$O$_3$–MgO, and the pseudo phase diagrams of those component were presented in Fig. 11. The most extensively studied ceramics in this system are Li$_2$Mg$_3$Nb/TaO$_6$ and Li$_3$Mg$_2$NbO$_6$. For instance, a large grain size (130 $\mu$m) was recorded after using reaction sintering process to generate Li$_3$Mg$_2$NbO$_6$ [287]. Single cation doped solid solution of Li$_3$(Mg$_{1-x}$Co$_x$)$_2$NbO$_6$ [288], Li$_3$(Mg$_{1-x}$Mn$_x$)$_2$NbO$_6$ [289], Li$_3$Mg$_2$Nb$_{1-x}$Mo$_x$O$_{6+x/2}$ [290],

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**Fig. 9** Schematic representation of the Li$_{2-3x}$Mg$_{3x}$Mg$_{1-x}$O$_6$ ($x = 0–4/7$) placement for providing ZrO$_2$-burying protective atmosphere and Li-rich sintering atmosphere. Reproduced with permission from Ref. [277], © The American Ceramic Society 2017.

**Fig. 10** Ternary phase diagram of Li$_2$O–3MgO–$m$TiO$_2$ systems. Reproduced with permission from Ref. [279], © Elsevier Ltd and Techna Group S.r.l. 2016.
Li₃Mg₂Nb₁₋ₓTaₓO₆ [291], Li₃Mg₂Nb₁₋ₓVₓO₆ [292], Li₃Mg₂Sb₁₋ₓO₆ [293], Li₃Mg₂-ZnₓSbO₆ [294], Li₃Mg₂(Nb₁₋ₓWₓ)O₆ [295], Li₃Mg₂Nb₁₋ₓTiₓO₆ [296], Li₃Mg₂Nb₁₋ₓTiₓO₆ [297], and Li₃Mg₂NbₓO₆(M,W₁₋ₓ)O₆ (M = Li⁺, Mg²⁺, Al³⁺, Ti⁴⁺) [298] or non-stoichiometric Li₃Mg₂SbO₆ [299] have been probed and analyzed to explain the variation of dielectric properties through current theory including P–V–L theory, packing fraction, and C–M equations. It was interesting that the “dark hole” phenomenon of Li₂TiO₃ was cured by adding Li₃Mg₂NbO₆ and the τᵣ value of 0.96Li₂TiO₃–0.04 Li₃Mg₂NbO₆ was 2.6 ppm/°C [300]. Since yet there was no literature about the structure transformation of Li₂TiO₃–Li₃NbO₄–MgO to renew the understanding of rock-salt ceramics, Zhang et al. [247,301,302] gradually updated the reports about Li₃Mg₂NbO₆-based ceramics. The phase transitions among the orthorhombic, cubic, and monoclinic were verified by XRD (Fig. 12) and TEM analysis (Fig. 13). The systematical analysis of lattice evolution and ordering transformation indicated that the low dielectric loss of this system was mainly ascribed to the superlattice. The THz time-domain spectroscopy was firstly used in this system to evaluate the intrinsic dielectric loss associated with phonon oscillation. Meanwhile, the configurational entropy was calculated to explain the change of disordered and ordered crystal structures, where the disordering cubic phase generated much larger configurational entropy than the ordered orthorhombic and monoclinic phase (Fig. 14).

Fig. 11  Pseudo phase diagrams of (a) Li₂TiO₃–Li₃NbO₄–MgO and (b) Li₂SnO₃–Li₃NbO₄–MgO ternary systems. Reproduced with permission from Ref. [246], © Elsevier Ltd and Techna Group S.r.l. 2020.

Fig. 12  (a) XRD patterns of Li₃Mg₂SnₓNb₁₋₂ₓO₆ (x = 0–1.5) MWDCs sintered at 1290 °C for 4 h. (b) Amplified spectra of the XRD patterns from 17° to 25°. (c) Amplified spectra of the XRD patterns from 41° to 45°. Reproduced with permission from Ref. [302], © American Chemical Society 2020.
In contrast to the large scale studies of \( \text{Li}_3\text{Mg}_2\text{NbO}_6 \)-based ceramics, only \( \text{Li}_4\text{MgSn}(2–1.25x)\text{Nb}_x\text{O}_7 \) \( (0 \leq x \leq 0.15) \) was reported to evaluate the change of microstructure in \( \text{Ba}_4\text{Ti}_7\text{O}_{23} \). The mean grain size of the doped ceramics ranged from 1.35 to 4.01 μm and the cracks appeared along with the occurrence of the secondary phase [303].

2.4 Tungsten bronze structure and titanate based on \( \text{BaO}–\text{TiO}_2 \)

Since 1970, the exploration of \( \text{BaO}–\text{TiO}_2 \) system has been continuous renewed. Among them, \( \text{BaO}–4\text{TiO}_2 \) and \( 2\text{BaO}–9\text{TiO}_2 \) are the most extensively investigated ceramics as the representative ceramics with medium dielectric constant. The pseudo phase diagram of tungsten bronze structure and binary system based on \( \text{BaO}–\text{TiO}_2 \) system is shown in Fig. 15. In contrast to other sections in this review, the investigations about the compounds within this phase diagrams are relatively less, because the study of ceramics in \( \text{BaO}–\text{R}_2\text{O}_3–\text{TiO}_2 \) (\( \text{R} = \text{La–Gd} \)) has been almost accomplished and widely used in the industry.

2.4.1 \( \text{BaO}–\text{TiO}_2\text{Nb}_x\text{O}_7/\text{Ta}_2\text{O}_5 \) system and \( \text{Re}_2\text{TiO}_5 \)

The frequency dependence of \( Q \times f \) value was observed for \( \text{Ba}_2\text{Ti}_9\text{O}_{26} \) ceramics, which was ascribed to the extrinsic dielectric loss [304]. After adding \( \text{Sm}_2\text{O}_3 \) into \( \text{BaTi}_4\text{O}_9 \), precursor of \( \text{BaTi}_4\text{O}_9 \) and \( \text{BaSm}_2\text{Ti}_4\text{O}_{12} \) was...
modeled by a cool iso-static press and calcined at 1300 °C, and a near-zero temperature coefficient of +2.2 ppm/°C was achieved with 40 mol% Sm2O3 [305]. (Zn1/3Nb2/3)3+ substitution for Ti4+ in Ba2Ti5O12 modified the τf value to +7 ppm/°C [306]. Pseudobrookite-type A3B2O15 (A = Ba, Sr, Mg; B = Nb, Ta) was firstly investigated by Jawahar et al. [307], which showed εr ≈ 11–51, Q′f value ≈ 2400–88,000 GHz, and τf ≈ (−73)–232 ppm/°C. Based on sol–gel method, Mg2Nd2O15 nano-powders were obtained at 600 °C, and then the sintering temperature can be reduced to 1300 °C [204]. On the basis of P–V–L chemical bond theory, the relationship of chemical bond characteristic and microwave dielectric properties of Eu2TiO5 was investigated by Jawahar et al. [307], which showed εr ≈ 11–51, Q′f value ≈ 2400–88,000 GHz, and τf ≈ (−73)–232 ppm/°C. Based on sol–gel method, Mg2Nd2O15 nano-powders were obtained at 600 °C, and then the sintering temperature can be reduced to 1300 °C [204]. On the basis of P–V–L chemical bond theory, the relationship of chemical bond characteristic and microwave dielectric properties of Eu2TiO5 was discussed deeply [308]. Meanwhile, the electron localization function (ELF) based on the first-principles calculation was evaluated to provide the information of bond covalency [309], which provided a strategy to estimate the chemical bond characterization.

2.4.2 Tungsten bronze structure

The different compositions of tungstenbronze-type with Ba6–3R8+2x2Ti18O54 solid solution reported by Ohsato [310] in 2001, and the compounds were presented in Fig. 16. The relative permittivity of BaO–R2O3–TiO2 (R = rare earth) ternary system. Three distinct phases were formed using variable size TiO2 reagents into BaO–Nd2O3–TiO2 system. After 2010, there are only a few studies focused on this system. Three distinct phases were formed using variable size TiO2 reagents into BaO–Nd2O3–TiO2 [312]. Ba6–3R8+2x2Ti18O54 (BRT, R = La, Pr, Nd, Sm)

![Fig. 16 BaO–R2O3–TiO2 (R = rare earth) ternary system. Reproduced with permission from Ref. [310], © Elsevier Science Ltd. 2001.](image-url)

solid solution family was reported with high permittivity. When x = 2/3, BaNd0.33Ti18O54 was regarded as the most investigated ceramics to lower its τf value and sintering temperature or improve its Q′f value. Yao et al. [313] and Chen et al. [314] proposed that with Al2O3 added BaO–Nd2O3–TiO2 ceramics, the Q′f value would increase obviously. The temperature-stable ceramics could be obtained by Pb and Sr substitution for Ba3.75Nd6.5Ti18O54 [315]; Ba4.5Re9Ti18O54 (Re = La, Nd) [316], solid solution of Ba2Nd8.5Ti18–xSn18.5O54 [317]; (Ba0.98Sr0.02)3.75Nd9.5Ti18(Al1.2Nd1.8)O54 [318], Ba6–3Nd8.28Ti18–y(Cr1/2Nd1/2)yO54 [319], Ba4Nd3.33(Al0.5Nb0.5)O54 [320], Ba3.75Nd6.5Ti18–x(Al1/2Nd1/2)yO54 [321], and Ba3.75Nd9.5Ti18O54 [322]; NaAlO2 [323] addition to Ba12Sm2Ti18O54; MgO, Al2O3, and MnO2 substituted for Ti4+ [324] in Ba2Sm2Ti18O54, Ba3La2Zn2Ti18O54, Ba2Sn2O5; Ba12Sm2Ti18O54, Ba4(Pr0.4Sm0.6)28/3Ti18O54 [325], and Ba4(Pr0.4Sm0.6)28/3Al4O54 [326]. Among those reports, the analysis of Raman spectrum of Ba3.75Nd9.5Ti18–x(Al1/2Nd1/2)yO54 enriched the theoretical study of tungstenbronze-type.

2.4.3 BaO–ZnO–TiO2 system

Ceramics based on the BaO–ZnO–TiO2 system have been concluded as Ba3.75Nd9.5Ti18O54, Ba2ZnTi5O13, and BaZn2Ti4O11–0.2BaNd2Ti4O12 ceramics [331]. The substitution of Cu for Zn dramatically increased the τf value because of the restrain of the formation of Ti4+ ions [328]. Considering the opposite τf values of BaTi4O9 and BaZn2Ti4O11, the τf values of composite ceramic based on those two phases varied gradually from 12 to −13 ppm/°C [329]. CuO also worked as flux former to enhance the densification in the BaTi4O9–BaZn2Ti4O11 composite ceramics, and the 0.85BaTi4O9–0.15BaZn2Ti4O11 wt% CuO presented the properties as eεr ≈ 36.4, Q′f value ≈ 62,600 GHz, and τf ≈ −0.2 ppm/°C [330]. Phase evolution of BaZn2Ti4O11–BaNd2Ti4O12 ceramics was determined by Yu et al. [331], where 0.8BaZn2Ti4O11–0.2BaNd2Ti4O12 ceramics possessed properties as eεr ≈ 39.1, Q′f value ≈ 37,850 GHz, and τf ≈ −9 ppm/°C.

2.5 Perovskite related structure

The ideal perovskite (written as ABO3) is cubically symmetric with a space group of Pm3m, and the represented material is SrTiO3. Due to the flexibility of ABO3 perovskite, variants of perovskite have been investigated, and the classification of perovskite-related structure with representative structure is summarized in Fig. 17. The perovskite-related structure...
contained cubic-type, orthorhombic-type, and hexagonal-type structures. For hexagonal-type structure, the twinned hexagonal structure means the closely packed AO layers were stacked in the order of (cch)c, while the shifted hexagonal structure corresponds to cccchh order. The typical representative of twinned structure is Ba₈CoTa₆O₂₄ and the shifted structure is Ba₈CoNb₆O₂₄ with eight-layer hexagonal perovskite structure [332]. The pseudo phase diagram of ABO₃ and complex ABO₃ type is provided in Fig. 18. From cubic and orthorhombic to hexagonal perovskite structure, researchers have proposed that tolerance factor, distortion of octahedron, and temperature of phase transition determined the variation of τₑ value, and the ordered/disordered cations were primarily related to quality factor.

2.5.1 ABO₃ formula

This section contains the ceramics with a general formula of ABO₃ and their related structure or system. Perovskite family is entirely studied because of their pyro and piezo electricity, linear and non-linear electric–optic properties, and superconducting properties. A series of investigations of CaTiO₃ with MgTiO₃-based [333–339], LaAlO₃-based [340–347], LaGaO₃ [348], Bi₂Sr₂CaCu₂O₈+δ [349], NdMg₀.₇Zn₀.₃Ti₀.₄O₃ [350], Bi₂Sr₂CaCu₂O₈+δ [351], NdMg₀.₇Zn₀.₃Ti₀.₄O₃ [352], Sm₀.₉Nd₀.₁AlO₃ [353], Ca(Mg₁/₃Nb₂/₃)O₃ [354], (Li₀.₅La₀.₅)TiO₃ [355], Li₀.₅Nd₀.₅TiO₃ [356], Li₀.₅Sm₀.₅TiO₃ [357], Mg₀.₉5Ca₀.₀₅TiO₃ [358], (Sm,Nd)AlO₃ [359–364], Zn₂SnO₄ [365], Li₃NbO₄ [366], CaMgₐₓZn₁₋ₓO₃ [367], Na₀.₃Nd₀.₅TiO₃ [368], Nd(Mg₁₂Ti₁₂)O₃ [369,370], Bi₀.₉Nd₀.₁TeO₃ [371], 3CaO–Re₂O₅–2WO₃ system [372], Ba₉Sr₉La₄Ti₄O₁₅ [373], La₄MgGeO₆ [374], (Ca₀.₉Sr₂)(Sn₀.₃Ti₁₋ₐ)O₃ [375], Ca₁₋ₓTi₃₋ₐ(Al₂₋ₐGaₐ)O₃ [376], CaₓNd₂/₃TiO₃ [377], Ca₀ₓLa₀ₓTiO₃ [378], Ca₀.₈Nd₀.₂₄TiO₃ [379], Ca₀.₈Nd₀.₂₄TiO₃ [380], Ca₀.₄₋ₓMgₓSr₀.₄Si₀.₄TiO₃ [381], CaTi₁₋ₓ(Nb₀.₃Ga₀.₇)O₃ [382], Ca₀.₆Nd₀.₄Ta₂O₅ [383], Ca₀.₆Nd₀.₄Ta₂O₅ [384], CaTi₁₋ₓ(Nd₀.₃Nd₀.₇)O₃ [385,386], Ca₀.₆Nd₀.₄Ta₂O₅ [387], Ca₀.₄₋ₓMgₓSr₀.₄Si₀.₄TiO₃ [388], Ca₀.₃₃Li₂O₂Nd₀.₃₅Ta₂O₅ [389], Ca₀.₆Nd₀.₂₄Ta₂O₅ [390], CaTi₁₋ₓ(Mg₀.₃W₁₋ₓ)O₃ [391], and Ca(HfₓTi₁₋ₓ)O₃ [392] ceramics have been reported thoroughly. Different thermally treated methods to minimize the dielectric loss for CaTiO₃ were proposed by Hu et al. [393]. The dielectric constant values saturated at 7.7–8.5 of Ca₀.₈Sr₀.₂SnO₃ ceramics in the sintering temperature range of 1450–1540 °C [394]. 0.₄Nd₂₀.₃₃Ba₀.₃(Mg₀.₅Sn₀.₅)O₃–0.₆Ca₀.₈Sr₀.₂TiO₃ ceramics modified the τₑ value to –7 ppm/°C when sintered at 1600 °C [395]. Although numbers of

Fig. 17 Classification and the representative structure of perovskite-related structure.

Fig. 18 Pseudo phase diagram of perovskite related structure.
investigations about optimizing the properties of CaTiO$_3$ ceramics have been reported, the vibrational characteristic of CaTiO$_3$ was verified by Shi et al. [396] in 2020.

For solid solution of Ba$_{1-x}$Ga$_x$Ti$_2$O$_5$, a near zero $\tau$ value of $-1.1$ ppm/°C was obtained with $x = 0.5$ [397], while a $\tau$ value of $8.2$ ppm/°C was achieved for (Sr$_{0.2}$Ga$_{0.48}$Nd$_{0.28}$)$_3$Ti$_4$O$_{12}$ with $x = 0.5$ [398]. A dramatical decrease of $\tau$ value from 1171 to $-82$ ppm/°C was obtained for Sr(Zr$_{0.5}$Ti$_{0.5}$)O$_3$ [399]. In the chemical formula of SrO(Sr$_{0.1}$Ba$_{0.9}$)TiO$_3$ (x = 0, 0.5; n = 1–4), it is demonstrated that samples with $n = 1, 2$ had no dielectric non-linear behavior in the temperature range of $(-165)$–$50$ °C, while the tunability increased with $n$ increasing [400]. Two second phases containing BaWO$_4$ and Ba$_2$TiO$_5$:Sr$_2$O$_7$ were observed in Ba$_{0.9}$Sr$_{0.1}$TiO$_3$ system with $y \geq 0.02$ [401], and BaTiSiO$_5$ phase was indexed in Ba$_{0.8}$Sr$_{0.2}$Ti$_{1.5}$O$_{4.5}$ [402]. The dielectric constant can be adjusted apparently in the Ba$_{0.9}$Sr$_{0.1}$Ti$_3$O$_9$–BaMoO$_4$ and Ba$_{0.5}$Sr$_{0.5}$Ti$_5$O$_{15}$–AMoO$_4$ (A = Ba, Sr) composite ceramics, where only cubic perovskite structure and scheelite structure were detected [403,404]. However, the BaMoO$_4$ was observed when MgMoO$_4$ added into Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ [405]. Adding Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ into Ba$_{0.4}$Sr$_{0.6}$Ti$_3$O$_9$, the dielectric constant and dielectric loss increased with the increase of the content of Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ [406]. Adding Fe power in Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ ceramics and Ba$_{2}$Mg$_{0.95}$Zn$_{0.05}$WO$_6$, and the grain size distributed in a narrow range around 0.8 μm [423,424]. A $\tau$ value of $-2.4$ ppm/°C was achieved for B-site deficient Ba(Mg$_{1-y}$Zn$_y$)$_2$Ti$_2$O$_7$O$_2$ [425]. In the non-stoichiometric system of (Sr$_{0.4}$Ce$_{0.4}$)$_{1-x}$Nd$_x$Ti$_{0.8}$Mg$_{0.2}$O$_3$, solid solution was obtained when $x \leq 0.2$, while the satisfied properties were $\varepsilon = 53$, $Q'\tau$ value $= 26,700$ GHz, and $\tau = 2.8$ ppm/°C with $x = 0.4$ [426]. Meanwhile, compositional dependence of microwave dielectric properties of doped SrTiO$_3$ sintered in air is presented as Fig. 19. It was demonstrated that SrTiO$_3$ added into ZnAl$_2$O$_4$–Zn$_2$SiO$_4$–2SiO$_2$ could reduce the sintering temperature from 1320 to 1180–1200 °C [427].

With the same general formula of ABO$_3$, the investigations of NdGaO$_3$, NdNbO$_3$, and AgTaNbO$_3$ are listed adjacent to CaTiO$_3$ and SrTiO$_3$. Phase composition was identified for NdGaO$_3$–Bi$_2$O$_3$–Nd$_2$O$_3$–TiO$_2$ system, and new temperature-stable ceramics with 0.4NdGaO$_3$–0.6Bi$_2$O$_3$–Nd$_2$O$_3$–TiO$_2$ was obtained [428]. Order–disorder transformation of A-site-deficient perovskites plays a significant role in conductivity of materials. The investigation of crystal structure and dielectric properties of the Nd$_{1-x}$O$_x$M$_{1-y}$Nb$_y$O$_3$ ($M$ = Li, Ag; $0 \leq x \leq 0.2$) suggested that the dielectric loss majorly by the lithium or silver ionic conduction at low frequencies [429]. Solid solution of AgNbTaO$_6$-based ceramics was then studied extensively [430,431]. Temperature-stable MWDCs with the formula of (La$_{0.5}$Nd$_{0.5}$)$_2$TiO$_7$ were studied by Saleem et al. [432].

MgTiO$_3$ also belongs to the general formula of ABO$_3$. The substitution for MgTiO$_3$ such as Ni, Zn, Co, and Mn for Mg has been investigated systematically [433–436], where (Mg$_{0.5}$Co$_{0.5}$)TiO$_3$ ceramics were crystalized as ilmenite structure when $x \leq 0.5$, and the
secondary phase was detected with more doping cations [437]. (Zn_{1–x}Mg_{x})TiO_3 was prepared and demonstrated that the dielectric constant and loss decreased with Mg increase [438]. For Sn doped into Ti site in MgTiO_3, in the range of x = 0.05–0.07, the ceramics exhibited excellent microwave dielectric properties of ε_r ≈ 16.8–17.1, Q × f value ≈ 298,000–312,000 GHz, and τ_f ≈ (–53)–(–50) ppm/℃ [439]. Mg_{0.95}Co_{0.05}TiO_3 ceramics possessed properties as ε_r ≈ 17.03, Q × f value ≈ 170 THz, and τ_f ≈ –40 ppm/℃ when prepared by Semi Alkoxide precursor method [440]. Gong et al. [441] obtained Mg(Sn_{0.05}Ti_{0.95})O_3 ceramics with microwave dielectric properties ε_r ≈ 17.6, Q × f value ≈ 328,543 GHz, and τ_f ≈ –42 ppm/℃, and Jia et al. [442] proposed that Mg(Ti_{1–x}Nb_x)O_3 showed microwave dielectric properties: ε_r ≈ 18.12, Q × f value ≈ 163,618 GHz, and τ_f ≈ –40.1 ppm/℃. Through sol–gel process, the quality factor of geikielite-type MgTiO_3 saturated when the ceramics sintered at 1200 ℃ [443]. After adding B_2O_3 into MgTiO_3, the composite ceramics could be densified at 1100 ℃ [444]. Investigation of introduction SrTiO_3 into Mg(Zr_{0.05}Ti_{0.95})O_3 ceramics suggested that a close zero τ_f value could achieve at 0.96Mg(Zr_{0.05}Ti_{0.95})O_3–0.04SrTiO_3 [445,446]. In the study of a designed composition of MgTiO_3 (Mg/Ti = 1, 1.02, 1.04, 1.05, 1.07), the generation of MgTi_2O_5 which derived from Mg/Ti = 1 was restrained, and then pure phase of MgTiO_3 was obtained when Mg/Ti = 1.02 [447]. (Co_{1–x}Zn_x)TiO_3 sintered at 1350 ℃ possessed ε_r = 20, Q × f value = 107,000GHz, and τ_f ≈ –60 ppm/℃ with x = 0.05 [448]. The choice of raw material of MgO and Mg(OH)_2 had a major influence on the phase formation and dielectric loss for 0.97MgTiO_3–0.03SrTiO_3 [449]. In the system of (1–x)MgTiO_3–xMg_2SiO_4–0.06CaTiO_3, τ_f ≈ 1.45 ppm/℃ was obtained with x = 0.2 [450]. ZnTiO_3-type phase, Zn_2TiO_4-type, and TiO_2 phase were co-existed in (Zn_{0.3}Co_{0.7})Ti_{1–x}Sn_xO_3, and the satisfied microwave dielectric properties were ε_r ≈ 24, Q × f value ≈ 66,700GHz, and τ_f ≈ –5.43 ppm/℃ with x = 0.02 [451]. It was interesting that MgTiO_3 and Mg_2TiO_4 were the main phases in Mg_{n+1}Ti_3O_{3n+1} (n = 2, 3, 4, 5, 6, and 7), and the Mg_2TiO_4 was effectively inhibited with n increasing [452]. New cofired tri-layer ceramic architecture of MgTiO_3/TiO_2/MgTiO_3 was designed to realize the temperature-stable and ultrahigh-Q ceramics, where the property comparison of MgO–TiO_2 system (Fig. 20) indicated that this new strategy was effective for developing high-performance dielectric resonators [4]. 2 wt% B_2O_3 as an additive could effectively reduce the sintering temperature from

![Fig. 19](image-url)  
Compositional dependence of microwave dielectric characteristics of Nd_2O_3, CeO_2, Al_2O_3, and Nb_2O_3 doped SrTiO_3 compound sintered in air, closed pipe, and nitrogen atmosphere with (a) relative permittivity (ε_r), (b) TCF (τ_f), and (c) Q × f value, respectively. Reproduced with permission from Ref. [426], © The Chinese Ceramic Society 2020.
1275 to 1175 °C in 0.9625MgTiO3–0.0375Ca0.5Sn0.5TiO3 [453]. Mg2TiO4-related and Mg6TiO16-based ceramics in MgO–TiO2 system were also reported. Mg2TiO4-based MWDCs were systematically investigated by Yu et al. [454], where the \( r_T \) value could be adjusted to \(-3\) ppm/\( °C \) by \( Ca^{2+} \) substitution. To explore the application for mobile communication, \( Nb^{5+} \) ion was added into Mg2SnO4 to improve the quality factor [455]. By mechanical synthesis method, the value of quality factor was sensitive to the initial particle size and microstructure of Mg2TiO4 [456]. Solid solution of particle size and microstructure of Mg2TiO4 was demonstrated as the optimal composition in the solid solution of (Mg,

Mg2Ti1–xGa4xO4 [457, 458]. A maximum quality factor value was 210,700 GHz [459], and infrared spectra was presented by Li et al. [460]. A zero \( r_T \) value of 210,700 GHz appeared in Mg2TiO4 [462].

2.5.2 A2B’B”O6 formula

Due to the flexibility and adjustability of the crystal structure of perovskite, the investigation of complex perovskite with various cations occupying Ti site gradually emerged. The structural studies of A2B’B”O6 (A = Ba, Sr, Ca; B’ = lanthanide, Mg, Cr, Bi; B” = Nb, Ta, Sb, W) indicated that phase transitions were ascribed to the tilting of B’O6/B”O6. In the Ba2–xSr2xSnMnO6 system, phase transitions of \( Fm\overline{3}m, I\overline{2}m, \) and \( P2_1/n \) were observed and the \( r_T \) value shifted from +25 to \(-50\) ppm/\( °C \) [473]. Effect of non-stoichiometry \( Ba_{1+x}(MgW)_{1/2}O_3 \), \( Ba(Mg_{1+y}W)_{1/2}O_3 \), and \( Ba(MgW_{1/2}Ta_{1/2})O_3 \) and the sintering temperature on microwave dielectric properties was systematically investigated by Wu and Bian [474] and Chen et al. [475], respectively. A zero \( r_T \) value ceramic was obtained in Ba2Mg1–xCaWO6 system with \( x = 0.1 \) [474]. First-principles calculation of assignment for vibrational spectra of Ba(Mg1/2W1/2)O3 MWDCs is shown in Fig. 21 [476], which proposed that \( F1d(2) \) modes originated from Mg-O6 vibrations had the largest contribution to the dielectric properties. The investigation of microwave dielectric properties of giant permittivity ceramics with a A2B’B”O6 formula (Ba(Fe1/2Nb1/2)O3 and Sr(Fe1/2Nb1/2)O3) indicated that the permittivity was independent of frequency [477].

LnMg3CaO5 (Ln = La, Sm, Nd; B = Mg, Zn; C = Ti, Sn) ceramics belonging to the general formula of A2B’B”O6 have been reported as low dielectric loss materials with an adjustable temperature coefficient of resonant frequency. Among them, minor amount of low-melt point oxide of \( Bi_2O_3 \) and \( B_2O_3 \) was usually used to enhance the sintering densification of \( Sm(Mg_{0.5}Ti_{0.5})O_3 \) [478, 479], CuO was added into \( La_{2.98}Sr_{0.02}(Mg_{0.5}Sn_{0.5})O_3 \) to enhance the densification [480], and \( V_2O_5 \) was valid for reducing the sintering temperature of \( Nd(Zn_{0.5}Ti_{0.5})O_3 \) [481]. Solid solution of \( Nd_{1-x}Sm_{x}(Mg_{0.5}Sn_{0.5})O_3 \) [482], \( Nd(Mg_{0.5}Co_{0.5}Sn_{0.5})O_3 \) [483], \( Nd_{1-x}Sr_x(Mg_{0.5}Sn_{0.5})O_3 \) [484], \( Nd_{1-x}Ba_x(Mg_{0.5}Sn_{0.5})O_3 \) [485], and \( Nd_{1-x}Sr_x(Mg_{0.5}Sn_{0.5})O_3 \) [486],

Fig. 20 Summary of \( Q'\sigma' \) value versus \( r_T \) plot for MgO–TiO2 system MWDCs. Reproduced with permission from Ref. [4], © Elsevier Ltd and Techna Group S.r.l. 2018.
Fig. 21 Combinations of the symmetry coordinates (normalized) for IR-active Fg(2) modes. Reproduced with permission from Ref. [476], © The American Ceramic Society 2013.

A(B1/3B′1/3B″2/3)O3 formula

A(B1/3B′1/3B″2/3)O3 (A = Ba, Ca; B′ = Mg, Zn; B″ = Nb, Ta) ceramics have been commercially used due to their excellent Q×f value, and the near-zero τf value. The order structures of Ca1–0.3xLa0.2x[(Mg1/3Ta2/3)x–1/3Ti1/3]O3-based, Ba(Mg1/3Nb2/3)O3-based, Ba(Zn1/3Ta2/3)O3-based and Ba3CaNb2O9 ceramics were investigated by TEM and the vibrational spectra to explain the cation ordering [505–525]. Meanwhile, superstructure reflections were obviously recorded in this system, such as Ba(Zn1/3Ta2/3)O3 doped with Nb2O5, MnO2, and V2O3 [526,527]. The wavelength of 1:2 ordered superlattice modulation was about 0.71 nm, while that of disordered superlattice modulation was 0.41 nm of Ba((Co0.6–1/2Zn0.4–1/2Mg)x1/3Ta2/3)O3, shown as Fig. 23 [511]. Adding MnO2 into Ba(Co1/3Nb2/3)O3 would enhance the grain growth and restrain the evaporation of CoO [527]. Meanwhile, the influence of B″-site non-stoichiometry of Ba(Co0.56Y0.04Zn0.35)1/3Nb2/3+x on properties was reported by Tang et al. [528], where Ba5Nb4O15 as a secondary phase was recorded. Simulation is carried out for Ba(Zn1/3Ta2/3)O3 for the design of linear metal taper [529]. Peng et al. [530] reported that addition of La2O3 into Ba(Mg1/3Ta2/3)O3, Ba1–xCa1–x(Mg1/3Ta2/3)O3, and Ba[Mg1–xZnx]1/3Ta2/3O3 led to the appearance of Ba0.5TaO3, and τf value reached to near zero [531,532]. The optimal properties of Ba[Mg1–xSn1/2Ta3(1–x/2)]O3 exhibited as εr ≈ 24.1, Q×f value ≈ 138,500 GHz, and τf ≈ +0.2 ppm/℃ [533]. The variation of τf values for 1:1 and 1:2 complex perovskites was clarified to be mainly relevant with tolerance factors, which are summarized in Fig. 24 [524]. It has been verified that samples with non-stoichiometric Mg2+ and Ta5+ in Ba(Mg1/3Ta2/3)O3 exhibited a wide temperature stability [525,534], and the correlations between Q×f versus εr and τf versus εr of high-Q (≥ 100,000 GHz) MWDCs are presented in Fig. 25.

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Fig. 22  Schematic representations of the vibrational modes of Y$_2$MgTiO$_6$ system (Y at 4e site). Reproduced with permission from Ref. [504], © The American Ceramic Society 2019.

Fig. 23  SAED pattern with zone axis [1\bar{1}0], and the corresponding HRTEM images for Ba((Co$_{0.6-x}$/2Zn$_{0.4-x}$/2Mg$_x$)$_{1/3}$Nb$_{2/3}$)O$_3$ ceramics: (a) $x = 0.1$; (b) $x = 0$; (c) $x = 0.1$; (d) $x = 0.2$; (e) $x = 0.3$; (f) HRTEM image of an ordered area in high magnification. Reproduced with permission from Ref. [511], © The American Ceramic Society 2013.

2.5.4 $A_nB_nO_{3n+2}$ formula

Perovskite-related oxides of series $A_nB_nO_{3n+2} = ABO_x$ ($x = 3+2/n$) ($A = Ca$, Sr, or La and $B = Ti$ or Nb) with $n = 4, 4.33, 4.5, 5, 6, and 7$ have been a focus owing to their electronic and dielectric properties. The crystal type and the physical properties rely on the value of $n$, which describes the number of octahedral layers in the slabs [535]. Besides Ca$_5$Nb$_5$O$_{17}$, the A$_n$B$_n$O$_{3n+2}$ phases appeared in the binary system of La$_2$Ti$_2$O$_7$–CaTiO$_3$, Nd$_2$Ti$_2$O$_7$–CaTiO$_3$, and Ca$_2$Nb$_2$O$_7$–CaTiO$_3$. Joseph et al. [536] reported the microwave dielectric properties of Ca$_5$A$_4$TiO$_{17}$ ($A = Nb$, Ta) as $\varepsilon_r \approx 44.9$, $Q\times f$ value $\approx 17,600$ GHz, and $\tau_f \approx -112.9$ ppm/°C for Ca$_5$Nb$_4$TiO$_{17}$; $\varepsilon_r \approx 40.1$, $Q\times f$ value $\approx 16,500$ GHz, and $\tau_f \approx -53.6$ ppm/°C for Ca$_5$Ta$_4$TiO$_{17}$. The solid solution of Sr$_{1-x}$La$_x$Sm$_{2/3}$Ti$_3$O$_{17}$ ($0 \leq x \leq 4$) and Sr$_{1.1-x}$Ca$_x$La$_{4.4}$Ti$_2$O$_{17}$ ($0 \leq x \leq 1$) would lower the $\tau_f$ to zero with a dielectric constant of near 53 [537,538], while $\tau_f$ declined to $+70$ ppm/°C by Zr substituted for Ti of...
SrLa$_4$Ti$_5$O$_{17}$ [539]. The intermediate of two end member phases of CaLa$_4$Ti$_5$O$_{17}$ and Ca$_5$Nb$_4$TiO$_{17}$ showed that the $\varepsilon_r$ varied from 45 to 52, $Q \times f$ was in the range of 9870–5680 GHz, and $\tau_f$ value ranged between $-38$ and $-126.4$ ppm/°C [540]. La$_3$Ti$_2$TaO$_{11}$ is an member of $n = 3$ in this series, and the textured La$_3$Ti$_2$TaO$_{11}$ was fabricated by spark plasma sintering, showing that grain-orientation control was an effective way to tailor the properties of this ceramic [541]. SrCa$_4$Nb$_4$TiO$_{17}$ and Ca$_5$Nb$_4$TiO$_{17}$ sintered at their optimal temperature presented an elongated and plate-like grain [542]. From 0 to 4, the $\tau_f$ value shifted from $-117$ to 415 in NaCa$_{4-x}$Sr$_x$Nb$_5$O$_{17}$ [543], while the $\tau_f$ value changed in the range of ($-117$)–473 ppm/°C for Na$_{4-x}$K$_x$Ca$_5$Nb$_5$O$_{17}$ [544].

2.5.5 Ca$_4$La$_2$Ti$_5$O$_{17}$

The dielectric properties of Ca$_4$La$_2$Ti$_5$O$_{17}$ were firstly reported by Rejini et al. [545], which were crystalized as perovskite structure and the XRD results were matched well based on the formula of Ca$_{0.706}$La$_{0.353}$Ti$_{0.882}$O$_3$. There are rare studies about this system, which just concentrated on the modification of $\tau_f$ value. For example, the dielectric constant declined from 71.86 to 35.23 in the solid solution of Ca$_4$La$_2$Ti$_5$-$_x$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_{17}$ (0 $\leq$ $x$ $\leq$ 4), and a near-zero $\tau_f$ value (1.62 ppm/°C) was achieved at $x$ = 3 [546]. Meanwhile, a near-zero $\tau_f$ value was measured for 0.4Ca$_4$La$_2$Ti$_5$O$_{17}$–0.6NdAlO$_3$ ceramics [547] and Mg$_4$La$_2$Ti$_5$O$_{17}$ ceramics [548].

2.5.6 $A_nB_{n-1}O_{3n}$ formula

A series of $A_nB_{n-1}$O$_{3n}$-type cation-deficient perovskite ceramics were consistent with the formula of Sr$_4$–$_m$La$_m$Ti$_m$–$_1$Ta$_4$–$_m$O$_{12}$ ($m$ = 1, 2, 3). Sr$_3$LaNb$_3$O$_{12}$ and SrLa$_3$Ti$_2$NbO$_{12}$ were firstly characterized by Fang et al. [549,550]. B-site deficient twinned perovskites such as Ba$_8$Ti$_3$Nb$_4$O$_{24}$, Ba$_8$MTa$_6$O$_{24}$ (M = Mg, Zn, Ni, Co, Cu), and Ba$_8$Ga$_4$–$_x$Ta$_4$–$_x$O$_{24}$ are classified as $A_nB_{n-1}O_{3n}$.
hexagonal perovskites. $\text{Ba}_6\text{ZnTa}_8\text{O}_{24}$ is a secondary phase of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$-based systems, and the dielectric properties in the range of 5 Hz–50 MHz of Sb substitution for Nb-site have been systematically studied by Suresh et al. [551,552] through spectroscopic methods. In the microwave frequency region, the $Q\times f$ value and $\tau_f$ values of $\text{Ba}_8(\text{Mg}_{1-x}\text{Zn}_x)\text{Ta}_6\text{O}_{24}$ ceramics decreased with the augment of $x$ [553]. Similarly, a single phase with hexagonal 8H perovskite structure of $\text{Ba}_8\text{Ti}_3\text{Nb}_{4-x}\text{Sb}_x\text{O}_{24}$ ceramics was prepared, and $\tau_f$ value declined from 110 to 2 ppm/℃ [554]. $\text{BaWO}_4$ was used to adjust the large $\tau_f$ value of 8H hexagonal perovskite $\text{Ba}_4\text{LiNb}_3\text{O}_{12}$, and the properties of $\varepsilon_r \approx 16.9$, $Q\times f$ value $\approx 75,500$ GHz, and $\tau_f \approx +8.7$ ppm/℃ were obtained [555]. Phase transformation in the sequence of hexagonal, hexagonal along with cubic, and cubic was observed in $\text{Ba}_4\text{LiNb}_3-x\text{Sb}_x\text{O}_{12}$ and $\text{Ba}_4\text{LiTa}_3-x\text{Sb}_x\text{O}_{12}$ system. Especially, the optimal microwave dielectric properties were achieved for $\text{Ba}_4\text{LiNb}_2\text{Sb}_x\text{O}_{12}$ with a zero $\tau_f$ [556,557]. $\tau_f$ value dropped from positive to negative in $\text{Ba}_3\text{LiTa}_{3-x}\text{Sb}_x\text{Ti}_5\text{O}_{21}$ [558], and $\text{Ba}_3\text{LiNb}_{3-x}\text{Sb}_x\text{Ti}_5\text{O}_{21}$ [559], while the $\tau_f$ value just reduced from 205 to 70 ppm/℃ for $\text{Ba}_3\text{LiTa}_{3-x}\text{Sb}_x\text{O}_{12}$ [560]. A-site deficient perovskite structure was well matched for $\text{LiSmTa}_4\text{O}_{12}$ ceramics with tetragonal perovskite structure (A-site deficient perovskite structure), and the optimal microwave dielectric properties were $\varepsilon_r \approx 59.60$, $Q\times f$ value $\approx 77,600$ GHz, and $\tau_f \approx +41.8$ ppm/℃ [561].

2.5.7 $\text{Sr}_{n+1}\text{TinO}_{3n+1}$ ($n = 1, 2, 3, 4, \infty$) formula

Researchers paid their attention to Ruddlesden–Popper (R–P) structure until the dielectric properties of $\text{CaReAlO}_4$ (Re = Nd, Sm, Y) were reported. The general formula of R–P compounds was written as $(\text{A},\text{A}')_{n+1}\text{B}_n\text{O}_{3n+1}$, where the structure was built by corner-sharing $(\text{BO}_6)$ octahedral and interlayer of $(\text{A},\text{A}')\text{O}$. $\text{MLnAlO}_4$ and $\text{SrLn}_2\text{Al}_2\text{O}_7$ ($M = \text{Ca}, \text{Sr}; \text{R} = \text{Y}, \text{Sm}, \text{Nd, La}$) belong to the R–P series with $n = 1$ and 2, respectively. The crystal structures of $\text{SrLaAlO}_4$ and $\text{SrLa}_2\text{Al}_2\text{O}_7$ are presented in Fig. 26. Single crystals of $\text{ABC}_4$ layered compounds with $\text{K}_2\text{NiF}_4$ structure were used as substrates for high-temperature superconductive thin films, while dielectric properties in this system were mainly investigated by Chen and his co-workers [562–574]. They contributed to analyze the relation between the intrinsic dielectric properties and crystal structure of $\text{MRAI}_4$ ($M = \text{Ca}, \text{Sr}$; and $\text{R} = \text{Y}, \text{Sm, Nd, La}$). Combining the compression/dilation effects of different cation–oxygen bonds and the stability of crystal structure with vibrational spectrum, they emphasized that the drop of the quality factor was ascribed to the abnormal variations of axial bonds and the theoretical dielectric loss was obtained after fitted the infrared reflectivity spectra. With $(\text{Zn}_{0.5}\text{Ti}_{0.5})^{3+}$ substituted for $\text{Al}^{3+}$ of $\text{SrLaAlO}_4$, the best combination of microwave dielectric properties was $\varepsilon_r \approx 23.5$, $Q\times f$ value $\approx 102,000$ GHz, and $\tau_f \approx -3.4$ ppm/℃ [572]. In the $\text{SrLaAlO}_4$–$\text{Sr}_2\text{TiO}_4$ system, some diffraction peaks shifted toward higher angles along with the variation of $x$, while some of them shifted toward lower angles, as shown in Fig. 27 [569]. This phenomenon was explained by the opposite change of $a$-axis and $c$-axis, where the octahedron elongated in the $ab$ plane with the shrinkage in the $c$ direction. The tolerance factor ($t$) of perovskite layer was used to evaluate the stability of those compounds, and the relation of $t$ and $r(M^{2+})/r(\text{Ln}^{3+})$ was plotted in Fig. 28 [573]. $\text{Sr}_{0.6}\text{Ca}_{0.4}\text{LaAlO}_4$ with 10 wt% $\text{TiO}_2$ presented a near zero $\tau_f \approx -2.5$ ppm/℃ [575].

Fig. 26  Crystal structures of $\text{SrLaAlO}_4$ and $\text{SrLa}_2\text{Al}_2\text{O}_7$.
On the other hand, the R–P structure such as Sr_{n+1}Ti_{3n}O_{3n+1} \ (n = 1, 2) [576], SrLn_{2}Al_{2}O_{7} \ (Ln = La, Nd, Sm) [577–581], was also established as K_{2}NiF_{4} structure. The interlayer polarization was verified to influence the microstructure and internal stress, and the complete structure information of SrLn_{2}Al_{2}O_{7} ceramics was obtained by TEM. Solid solution of (Sr_{1−x}Ca_{x})_{2}TiO_{4} [582], Sr_{2}Ti_{1−x}Sn_{x}O_{4} [583], Sr_{2}[Ti_{1−x}(Al_{0.5}Nb_{0.5})_{x}]O_{4} [584], and (Sr_{1−3x/2}La_{x})_{2}Ti_{1−y}Ce_{y}O_{4} [585] was prepared to reduce the large τ_{f} value of Sr_{2}TiO_{4}. Moreover, Sr_{2}CeO_{4} was obtained by Dai and Zuo [586], and the substitution of Ti^{4+} for Ce^{4+} in Sr_{2}CeO_{4} generated a ceramic with excellent properties of \varepsilon_{r} \approx 20.7, \ Q \times f \ value \approx 115,550 \ GHz, and \tau_{f} \approx –1.8 \ ppm/\degree C.

2.6 Other system and machine learning in MWDCs

Although the pseudo phase diagrams contain various primary systems, some ceramics such as CeO_{2}, MgAl_{2}O_{4}, Ca_{3}Ln_{2}W_{2}O_{12}, and Ln_{2}MoO_{6} \ (Ln = La, Y) do not classify. It is difficult to arrange those ceramics to any phase diagram and the relevant reports are relatively less, and thus, the investigations about the mentioned ceramics are listed in this section. Ce_{0.75}Y_{0.25}O_{1.875} ceramic was indexed as CeO_{2} phase, and the grain size changed from 0.64 to 1.23 μm contributing to a higher \ Q \times f \ value [587]. The \tau_{f} value
of (1–x)Bi2(Li0.5Ta1.5)O7–xTiO2 was tuned to –1.45 ppm/℃ with x = 0.04 [588]. 0.875CeO2–0.125TiO2 composition possessed properties of εr ≈ 27.38, Q×f value ≈ 12,950 GHz, and τf ≈ –2.49 ppm/℃, which could meet the criterion of practical application [589]. MgAl2O4 transparent ceramic was designed and optimal microwave dielectric properties were obtained: εr ≈ 8.2, Q×f value ≈ 110,510 GHz, and τf ≈ –74.1 ppm/℃ [590]. The (Mg0.5Ti0.4)3+ for Al3+ in MgAl2O4 could reduce the sintering temperature approximately 200 ℃ due to the less concentration of the Al–O bond [591]. Vibrational spectroscopy and microwave dielectric properties of Ca3Ln2W2O12 (Ln = La, Sm) were analyzed by Liu and Song [592], and the εr of those two phases were 18.7 and 19.5. Ln2MoO6 (Ln = La, Y) ceramics possessed a relative permittivity of 14.1–17.1, and the quality factor was 67,090 GHz for La2MoO6 and 27,760 GHz for Y2MoO6, respectively [593].

In the wake of the update of computer science, date-driven approaches including data mining and machine learning have been applied in many disciplines for obtaining the obscure quantitative relationships. For material science, machine learning was used to realize the property prediction, composition optimization, and experimental design [594–600]. Qin et al. [601] employed five commonly-used algorithms with 32 intrinsic chemical, structural, and thermodynamic features for modeling to predict low permittivity materials, where a database of 3300 materials has not been reported and the distribution of permittivity in virtual space of materials was shown in Fig. 29. Quantitative prediction of the Q×f value of gillespite-type ACuSi4O10 (A = Ca, Sr, Ba) ceramics was obtained by machine learning, and the results of (Ca0.8Sr0.2)CuSi4O10 and (Ba1.5Sr0.5)CuSi4O10 ceramics matched well with the experimental Q×f value, as shown in Fig. 30 [602].

3 Conclusions and further outlook

MWDCs with a suitable permittivity, low dielectric loss, and temperature stability are a perpetual pursuit for researchers. Those ceramics offer technoeconomic advantages including integration, lightweight, and reliability. With the continuous exploration, significant progress is presently being made in designing new compounds, analyzing the polarization mechanism.

![Fig. 29](https://example.com/Fig29.png)
along with the origin of dielectric loss, and predicting the microwave dielectric properties by theoretical model of machine learning. The relevant computational and experimental methods currently used to probe, predict, and understand intrinsic mechanisms are covered in this review. Because target ceramic system and their associated investigations are so diverse, we provide a brief classification on the composition of ceramics using pseudo phase diagram. The exploration of substitution of the given ceramics or new compounds is listed briefly following the pseudo phase diagram. Experimentally, it appears that substitution and composite ceramics are the most common used methods to optimize the microwave dielectric properties for a given system (reduce dielectric loss or adjust the $\tau_f$ value to near zero). The previous doping researches are concentrated on single ion substitution, while more development of the co-doping (group of two aliovalent cations with a certain mole ratio) appears recently. For the probe of new dielectric materials, the new system usually belongs to germanate and gallate, besides the familiar system of silicate, titanate, niobate, and tantalate. Comparing with conventional solid state reaction method, fabrication techniques containing solution-processed sol–gel method, high energy ball milling method, spark plasma sintering, and microwave sintering have been demonstrated as the promising approaches to improve the properties or sintering behaviors so far. Providing the atmosphere with the volatile element in the sintering procession is a valid method to reduce the pores. Multi-layer ceramic architecture has been verified as a design for temperature-stable ceramics, and the wide application for more system or in the industry is waiting for the exploration.

The influence factor of microwave dielectric properties evolves extrinsic and intrinsic parts. The defects such as porosity, microstructure, and secondary phase are related to the relative density and grain size, which are extrinsic factors. Those results of a unique ceramics can be easily obtained by XRD and SEM, while the investigation of dielectric responded mechanism of intrinsic part is difficult due to the restrain of characterization techniques and the lack of general theory. Theoretically, from Clausius–Mossotti equation, packing fraction, cation valence, distortion of octahedron to the combination of P–V–L theory, lattice dynamics, and THz time-domain spectroscopy with the first-principles calculation, the intrinsic mechanism for MWDCs is gradually created. Recent efforts to employ P–V–L theory and infrared reflectivity spectra to understanding the intrinsic mechanism seem to be an easy and potential approach to draw conclusions for prediction the microwave dielectric properties. However, the development of “try and error” situation in experiments is a long-term procession. Toward this state end, greater fundamental understanding of dielectric response mechanism and increased practical performance metrics are required. The experimental trials and theoretical calculation serve as a database of MWDCs, and then, the machine learning is applied to predict new materials and their microwave dielectric properties. There has been an emerging trend about machine learning to provide new insight to draw a general conclusion to verify the effect of each factor on the variation of microwave dielectric properties. Challenges remain in the reconciliation of conclusion between existing theoretical approaches, the evaluation of P–V–L theory on microwave dielectric properties, and the advancement of first-principles calculation for describing the state of bond. Based on the theoretical analysis of MWDCs and the careful control of extrinsic influence, more comprehensive application-specific analyses to justify their adoption in electronic market may be able to complete.

While there is always a need for fundamental research,
the acceleration of the commercial application of new materials and property optimized ceramics is another persistent target for researchers. This includes ending the limitation of currently available system and exploration materials with stable and excellent properties for electronic market. For example, alternative materials with satisfied microwave dielectric properties equal to perovskite ceramics are required in the industry. With the development of 5G and 6G, there is an urgent need for ceramics with ultra-low dielectric constant (< 5), low dielectric loss, and excellent temperature-stability in high frequencies. The compounds of borate, aluminate, silicate, and fluoride with low polarization should take into consideration as promising candidate. It may be a direction for discovering composite materials consisted of ceramics and organics. Meanwhile, reducing the sintering temperature of ceramics for meeting the need of LTCC is a highly challenging issue owing to its advantages in fabrication of electronic devices. On the other hand, the repeatability of microwave dielectric properties and the normalized evaluation method should be emphasized. The advancement of preparation method with simplified procedures should be taken into consideration as well. The investigation combining the discussion of the performance of a simulated and fabricated device with the analysis of fundamental mechanism of structure–property relationship should be more popularized to provide an entire and systematical exploration. As a summary, the microwave dielectric properties listed in the references are presented in Figs. 31(a) and 31(b).

Lastly, we hope this brief progress report helps to understand the recent experimental methods and suggests an insight to take a new research direction for MWDCs.

Fig. 31 Microwave dielectric properties of listed references: (a) \( \varepsilon_r \) versus \( Q\times f \) values and (b) \( \varepsilon_r \) versus \( \tau_f \) values.

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References

[1] Sebastian M T. Dielectric Materials for Wireless Communication. London, UK: Elsevier, 2008.
[2] Ohsato H, Tsunooka T, Sugiyama T, et al. Forsterite ceramics for millimeterwave dielectrics. J Electroceramics 2006, 17: 445–450.
[3] Zhang J, Luo Y, Yue ZX, et al. High-\( Q \) and temperature-stable microwave dielectrics in layer cofired \( \text{Zn_{1.01}Nb_2O_6} / \text{TiO_2/Zn_{1.01}Nb_2O_6} \) ceramic architectures. J Am Ceram Soc 2019, 102: 342–350.
[4] Zhang J, Yue ZX, Luo Y, et al. \( \text{MgTiO}_3/\text{TiO}_2/\text{MgTiO}_3 \): An ultrahigh-\( Q \) and temperature-stable microwave dielectric ceramic through cofired trilayer architecture. Ceram Int 2018, 44: 21000–21003.
[5] Luo WJ, Li LX, Zhang BW, et al. The mechanism of microwave response in layer-cofired \( \text{Zn}_3\text{Nb}_2\text{O}_8-\text{TiO}_2-\text{Zn}_3\text{Nb}_2\text{O}_8 \) ceramic architecture. J Alloys Compd 2020, 824: 153978.
[6] Levine BF. Bond susceptibilities and ionicities in complex crystal structures. J Chem Phys 1973, 59: 1463–1486.
[7] Sebastian MT, Jantunen H. Low loss dielectric materials for LTCC applications: A review. Int Mater Rev 2008, 53: 57–90.
[8] Sebastian MT, Wang H, Jantunen H. Low temperature co-fired ceramics with ultra-low sintering temperature: A review. Curr Opin Solid State Mater Sci 2016, 20: 151–170.
[9] Zhou D, Pang LX, Wang DW, et al. \( \text{BiVO}_4 \) based high \( k \) microwave dielectric materials: A review. J Mater Chem C 2018, 6: 9290–9313.
[10] Fang Y, Li L, Xiao Q, et al. Preparation and microwave dielectric properties of cristobalite ceramics. Ceram Int 2012, 38: 4511–4515.
[11] Li F, Liu P, Ruan P, et al. Microwave dielectric properties of (1−x)SiO2−xTiO2 ceramics. *Ceram Int* 2015, **41**: S582–S587.

[12] Sreekanth Chakradhar RP, Nagabhushana BM, Chandrappa GT, et al. Solution combustion derived nanocrystalline macroporous wollastonite ceramics. *Mater Chem Phys* 2006, **95**: 169–175.

[13] Wang HP, Zhang QL, Yang H, et al. Synthesis and microwave dielectric properties of CaSiO3 nanopowder by the sol–gel process. *Ceram Int* 2008, **34**: 1405–1408.

[14] Sun HP, Zhang QL, Yang H, et al. (Ca1−xMg)xSiO3: A low-permittivity microwave dielectric ceramic system. *Mater Sci Eng B* 2007, **138**: 46–50.

[15] Wang HP, Chen JM, Yang WY, et al. Effects of Al2O3 addition on the sintering behavior and microwave dielectric properties of CaSiO3 ceramics. *J Eur Ceram Soc* 2012, **32**: 541–545.

[16] Hu W, Liu HX, Hao H, et al. Influence of Al2O3 addition on the microstructure and microwave dielectric properties of α-CaSiO3 ceramics. *J Mater Sci: Mater Electron* 2015, **26**: 211–216.

[17] Hu W, Liu HX, Hao H, et al. Phase transition, microstructure and microwave dielectric properties of α-CaSiO3 ceramics with SiO2 addition. *J Mater Sci: Mater Electron* 2015, **26**: 1977–1981.

[18] Hu W, Liu HX, Hao H, et al. Influence of TiO2 additive on the microwave dielectric properties of α-CaSiO3–Al2O3 ceramics. *Ceram Int* 2015, **41**: S510–S514.

[19] Ma Q, Wu SP, Jiang C, et al. Microwave dielectric properties of SnO2-doped CaSiO3 ceramics. *Ceram Int* 2013, **39**: 2223–2229.

[20] Joseph T, Sebastian MT. Microwave dielectric properties of alkaline earth orthosilicates Mn2SiO4 (M=Ba,Sr,Ca). *Mater Lett* 2011, **65**: 891–893.

[21] Li LX, Wang YC, Xia WS, et al. Influence of Ca2+ and Mg2+ co-doping on the microstructure and microwave dielectric properties of Sr2MgSi2O7 ceramic. *J Mater Sci* 2015, **40**: 4823–4829.

[22] Liang Z, Han XN, Wang G, et al. Microwave dielectric properties and sintering behaviors of Zn1−xSiO3 ceramics. *J Mater Sci: Mater Electron* 2021, **32**: 517–523.

[23] Liu L, Feng YB, Qiu T, et al. Microstructures and microwave dielectric properties of Mg2SiO4-Ca0.8Sr0.2TiO3 ceramics. *J Mater Sci: Mater Electron* 2015, **26**: 1316–1321.

[24] Weng ZZ, Song CX, Xiong ZX, et al. Microstructure and broadband dielectric properties of Zn2SiO4 ceramics with nano-sized TiO2 addition. *Ceram Int* 2019, **45**: 13251–13256.

[25] Lai YM, Zeng YM, Han J, et al. Structure dependence of microwave dielectric properties in Zn2−xSiO4−xCuO ceramics. *J Eur Ceram Soc* 2021, **41**: 2602–2609.

[26] Li CC, Yin CZ, Chen JQ, et al. Crystal structure and microwave dielectric properties of Sm2SiO5 ceramics. *J Alloys Compd* 2012, **517**: 169–175.

[27] Xiao M, Wei YS, Zhang P. The effect of sintering temperature on the crystal structure and microwave dielectric properties of CaCoSi2O6 ceramics. *Mater Lett* 2018, **213**: 19–23.

[28] Liu YM, Su H, Wang G, et al. Improved microwave dielectric properties of CaMgSi2O6 ceramics through CuO doping. *J Alloys Compd* 2019, **772**: 40–48.

[29] Xiao M, Wei YS, Zhang P. The effect of sintering temperature on the crystal structure and microwave dielectric properties of CaCoSi2O6 ceramics. *Mater Lett* 2018, **213**: 19–23.

[30] Cai CY, Chen XQ, Li H, et al. Microwave dielectric properties of Ca1−xSr2MgSi2O6 ceramics. *Ceram Int* 2020, **46**: 27679–27685.

[31] Chen XQ, Li H, Zhang PC, et al. Phase composition, microstructure, and microwave dielectric properties of CaMnSi2O6 ceramics. *Ceram Int* 2021, **47**: 4083–4089.

[32] Li CC, Yin CZ, Chen JQ, et al. Crystal structure and dielectric properties of germanate melilites Ba2MGe2O7 (M=Mg and Zn) with low permittivity. *J Eur Ceram Soc* 2018, **38**: 5246–5251.

[33] Shin KS, Xie MQ, Song XQ, Lei W, et al. Effect of Ca2+ substitution on the structure, microstructure, and microwave dielectric properties of Sr2Al2SiO7 ceramic. *J Am Ceram Soc* 2013, **96**: 3842–3848.

[34] Shin KS, Xie MQ, Song XQ, Lei W, et al. Sintering behaviour, lattice energy and microwave dielectric properties of Sr2Al2SiO7 ceramics. *Mater Lett* 2018, **213**: 19–23.

[35] Xiao M, Wei YS, Zhang P. The effect of sintering temperature on the crystal structure and microwave dielectric properties of CaCoSi2O6 ceramics. *Mater Lett* 2018, **213**: 19–23.
melilite-type BaCo$_2$Si$_2$O$_7$ ceramics. *Mater Res Express* 2020, 6: 126322.

[43] Song XQ, Lu WZ, Lou YH, *et al.* Synthesis, lattice energy and microwave dielectric properties of BaCu$_2$CoSi$_2$O$_9$ ceramics. *J Eur Ceram Soc* 2020, 40: 3035–3041.

[44] Song XQ, Lou WY, Lu WZ, *et al.* Crystal structure, lattice energy and microwave dielectric properties of melilite-type Ba$_{0.5}$Sr$_{0.5}$Cu$_2$Si$_2$O$_9$ solid solutions. *J Alloys Compd* 2020, 835: 155340.

[45] Wu SP, Chen DF, Mei YX, *et al.* Synthesis and microwave dielectric properties of Ca$_3$SnSi$_2$O$_9$ ceramics. *J Alloys Compd* 2012, 521: 8–11.

[46] Bafrooei HB, Liu B, Su WT, *et al.* Ca$_3$MgSi$_2$O$_7$: Novel low-permittivity microwave dielectric ceramics for 5G application. *Mater Lett* 2020, 263: 127248.

[47] Song XQ, Lei W, Wang F, *et al.* Phase evolution, crystal structure, and microwave dielectric properties of gillespite-type ceramics. *J Am Ceram Soc* 2021, 104: 1740–1749.

[48] Li C, Ding SH, Zhang Y, *et al.* Effects of Ni$^{2+}$ substitution on the crystal structure, bond valence, and microwave dielectric properties of BaAl$_2$Ni$_2$Si$_2$O$_{8-x}$ ceramics. *J Eur Ceram Soc* 2021, 41: 2610–2616.

[49] Li C, Ding SH, Song TX, *et al.* Structure and microwave dielectric properties of BaAl$_{2-x}$Li$_x$Si$_2$O$_{8-x}$ ceramics. *Ceram Int* 2021, 47: 4895–4904.

[50] Felsche J. Rare earth silicates with the apatite structure. *J Solid State Chem* 1972, 5: 266–275.

[51] Manu KM, Karthik C, Leu LC, *et al.* Crystal structure and microwave dielectric properties of LiRE$_2$(SO$_4$)$_3$O$_2$ ceramics (RE = La, Pr, Nd, Eu, Gd, and Er). *J Am Ceram Soc* 2013, 96: 1504–1511.

[52] Thomas S, Sebastian MT. Microwave dielectric properties of Sr(RE)$_2$Si$_2$O$_7$ (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, and Y) ceramics. *J Am Ceram Soc* 2009, 92: 2975–2981.

[53] Du K, Lou WY, Song XQ, *et al.* Correlation between crystal structure and microwave dielectric properties of CaRE$_2$Si$_2$O$_7$ (RE = La, Nd, Sm, and Er). *J Mater Sci: Mater Electron* 2020, 31: 3274–3280.

[54] Ao LY, Tang Y, Li J, *et al.* Structure characterization and microwave dielectric properties of LiGa$_5$O$_8$ ceramic with low-$\varepsilon_r$ and low loss. *J Eur Ceram Soc* 2020, 40: 5498–5503.

[55] Ao LY, Li J, Tang Y, *et al.* Structure, far-infrared reflectance spectra, and microwave dielectric properties of Ba$_2$MgAl$_2$O$_6$ (M = Bi, La) ceramics. *Ceram Int* 2021, 47: 11899–11905.

[56] Li FH, Tang Y, Li J, *et al.* Effect of A-site cation on crystal structure and microwave dielectric properties of MgGeO$_3$ (A = Ba, Sr) ceramics. *J Eur Ceram Soc* 2021, 41: 4153–4159.

[57] Wang Y, Tang Y, Li J, *et al.* A$_7$Y$_3$Ge$_2$O$_{12}$ (A = Ca, Mg): Two novel microwave dielectric ceramics with contrasting $\tau_f$ and $Q_f$. *J Eur Ceram Soc* 2020, 40: 3989–3995.

[58] Lou WC, Song KX, Hussain F, *et al.* Bond characteristics and microwave dielectric properties of (Li$_{1/2}$Ga$_{1/2}$)$_x$ doped Mg$_2$Al$_2$O$_4$ ceramics. *Ceram Int* 2020, 46: 28631–28638.

[59] Wang Y, Tang Y, Li J, *et al.* Microwave dielectric properties of silico-carnotite Ca$_2$M$_2$Si$_2$O$_7$ (M = Yb, Y) ceramics synthesized via high energy ball milling. *Ceram Int* 2021, 47: 4831–4837.

[60] Su CX, Fang L, Ao LY, *et al.* Structure, Raman spectra and microwave dielectric properties of novel garnet-type Ca$_3$MgZrGe$_3$O$_7$ (M = Co, Zn) ceramics. *Asian Ceram Soc* 2021, 9: 424–432.

[61] Zhai YF, Tang Y, Li J, *et al.* Structure, Raman spectra and properties of two low-$\varepsilon$ microwave dielectric ceramics Ca$_2$B$_2$Ge$_2$O$_7$ (B = Al, Ga). *Ceram Int* 2020, 46: 28710–28715.

[62] Su CX, Ao LY, Zhai YF, *et al.* Novel low-permittivity microwave dielectric ceramics in garnet-type Ca$_2$ZrGe$_2$O$_7$. *Mater Lett* 2020, 275: 128149.

[63] Li J, Tang Y, Zhang ZW, *et al.* Two novel garnet Sr$_x$B$_2$Ge$_2$O$_7$ (B = Yb, Ho) microwave dielectric ceramics with low permittivity and high Q. *J Eur Ceram Soc* 2021, 41: 1317–1323.

[64] Tan ZY, Song KX, Bafrooei HB, *et al.* The effects of TiO$_2$ addition on microwave dielectric properties of Y$_2$MgAl$_2$Si$_2$O$_7$ ceramic for 5G application. *Ceram Int* 2020, 46: 15665–15669.

[65] Yang AH, Tang Y, Li J, *et al.* Structure and infrared reflectivity spectra of novel Mg$_2$Ga$_2$Ge$_2$O$_8$ microwave dielectric ceramic with high Q. *Ceram Int* 2021, 47: 2450–2455.

[66] Su CX, Ao LY, Zhang ZW, *et al.* Crystal structure, Raman spectra and microwave dielectric properties of novel temperature-stable LiYbSiO$_4$ ceramics. *Ceram Int* 2020, 46: 19996–20003.

[67] Du K, Wang F, Song XQ, *et al.* Correlation between crystal structure and dielectric characteristics of Ti$^{4+}$ substituted CaSnSiO$_3$ ceramics. *J Eur Ceram Soc* 2021, 41: 2568–2578.

[68] Du K, Fan J, Lou WY, *et al.* Crystal structure, phase compositions, and microwave dielectric properties of malayaite-type Ca$_{1-x}$Sr$_x$SnSiO$_3$ ceramics. *J Am Ceram Soc* 2020, 103: 6369–6377.

[69] Du K, Song XQ, Zou ZY, *et al.* Improved microwave dielectric properties of novel low-permittivity Sn-doped Ca$_2$Hf$_2$Si$_2$O$_7$ ceramics. *Mater Res Bull* 2020, 129: 110887.

[70] Templeton A, Wang XR, Penn SJ, *et al.* Microwave dielectric loss of titanium oxide. *J Am Ceram Soc* 2000, 83: 95–100.

[71] Kim ES, Kang DH. Relationships between crystal structure and microwave dielectric properties of (Zr$_{1-x}$Ti$_x$)$_2$O$_3$–TiO$_2$ (B$^{5+}$ = Nb, Ta) ceramics. *Ceram Int* 2008, 34: 883–888.

[72] Baumgarte A, Blachnik R. Phase relations in the system titaniumoxide-diniobium-zinc-hexoxide. *Mater Res Bull* 1992, 27: 1287–1294.
Preparation, J Adv Ceram 2021, 10(5): 885–932

[73] Yang HY, Zhang SR, Yang HC, et al. Usage of P–V–L bond theory in studying the structural/property regulation of microwave dielectric ceramics: A review. Inorg Chem Front 2020, 7: 4711–4753.

[74] Liao QW, Li LX, Ding X, et al. A new temperature stable microwave dielectric material Mg0.95Zn0.05TiNb2O8. J Am Ceram Soc 2012, 95: 1501–1503.

[75] Yang HY, Li EZ, Duan SX, et al. Structure, microwave properties and low temperature sintering of Ta2O5 and Co2O3 codoped Zn0.5Ti0.5NbO4 ceramics. Mater Chem Phys 2017, 199: 43–53.

[76] Li LX, Cai HC, Yu XX, et al. Structure analysis and microwave dielectric properties of Zn1−xSnxTi1.92Nb2O10 ceramics. J Alloys Compd 2014, 584: 315–321.

[77] Yang HY, Zhang SR, Yang HC, et al. Structural evolution and microwave dielectric properties of xZn0.5Sn0.5Nb2O4−(1−x)Zr0.5Sn0.5Ti0.5O2 ceramics. Inorg Chem 2018, 57: 8264–8275.

[78] Yang HY, Zhang SR, Yang HC, et al. Effects of ZrO2 substitution on crystal structure and microwave dielectric properties of Zn0.15Nb0.85(Ti1−xZr0.5)xO2 ceramics. Ceram Int 2018, 44: 22710–22717.

[79] Chen YW, Zhang SR, Yang HY, et al. Bond ionicity, lattice energy and structural evolution of Ta substituted 0.15ZnO–0.15Nb2O5–0.55TiO2 dielectric ceramics. Ceram Int 2019, 45: 8832–8839.

[80] Ramarao SD, Murthy VRK. Crystal structure refinement and microwave dielectric properties of new low dielectric loss AZrNb2O8 (A: Mn, Zn, Mg and Co) ceramics. Scripta Mater 2013, 69: 274–277.

[81] Jiang XS, Pan HL, Feng ZB, et al. Characterization of microwave dielectric materials NiZrNbO3 based on the chemical bond theory. J Mater Sci: Mater Electron 2016, 27: 10963–10969.

[82] Pan HL, Feng ZB, Bi JX, et al. Preparation, characterization, and dielectric properties of wolframite-structure MnZrNbO3 ceramics at microwave frequency. J Alloys Compd 2015, 651: 440–444.

[83] Xia WS, Yang FY, Zhang GY, et al. New low-dielectric-loss NiZrNbO3 ceramics for microwave application. J Alloys Compd 2016, 656: 470–475.

[84] Wu HT, Bi JX, Wang HJ, et al. Sintering characteristics and microwave dielectric properties of low loss ZnZrNb2O8 ceramics achieved by reaction sintering process. J Mater Sci: Mater Electron 2016, 27: 5670–5675.

[85] Wu HT, Feng ZB, Mei QJ, et al. Correlations of crystal structure, bond energy and microwave dielectric properties of A2ZrNbO3 (A = Zn, Co, Mg, Mn) ceramics. J Alloys Compd 2015, 648: 368–373.

[86] Cheng Y, Zuo RZ, Lv Y. Preparation and microwave dielectric properties of low-loss MgZrNb2O8 ceramics. Ceram Int 2013, 39: 8681–8685.

[87] Yang HY, Zhang SR, Li YP, et al. Investigations of dielectric properties of wolframite A0.5Zr0.5NbO3 ceramics by bond theory and far-infrared spectroscopy. Ceram Int 2020, 46: 3688–3694.

[88] Wu HT, Kim ES. Characterization of crystal structure and microwave dielectric properties of A2ZrNbO3 (A = Zn, Co, Mg, Mn) ceramics based on complex bond theory. Ceram Int 2016, 42: 5785–5791.

[89] Zhang Y, Ding SH, Li C, et al. Bond analysis of novel MnZrTaO3 microwave dielectric ceramics with monoclinic structure. J Mater Sci 2020, 55: 8491–8501.

[90] Yang HY, Zhang SR, Yang HC, et al. Structure, phase composition, Raman spectra, and microwave dielectric properties of novel Co0.5Zr3TaO4 ceramics. Ceram Int 2019, 45: 15445–15450.

[91] Xia WS, Zhang LY, Wang Y, et al. Extrinsic effects on microwave dielectric properties of high-Q MgZrTaO3 ceramics. J Mater Sci: Mater Electron 2016, 27: 11325–11330.

[92] Cai HC, Li LX, Sun H, et al. A microwave dielectric material Mg0.95Zn0.05Ta2O5. Mater Lett 2015, 144: 78–81.

[93] Xu J, Li LX, Sun H, et al. Microstructure and microwave dielectric characteristics of (Zn1−xCo)xZrNb2O8 ceramics. J Mater Sci: Mater Electron 2015, 26: 8954–8959.

[94] Yang ZL, Pan HL, Jiang XS, et al. Characterization of low loss microwave dielectric materials Zn0.92Co0.08ZrNb2O8 based on the complex chemical bond theory. J Mater Sci: Mater Electron 2017, 28: 1597–1604.

[95] Pan HL, Liu QQ, Zhang YH, et al. Crystal structure and microwave dielectric characteristics of Co-substituted Zn1−xCoZrNb2O8 (0 ≤ x ≤ 0.1) ceramics. RSC Adv 2016, 6: 86889–86903.

[96] Wang SY, Xiao BY, Li JY, et al. Structural evolution, Raman spectra, and microwave dielectric properties of Zr-substituted ZnTiTaO3 ceramics. J Mater Sci: Mater Electron 2020, 31: 10298–10305.

[97] Li LX, Zhang S, Ye J, et al. Crystal structure and microwave dielectric properties of the low dielectric loss ZnZrSnO3 ceramics. Ceram Int 2016, 42: 9157–9161.

[98] Ye J, Li LX, Li S, et al. A new microwave dielectric material Zn0.95Sn0.05Nb2O5. J Mater Sci: Mater Electron 2016, 27: 97–102.

[99] Xiao M, He SS, Lou J, et al. Structure and microwave dielectric properties of MgZr(Nb1−xSn)x2O6 (0 ≤ x ≤ 0.1) ceramics. J Alloys Compd 2019, 777: 350–357.

[100] Zhao YG, Zhang P. A novel low loss microwave dielectric ceramic ZnZrNb1.5Sn0.5O3 with wolframite structure. J Mater Sci: Mater Electron 2016, 27: 2933–2937.

[101] Li LX, Sun H, Lv X, et al. A new microwave dielectric material ZnZrTa2O5. Mater Lett 2015, 160: 363–365.

[102] Xiao M, He SS, Meng J, et al. Dependence of microwave dielectric properties on the substitution of isovalent composite ion for Nb-site of MgZnNb2−x(Sn0.5W1.5)xO8 (0 ≤ x ≤ 0.15) ceramics. J Mater Sci: Mater Electron 2019, 30: 18280–18286.
bond energy and the microwave dielectric properties of non-stoichiometric MgZrNb$_{2-x}$O$_{6}$ ceramics. *Mater Chem Phys* 2020, **242**: 122412.

[104] Zhang J, Zuo RZ, Cheng Y. Relationship of the structural phase transition and microwave dielectric properties in MgZrNb$_{2-x}$Ti$_{2}$O$_{7}$ ceramics. *Ceram Int* 2016, **42**: 7681–7689.

[105] Lyu XS, Li LX, Zhang S, *et al.* Crystal structure and microwave dielectric properties of novel (1−x)ZnZrNb$_{2}$O$_{6}$−xTiO$_{2}$ ceramics. *Mater Lett* 2016, **171**: 129–132.

[106] Wu HT, Guo JD, Bi JX, *et al.* Effect of H$_{3}$BO$_{3}$ addition on the sintering behavior and microwave dielectric properties of wolframite-type MgZrNb$_{2}$O$_{6}$ ceramics. *J Alloys Compd* 2016, **661**: 535–540.

[107] Wu HT, Mei QJ, Xing CF, *et al.* Effects of B$_{2}$O$_{3}$ addition on sintering behavior and microwave dielectric properties of ixiolite-structure ZnTiNb$_{2}$O$_{8}$ ceramics. *J Alloys Compd* 2016, **679**: 26–31.

[108] Bi JX, Xing CF, Jiang XS, *et al.* Effect of H$_{3}$BO$_{3}$ on sintering behavior and microwave dielectric properties of monoclinic structure ZnZrNb$_{2}$O$_{6}$ ceramics. *J Mater Sci: Mater Electron* 2016, **27**: 8055–8061.

[109] Liao QW, Li LX, Ren X, *et al.* A new microwave dielectric material Ni$_{0.5}$Ti$_{0.5}$NbO$_{4}$. *Mater Lett* 2012, **89**: 351–353.

[110] Tseng CF. Microwave dielectric properties of a new Cu$_{0.5}$Ti$_{0.5}$NbO$_{4}$ ceramics. *J Eur Ceram Soc* 2015, **35**: 383–387.

[111] Tseng CF. Microwave dielectric properties of low loss microwave dielectric ceramics: A$_{0.5}$Ti$_{0.5}$NbO$_{4}$ (A = Zn, Co). *J Eur Ceram Soc* 2014, **34**: 3641–3648.

[112] Zhang Y, Zhang YC. Microwave dielectric properties of sol–gel derived CoTiNb$_{2}$O$_{8}$ ceramics. *J Alloys Compd* 2016, **683**: 86–91.

[113] Chen TK, Ma WB, Sun QC, *et al.* The microwave dielectric properties of (Ni,Zn)$_{0.5}$Ti$_{0.5}$NbO$_{4}$ solid solution. *Mater Lett* 2013, **113**: 111–113.

[114] Zhang Y, Zhang YC, Xiang MQ. Microwave dielectric properties of temperature stable CoTiNb$_{2}$O$_{6}$–CoNb$_{2}$O$_{4}$ composite ceramics. *Mater Lett* 2016, **178**: 175–177.

[115] Zhang Y, Ding SH, You L, *et al.* Temperature stable microwave dielectric ceramic CoTiNb$_{2}$O$_{6}$–Zn$_{1.0}$Nb$_{2}$O$_{4}$ with ultra-low dielectric loss. *J Electron Mater* 2019, **48**: 867–872.

[116] Zhang Y, Zhang YC, Xiang MQ. Crystal structure and microwave dielectric properties of Zr-structured CoTiNb$_{2}$O$_{6}$ ceramics. *J Eur Ceram Soc* 2016, **36**: 1945–1951.

[117] Li YY, Lu XC, Zhang Y, *et al.* Characterization of Co$_{0.5}$Ti$_{1-x}$Zr$_{x}$NbO$_{4}$ microwave dielectric ceramics based on structural refinement. *Ceram Int* 2017, **43**: 11516–11522.

[118] Wang J, Lu XC, Li YY, *et al.* Correlations between microwave dielectric properties and crystal structures of Sb-doped Co$_{0.5}$Ti$_{0.5}$NbO$_{4}$ ceramics. *Ceram Int* 2020, **46**: 3464–3470.

[119] Kremer RK, Greedan JE. Magnetic ordering in CoTa$_{2}$O$_{6}$ and NiTa$_{2}$O$_{6}$. *J Solid State Chem* 1988, **73**: 579–582.

[120] Reimers JN, Greedan JE, Stager CV, *et al.* Crystal structure and magnetism in Co$_{2}$Sb$_{2}$O$_{7}$ and CoTa$_{2}$O$_{6}$. *J Solid State Chem* 1989, **83**: 20–30.

[121] Yang HY, Zhang SR, Chen YW, *et al.* Crystal chemistry, Raman spectra, and bond characteristics of rutile-type Co$_{0.5}$Ti$_{0.5}$TaO$_{4}$ microwave dielectric ceramics. *Inorg Chem* 2019, **58**: 968–976.

[122] Kumada N, Koike N, Nakano K, *et al.* Synthesis of rutile-type solid solution Ni$_{1-y}$Co$_{y}$Ti(Nb$_{1-x}$Ta$_{x}$)$_{2}$O$_{6}$ (0 ≤ x ≤ 1, 0 ≤ y ≤ 1) and its optical property. *J Asian Ceram Soc* 2017, **5**: 284–289.

[123] Li EZ, Wen QY, Yang HC, *et al.* Novel temperature stable NiSnTa$_{2}$O$_{8}$ microwave dielectric ceramics with trirutile structure. *Ceram Int* 2020, **46**: 6079–6084.

[124] Baumgarte A, Blachnik R. Isothermal sections in the systems ZnO–AO$_{2}$–Nb$_{2}$O$_{5}$ (A=Ti,Zr,Sn) at 1473 K. *J Alloys Compd* 1994, **210**: 75–81.

[125] Huan ZL, Sun QC, Ma WB, *et al.* Crystal structure and microwave dielectric properties of (Zn$_{1-x}$Co)$_{2}$TiO$_{3}$O$_{8}$ ceramics. *J Alloys Compd* 2013, **551**: 630–635.

[126] Li LX, Sun H, Lv X, *et al.* Microstructure and microwave dielectric characteristics of the Ca$_{2}$Zn$_{3-x}$Ti$_{14-x}$O$_{32}$ temperature stable ceramics. *J Mater Sci: Mater Electron* 2016, **27**: 126–133.

[127] Liao QW, Li LX, Zhang P, *et al.* Correlation of crystal structure and microwave dielectric properties for Zn(Ti$_{1-x}$Sn$_{x}$)$_{2}$O$_{7}$ ceramics. *Mater Sci Eng: B* 2011, **176**: 41–44.

[128] Liao QW, Li LX, Ding X. Phase constitution, structure analysis and microwave dielectric properties of Zn$_{0.5}$Ti$_{1.5}$Zr$_{0.5}$NbO$_{4}$ ceramics. *Solid State Sci* 2012, **14**: 1385–1391.

[129] Liao QW, Li LX, Zhang P, *et al.* Correlation of crystal structure and microwave dielectric properties for ZnTi(Nb$_{1-x}$Ta$_{x}$)$_{2}$O$_{6}$ ceramics. *Solid State Sci* 2011, **13**: 1201–1204.

[130] Liao QW, Li LX, Ren X, *et al.* New low-loss microwave dielectric material ZnTiNbTaO$_{5}$. *J Am Ceram Soc* 2011, **94**: 3237–3240.

[131] Park JH, Choi YJ, Nahm S, *et al.* Crystal structure and microwave dielectric properties of ZnTi(Nb$_{1-x}$Ta$_{x}$)$_{2}$O$_{8}$ ceramics. *J Alloys Compd* 2011, **509**: 6908–6912.

[132] Liao QW, Li LX. Structural dependence of microwave dielectric characteristics of ixiolite-structure ZnTiNb$_{2}$O$_{8}$ ceramics. *Ceram Int* 2011, **37**: 41–44.

[133] Ruan P, Liu P, Guo BC, *et al.* Microwave dielectric properties of ZnO–Nb$_{2}$O$_{5}$–TiO$_{2}$ ceramics prepared by reaction-sintering process. *J Mater Sci: Mater Electron* 2016, **27**: 4201–4205.

[134] Bafrooei HB, Feizpour M, Sayyadi-Shahraki A, *et al.* High-performance ZnTiNb$_{2}$O$_{8}$ microwave dielectric
ceramics produced from ZnNB2O6–TiO2 nano powders. J Alloys Compd 2020, 834: 155082.

[135] Luo WJ, Li LX, Yu SH, et al. Bond theory, terahertz spectra, and dielectric studies in donor-acceptor (Nb–Al) substituted ZnTiNB6O15 system. J Am Ceram Soc 2019, 102: 4621–4620.

[136] Mei QJ, Li CY, Guo JD, et al. Synthesis, characterization, and microwave dielectric properties of ternary-phase iliolite-structure MgTiNB6O15 ceramics. Mater Lett 2015, 145: 7–10.

[137] Lee HJ, Kim IT, Hong KS. Dielectric properties of AB2O6 compounds at microwave frequencies (A = Ca, Mg, Mn, Co, Ni, Zn, and B = Nb, Ta). Jpn J Appl Phys 1997, 36: L1318–L1320.

[138] Blasse G Qualitative approach to the structural differences between some mixed metal oxides containing Sh5+, Nb6+ and Ta5+. J Inorg Nucl Chem 1964, 26: 1191–1199.

[139] Lee HJ, Hong KS, Kim SJ, et al. Dielectric properties of MNB2O6 compounds (where M = Ca, Mn, Co, Ni, or Zn). Mater Res Bull 1997, 32: 847–855.

[140] Pullar RC, Breeze JD, Alford NM. Characterization and microwave dielectric properties of M2+NB6O15 ceramics. J Am Ceram Soc 2005, 88: 2466–2471.

[141] Chen YC, Weng MZ, Chang KC. Effect of sintering temperature and time on microwave dielectric properties of CaNB2O6 ceramics. J Mater Sci: Mater Electron 2014, 25: 844–851.

[142] Wu HT, Jiang YS, Wu WB, et al. Synthesis and microwave dielectric properties of columbite-structure MgNB2O6 ceramics by aqueous sol–gel technique. J Electroceramics 2012, 28: 191–196.

[143] Xia WS, Li LX, Ji LJ, et al. Phase evolution, bond valence and microwave characterization of (Zn1−xMx)Ta2O6 ceramics. Mater Lett 2012, 66: 296–298.

[144] Xia WS, Li LX, Ning PF, et al. Relationship between bond ionicity, lattice energy, and microwave dielectric properties of ZnTa1−xNB2O6 ceramics. J Am Ceram Soc 2012, 95: 2587–2592.

[145] Xia WS, Zhang GY, Shi LW, et al. Enhanced microwave dielectric properties of ZnTa2O6 ceramics with Sbx+ ion substitution. Mater Lett 2014, 124: 64–66.

[146] Sp W, Jh L. Mg-substituted ZnNB2O6–TiO2 composite ceramics for RF/microwaves ceramic capacitors. J Alloys Compd 2011, 509: 8126–8129.

[147] Fu BJ, Zhang YC, Yue H. Microwave dielectric properties of (1−x)ZnTa2O6–xMgNb2O6 ceramics. Ceram Int 2013, 39: 3789–3793.

[148] Zhang YC, You CY, Fu BJ, et al. Tailoring of microwave dielectric properties in (1−x)ZnTa2O6–xNiNb2O6 ceramics. Ferroelectrics 2013, 451: 54–61.

[149] Yu SQ, Tang B, Zhang SR, et al. Phase structure and microwave dielectric properties of Mn-doped (1−x)ZrTi2O6–xZnNB6O15 ceramics. J Mater Sci: Mater Electron 2013, 24: 418–422.

[150] Liu XC, Deng JP. Phase structure and dielectric property of the ZnNB2O6–(Mg0.5Zn0.5)TiO3 multphase ceramics. J Mater Sci: Mater Electron 2012, 23: 506–510.

[151] Yan Z, Huang JL, Gu YJ, et al. Effects of V2O5 addition on the microstructure and microwave dielectric properties of ZnNB6O15 ceramics. Adv Mat Res 2012, 476–478: 940–943.

[152] Wu HT, Jiang YS, Yue YL. Low-temperature synthesis and microwave dielectric properties of trirutile-structure MgTa2O6 ceramics by aqueous sol–gel process. Ceram Int 2012, 38: 5151–5156.

[153] Liu LT, Matushevich A, Garg C, et al. The dominance of paramagnetic loss in microwave dielectric ceramics at cryogenic temperatures. Appl Phys Lett 2012, 101: 252901.

[154] Park JH, Nam S, Park JG. Crystal structure and microwave dielectric properties of (1−x)ZnTa2O6–xTiO2 ceramics. J Alloys Compd 2012, 537: 221–226.

[155] Shahghioli N, Asadian K, Ebadzadeh T. Microstructural and microwave dielectric properties of ZnNB6O15 ceramics prepared through microwave sintering. Ceram Int 2014, 40: 14335–14339.

[156] Yang HY, Zhang SR, Yang HC, et al. Intrinsic dielectric properties of columbite ZnNB6O15 ceramics studied by P–V–L bond theory and Infrared spectroscopy. J Am Ceram Soc 2019, 102: 5365–5374.

[157] Sebastian MT, Solomon S, Ratheesh R, et al. Preparation, characterization, and microwave properties of RETiNbO6 (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, and Yb) dielectric ceramics. J Am Ceram Soc 2001, 84: 1487–1489.

[158] Surendran KP, Solomon S, Varma MR, et al. Microwave dielectric properties of RETiTaO6 (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al, and In) ceramics. J Mater Res 2002, 17: 2561–2566.

[159] Lei Y, Reaney IM, Liu YC, et al. Microwave dielectric properties and microstructures of RETiNbO6 (RE = La, Sm, and Y). Adv Mat Res 2011, 197–198: 285–289.

[160] Zhang J, Zuo RZ. A novel self-composite property-tunable LaTiNbO6 microwave dielectric ceramic. Mater Res Bull 2016, 83: 568–572.

[161] Zhang J, Zuo RZ. Sintering behavior, structural phase transition, and microwave dielectric properties of La1−xZnTiNbO6+2 ceramics. J Am Ceram Soc 2017, 100: 4362–4368.

[162] Zhang J, Zuo RZ. Phase structural transition and microwave dielectric properties in isovalently substituted La1−xLnTiNbO6 (Ln = Ce, Sm) ceramics. Ceram Int 2017, 43: 7065–7072.

[163] Zhang J, Zuo RZ. Octahedral distortion, phase structural stability, and microwave dielectric properties in equivalently substituted LaTiNbO6 ceramics. J Am Ceram Soc 2017, 100: 5249–5258.

[164] Zhang J, Zuo RZ. Raman scattering and infrared reflectivity study of orthorhombic/moniclinic LaTiNbO6 microwave dielectric ceramics by A/B-site substitution.
[165] John F, Solomon S. Dielectric and optical properties of Ln₃⁺La₂⁺TiNbO₄ (Ln = Ce, Pr, Nd & Sm) ceramics. Phys Lett A 2020, 384: 126731.

[166] Kim DW, Kwon DK, Yoon SH, et al. Microwave dielectric properties of rare-earth ortho-niobates with ferroelasticity. J Am Ceram Soc 2006, 89: 3861–3864.

[167] Zhang P, Song ZK, Wang Y, et al. Effect of ion substitution for Nd³⁺ based on structural characteristic on the microwave dielectric properties of NdNbO₄ ceramic system. J Am Ceram Soc 2014, 97: 976–981.

[168] Song ZK, Zhang P, Wang Y, et al. Improved quality factor of NdNbO₄ microwave dielectric ceramic by Mn²⁺ substitution. J Alloys Compd 2016, 654: 546–549.

[169] Chen YH, Wang H, Pang LX, et al. Effect of Zn²⁺ substitution on sintering behavior and dielectric properties of NdNbO₄ ceramics. Ferroelectrics 2010, 407: 61–68.

[170] Xiao M, Gu QQ, Zhou QZ, et al. Study of the microwave dielectric properties of (La₁−xSmₓ)NbO₄ (x = 0–0.10) ceramics via bond valence and packing fraction. J Am Ceram Soc 2017, 100: 3952–3960.

[171] Zhang P, Zhao YG. Influence of Sm³⁺ substitutions for Nd³⁺ on the microwave dielectric properties of (Nd₁−xSmₓ)NbO₄ (x = 0.02–0.15) ceramics. J Alloys Compd 2016, 654: 240–245.

[172] Zhao YG, Zhang P. Complex chemical bond theory, Raman spectra and microwave dielectric properties of low loss ceramics NdNbO₄−ₓAl₂O₃. J Mater Sci: Mater Electron 2016, 27: 2511–2522.

[173] Zhang P, Zhao YG. New temperature stable (Nd₁−Laₓ)₀.₇₂Nb₀.₹₈O₄ microwave dielectric ceramics. Mater Lett 2015, 161: 620–623.

[174] Zhang P, Zhao YG, Li LX. The correlations among bond ionicity, lattice energy and microwave dielectric properties of (Nd₁−Laₓ)NbO₄ ceramics. Phys Chem Chem Phys 2015, 17: 16692–16698.

[175] Pang LX, Zhou D. Modification of NdNbO₄ microwave dielectric ceramic by Bi substitutions. J Am Ceram Soc 2019, 102: 2278–2282.

[176] Zhang P, Zhao Y, Liu J, et al. Correlation of crystal structure and microwave dielectric properties of Nd₀.₆₂(Nb₁₋ₓTaₓ)₀.₹₈O₄ ceramic. Dalton Trans 2015, 44: 5053–5057.

[177] Zhang P, Zhao YG, Liu J, et al. Enhanced microwave dielectric properties of NdNbO₄ ceramic by Ta⁷⁺ substitution. J Alloys Compd 2015, 640: 90–94.

[178] Zhang P, Zhao YG, Wang XY. The relationship between bond ionicity, lattice energy, coefficient of thermal expansion and microwave dielectric properties of Nd(Nb₁₋ₓSbx)O₃ ceramics. Dalton Trans 2015, 44: 10932–10938.

[179] Zhang P, Zhao YG, Wang XY. The correlations between electronic polarizability, packing fraction, bond energy and microwave dielectric properties of Nd(Nb₁₋ₓSbx)O₃ ceramics. J Alloys Compd 2015, 644: 621–625.

[180] Yang HC, Zhang SR, Yang HY, et al. Influence of (Al₁₋ₓWₓ)³⁺ co-substitution for Nb⁵⁺ in NdNbO₄ and the impact on the crystal structure and microwave dielectric properties. Dalton Trans 2018, 47: 15808–15815.

[181] Yang HC, Zhang SR, Yang HY, et al. Structure stability, bond characteristics and microwave dielectric properties of co-substituted NdNbO₄ ceramics. Ceram Int 2019, 45: 3620–3626.

[182] Yang HC, Zhang SR, Yang HY, et al. NdNb₁₋ₓ(MgₓW₁₋ₓ)O₄ (0.02 ≤ x ≤ 0.06) solid solution characterized by infrared spectrum and complex chemical theory. J Alloys Compd 2019, 787: 358–366.

[183] Yang HC, Zhang SR, Yang HY, et al. Bond characteristics, vibrational spectrum and optimized microwave dielectric properties of chemically substituted NdNbO₄. Ceram Int 2019, 45: 16940–16947.

[184] Zhang P, Song ZK, Wang Y, et al. Effect of CaTiO₃ addition on microwave dielectric properties of NdNbO₄ ceramics as multi-function material. J Alloys Compd 2013, 581: 741–746.

[185] Zhang P, Wang T, Xia WS, et al. Microwave dielectric properties of a new ceramic system NdNbO₄ with CaF₂ addition. J Alloys Compd 2012, 535: 1–4.

[186] Peng Y, Xia WS, Yi C, et al. Effects of MgO additive on microwave dielectric properties of NdNbO₄ ceramics. J Mater Sci: Mater Electron 2020, 31: 785–790.

[187] Liu LT, Chen YG, Feng ZB, et al. Crystal structure, infrared spectra, and microwave dielectric properties of the EuNbO₄ ceramic. Ceram Int 2021, 47: 4321–4326.

[188] Guo D, Zhou D, Li WB, et al. Phase evolution, crystal structure, and microwave dielectric properties of water-insoluble (1−x)LaNbO₄−ₓLaVO₄ (0 ≤ x ≤ 0.9) ceramics. Inorg Chem 2017, 56: 9321–9329.

[189] Tang TL, Xia WS, Zhang B, et al. Optimization on quality factor of LaNbO₄ microwave dielectric ceramics. J Mater Sci: Mater Electron 2019, 30: 15293–15298.

[190] Chen JW, Fang L, Li J, et al. Packing fraction, bond valence and crystal structure of AVO₄ (A = Eu, Y) microwave dielectric ceramics with low permittivity. J Mater Sci: Mater Electron 2020, 31: 19180–19187.

[191] Zhou D, Guo HH, Fu MS, et al. Anomalous dielectric behaviour during the monoclinic to tetragonal phase transition in La(Nb₀.₉₅V₀.₀₅)O₄. Inorg Chem Front 2021, 8: 156–163.

[192] Deng JY, Xia WS, Zhang WH, et al. Optimization of sintering behavior and microwave dielectric properties of LaNbO₄ ceramics with NiO/CoO additive. J Alloys Compd 2021, 859: 158378.

[193] Chen L, Hu MY, Wu P, et al. Thermal expansion performance and intrinsic lattice thermal conductivity of ferroelastic RETaO₄ ceramics. J Am Ceram Soc 2019, 102: 4809–4821.

[194] Wu P, Hu MY, Chen L, et al. The effect of ZrO₂ alloying on the microstructures and thermal properties of DyTaO₄ for high-temperature application. J Am Ceram Soc 2019,
Wu HT, Lu MY, Chen L, et al. Investigation on microstructures and thermo-physical properties of ferroelectrics (Y1−xDyx)TaO4 ceramics. Materialia 2018, 4: 478–486.

Wu P, Chong XY, Feng J. Effect of Al3+ doping on mechanical and thermal properties of Dy2TaO4 as promising thermal barrier coating application. J Am Ceram Soc 2018, 101: 1818–1823.

Ma Z, Zheng J, Wang S, et al. First-principle calculations of crystal structures, electronic structures, and optical properties of RETaO4 (RE = Y, La, Sm, Eu, Dy, Er). Opt Eng 2018, 57: 017107.

Devesa S, Teixeira SS, Rooney AP, et al. Structural, morphological and dielectric properties of ErNbO4 prepared by the sol–gel method. J Phys Chem Solids 2020, 146: 109619.

Nedelcu L, Geambasu CD, Enculescu M, et al. Intrinsic dielectric loss in Zn0.9Sn0.1TiO3 ceramics investigated by terahertz time domain spectroscopy. Materials 2021, 14: 216.

Kumada N, Taki K, Kimura N. Single crystal structure and microwave dielectric properties of ErNbO4 (RE = Y, La, Sm, Eu, Dy, Er). Ceram Int 2018, 44: 889–895.

Li BJ, Wang SY, Lin SH, et al. Dielectric properties and mixture behavior of y(Mg0.995Co0.005)TaO4–(1–y)CaTiO3 ceramic system at microwave frequency. J Alloys Compd 2016, 661: 357–362.

Pakavanit P, Ananta S. Influence of sintering temperature on densification and microstructure of Zn1-xNbxO3 ceramics derived from nanopowders. Adv Mater Res 2011, 194–196: 656–659.

Amonpattaratkit P, Ngamjarurojana A, Ananta S. Microstructure and dielectric properties of Zn1-xNbxO3 ceramics prepared by a two-stage sintering method. Ceram Int 2013, 39: S331–S334.

Bian JJ, Wang L, Yuan LL. Microwave dielectric properties of Li2O−O2−Ta2O5 ceramics with (B x+ y + z)-substitutions and microwave dielectric properties of Mg4Ta2O9 ceramics. J Eur Ceram Soc 2010, 30: 433–442.

Bian JJ, Dong YF. Sintering behavior, microstructure and microwave dielectric properties of Li2+xTa2O5 (0 ≤ x ≤ 0.2). Mater Sci Eng: B 2011, 176: 147–151.

Hao YZ, Zhang QL, Zhang J, et al. Enhanced sintering characteristics and microwave dielectric properties of Li2TaO5 due to nano-size and nonstoichiometry effect. J Mater Chem 2012, 22: 23885.

Izquierdo G, West AR. Phase equilibria in the system Li2O–TiO2. Mater Res Bull 1980, 15: 1655–1660.

Mikkelsen JC. Pseudo-binary phase relations of Li2Ti3O7. J Eur Ceram Soc 2010, 30: 13–17.

Chen GH, Xu HR, Yuan CL. Microstructure and microwave dielectric properties of Li2+xTi1–xO3 (0 ≤ x ≤ 0.2). Mater Sci Eng: B 2011, 176: 147–151.

Guo HH, Zhou D, Pang LX, et al. Influence of (Mg1/3−x/3Ta2/3)x+ substitutions on crystal structures and microwave dielectric properties of Mg4Ta2O9 ceramics. J Materiomics 2018, 4: 368–382.

Chen WS, Hung ML, Hsu CH. Effects of (Co0.5Ta1–xO3+1/2)-substitution on microstructure and microwave dielectric properties of Li2+xTa1–x(O1–x)O3 ceramics for applications in ceramic antenna. J Asian Ceram Soc 2021, 9: 433–442.

Guo HH, Fu MS, Zhou D, et al. Design of a high-efficiency and -gain antenna using novel low-loss, temperature-stable Li2+xTa1–x(Cu1/3Nb2/3)3O15 microwave dielectric ceramics. ACS Appl Mater Interfaces 2021, 13: 912–923.

Bian JJ, Dong YF. New high Q microwave dielectric ceramics with rock salt structures: (1–x)Li2TaO4+xMgO system (0 ≤ x ≤ 0.5). J Eur Ceram Soc 2010, 30: 325–330.

Huang CL, Tseng YW, Chen JY. High-Q dielectrics using ZnO-modified Li2TaO4 ceramics for microwave applications. J Eur Ceram Soc 2012, 32: 3287–3295.

Bian JJ, Liang Z, Wang L. Structural evolution and microwave dielectric properties of Li1+x/3−x/3M2/3Nb2/3−xO4 (M = Mg, Zn; 0 ≤ x ≤ 0.5). J Am Ceram Soc 2011, 94:
1447–1453.

[225] Wu NX, Bian JJ. Microstructure and microwave dielectric properties of (1–y)Li1/2Mg1/2TiO3-yLi2/3SnO3 ternary ceramics. J Mater Sci: Mater Electron 2016, 27: 302–308.

[226] Tseng YW, Chen JY, Kuo YC, et al. Low-loss microwave dielectrics using rock salt oxide Li2MgTiO4. J Alloys Compd 2011, 509: L308–L310.

[227] Chen XL, Zhou HF, Fang L, et al. Microwave dielectric properties and its compatibility with silver electrode of Li2MgTi3O8 ceramics. J Alloys Compd 2011, 509: 5829–5832.

[228] Fang L, Chu DJ, Zhou HF, et al. Preparation, phase ordering transformation and microwave dielectric properties of Li2CoTi3O8 ceramic. J Eur Ceram Soc 2010, 30: 269–272.

[229] Taghipour Armaki H, Taheri-Nassaj E, Bari M. A new series of low-loss multicomponent oxide microwave dielectrics with a rock salt structure: Li3MgABO8 (A = Ti, Sn; B = Nb, Ta). J Alloys Compd 2013, 581: 757–761.

[230] Lyu XS, Li LX, Cai HC, et al. A new microwave dielectric material LiNi0.5Ti0.5O4. Ceram Int 2015, 41: 9168–9171.

[231] Zhou HF, Liu XB, Chen XL, et al. ZnLi1/3Ti1/3O3: A new low loss spinel microwave dielectric ceramic. J Eur Ceram Soc 2012, 32: 261–265.

[232] Zhou HF, Liu XB, Chen XL, et al. Preparation, phase structure and microwave dielectric properties of a new low cost MgLi1/2Ti1/2O4 compound. Mater Chem Phys 2012, 137: 22–25.

[233] Zhou HF, Liu XB, Chen XL, et al. Preparation, phase structure and microwave dielectric properties of CoLi2/3Ti4/3O4 ceramic. Mater Res Bull 2012, 47: 1278–1280.

[234] Bi JX, Xing CF, Jiang XS, et al. Characterization and microwave dielectric properties of new low loss Li2MgZrO4 ceramics. Mater Lett 2016, 184: 269–272.

[235] Fu ZF, Liu P, Ma JL, et al. New high Q low-fired Li2Mg2Ti3O10 microwave dielectric ceramics with rock salt structure. Mater Lett 2016, 164: 436–439.

[236] Zhou HF, Gong JZ, Fan GC, et al. Enhanced sintering ability and microwave dielectric properties of Li2ZnNbO4 ceramics with pretreatment of raw materials. J Alloys Compd 2016, 665: 113–118.

[237] Su CH, Huang CL. Investigation of the microwave dielectric properties of Li2ZnTi3O12 ceramics. J Alloys Compd 2016, 678: 102–108.

[238] Liu QQ, Pan HL, Tao WH, et al. New rock salt structure dielectric material Li2Ni1/3TiO3, at microwave frequency. J Mater Sci: Mater Electron 2017, 28: 9892–9899.

[239] Bi JX, Li CC, Zhang YH, et al. Crystal structure, infrared spectra and microwave dielectric properties of ultra-low-loss Li2Mg2Ti3O9 ceramics. Mater Lett 2017, 196: 128–131.

[240] Pan HL, Wu HT. Crystal structure, infrared spectra and microwave dielectric properties of new ultra low-loss Li3MgTi3O10 ceramics. Ceram Int 2017, 43: 14484–14487.

[241] Zuo RZ, Qi H, Qin F, et al. A new Li-based ceramic Li3MgSn2O7: Synthesis, phase evolution and microwave dielectric properties. J Eur Ceram Soc 2018, 38: 5442–5447.

[242] Jiang PB, Hu YD, Bao SX, et al. A novel microwave dielectric ceramic Li2NiZrO4 with rock salt structure. RSC Adv 2019, 9: 32936–32939.

[243] Wu HT, Kim ES. Characterization of low loss microwave dielectric materials Li1MgNbO4 based on the chemical bond theory. J Alloys Compd 2016, 669: 134–140.

[244] Pei CJ, Hou CD, Li Y, et al. A low εr and temperature-stable Li3Mg2NbO6 microwave dielectric ceramics. J Alloys Compd 2019, 792: 46–49.

[245] Li J, Zhang ZW, Tian YF, et al. Crystal structure and microwave dielectric properties of a novel rock-salt type Li3MgNbO6 ceramic. J Mater Sci 2020, 55: 15643–15652.

[246] Zhang X, Jiang ZH, Tang B, et al. New rock salt structure, and microwave dielectric properties of Li2Mg0.95A0.05TiO4 (A = Ni, Co, Mn, Zn) ceramics. J Adv Ceram 2015, 4: 32–36.

[247] Zuo RZ, Qi H, Qin F, et al. A new microwave dielectric ceramic Li2Mg2SnO6 solid-solution system: A newly developed pseudo ternary phase diagram. Acta Mater 2021, 206: 116636.

[248] Gu FF, Chen GH, Li XQ, et al. Structural and microwave dielectric properties of (1−δ)Li1Na0.5NbO3−δMg0.5Nb2/3O3 thermally stable ceramics. Mater Chem Phys 2015, 167: 354–359.

[249] Yao GG, Hu XS, Tian XL, et al. Synthesis and microwave dielectric properties of Li2MgTiO4 ceramics. Ceram Int 2015, 41: S563–S566.

[250] Du H, Li CC, Liu FL, et al. Influence of ionic substitution on the microwave dielectric properties of Li2Mg0.95A0.05TiO4 (A = Ni, Co, Mn, Zn) ceramics. J Mater Sci: Mater Electron 2017, 28: 8304–8308.

[251] Wang P, Wang YR, Bi JX, et al. Effects of Zn⁺ substitution on the crystal structure, Raman spectra, bond energy and microwave dielectric properties of Li2MgTiO4 ceramics. J Alloys Compd 2017, 721: 143–148.

[252] Xing CF, Liu QQ, Wu HT. Sintering characteristics, crystal structure, and microwave dielectric properties of Li2(Mg0.9A0.1)2TiO4 (A = Ni, Co, Mn, Zn) ceramics. J Mater Sci: Mater Electron 2020, 30: 302–307.

[253] Xing CF, Wu HT. Crystal structure and microwave dielectric properties of Li2Mg0.95Zn0.05TiO4 (x = 0–0.4) ceramics. Ceram Int 2019, 45: 4142–4145.

[254] Lu XP, Zheng Y, Huang Q, et al. Correlation of heating rates, crystal structures, and microwave dielectric properties of Li2ZnTi3O8 ceramics. J Electron Mater 2015, 44: 4243–4249.

[255] Zhou HF, Wang N, Gong JZ, et al. Processing of low-fired glass-free Li2Mg2Ti3O9 microwave dielectric ceramics. J Alloys Compd 2016, 688: 8–13.
[256] Tajik Z, Sayyadi-Shahraki A, Taheri-Nassaj E, et al. Effect of synthesis and sintering technique on the long-range 1:3 cation ordering and microwave dielectric loss of Li2ZnTi3O8 ceramics. Ceram Int 2020, 46: 20905–20913.

[257] Huang CL, Su CH, Chang CM. High Q microwave dielectric ceramics in the Li2(Zn1−xAlx)Ti3O8 (A = Mg, Co; x = 0.02–0.1) system. J Am Ceram Soc 2011, 94: 4146–4149.

[258] Fang L, Chu DJ, Zhou HF, et al. Microwave dielectric properties of temperature stable Li2ZnCo1−xTi3O8 ceramics. J Alloys Compd 2011, 509: 8840–8844.

[259] Wang LJ, Sun QC, Ma WB, et al. Microwave dielectric characteristics of Li5(Mg0.86Mo0.14)Ti3O8 (M = Zn, Co, and Mn) ceramics. Ceram Int 2013, 39: 5185–5190.

[260] Ren HS, Wu ZL, He F, et al. Investigation on phase and microstructures of a temperature stable high-Q Li2Zn0.99Sn0.01Ti3O8 microwave dielectric ceramic. J Mater Sci: Mater Electron 2019, 30: 8154–8159.

[261] Ren HS, Xie TY, Wu ZL, et al. Crystal structure, phase evolution and dielectric properties in the Li2ZnTi3O8−SrTiO3 system as temperature stable high-Q material. J Alloys Compd 2019, 797: 18–25.

[262] Tian S, Liao ZL, Wang H, et al. Influence of Ca4Sr1−x (0 ≤ x ≤ 1) substitution for Zn on microwave dielectric properties of Li2ZnTi3O8 ceramic as temperature stable materials. J Wuhan Univ Technol Mater Sci Ed 2020, 35: 686–690.

[263] Liu XB, Zhou HF, Chen XL, et al. Phase structure and microwave dielectric properties of (1−x)Li2ZnTi3O8−xTiO2 ceramics. J Alloys Compd 2012, 515: 22–25.

[264] Wang W, Zhou HF, Chen XL, et al. Crystal structure and optimized microwave dielectric properties of (1−x)LiZn0.99Sn0.01−xTiO2 ceramics for application in dielectric resonator. J Mater Sci: Mater Electron 2013, 24: 2641–2645.

[265] Bari M, Taheri-Nassaj E, Taghipour-Armaki H. Phase evolution, microstructure, and microwave dielectric properties of reaction-sintered Li2ZnTi3O8 ceramic obtained using nanosized TiO2 reagent. J Electron Mater 2015, 44: 3670–3676.

[266] Bari M, Taheri-Nassaj E, Taghipour-Armaki H. Role of nano- and micron-sized particles of TiO2 additive on microwave dielectric properties of Li2ZnTi3O8−4 wt%TiO2 ceramics. J Am Ceram Soc 2013, 96: 3737–3741.

[267] Zhang P, Wang Y, Liu J, et al. A high improved quality factor of Li2Mg0.6TiO3 microwave dielectric ceramics system. Mater Lett 2014, 123: 195–197.

[268] Zhang P, Zhao YG. High-Q microwave dielectric materials of Li2ZnTi3O8 ceramics with SnO2 additive. Ceram Int 2016, 42: 2882–2886.

[269] Zhang YD, Han J, Liang R, et al. Novel temperature stable Li2TiO3-based microwave dielectric ceramics with low loss. Mater Lett 2015, 153: 118–120.

[270] Li W, Li JH, Shen JX, et al. Crystal structure, Raman spectra, and microwave dielectric properties of high-Q Li2ZnTi3O8 systems with Nb2O5 addition. Ceram Int 2021, 47: 8601–8609.

[271] Zhang BW, Li LX, Luo WJ. Oxygen vacancy regulation and its high frequency response mechanism in microwave ceramics. J Mater Chem C 2018, 6: 11023–11034.

[272] Zhang P, Xie H, Zhao YG, et al. Microwave dielectric properties of low loss Li2(Mg0.65Sn0.35)TiO4 (A = Ca2+, Ni2+, Zn2+, Mn2+) ceramics system. J Alloys Compd 2016, 689: 246–249.

[273] Shi XL, Zhang HW, Zhang DN, et al. Structure and microwave dielectric properties of Li2Mg3Ti1−x, (Al1−x, Nb2)xO6 ceramics. Ceram Int 2020, 46: 13737–13742.

[274] Zhan Y, Li LX. Low-permittivity and high-Q value Li2Mg3Ti1−x, (Zn3−x, Nb2)xO6 microwave dielectric ceramics for microstrip antenna applications in 5G millimeter wave. J Alloys Compd 2021, 857: 157608.

[275] Fang ZX, Tang B, Si F, et al. Phase evolution, structure and microwave dielectric properties of Li2Zn3Ti4O12 (x = 0.00–0.12) ceramics. Ceram Int 2017, 43: 13645–13652.

[276] Fang ZX, Tang B, Si F, et al. Temperature stable and high-Q microwave dielectric ceramics in the Li2Zn3−x, CaTiO3 system (x = 0.00–0.18). Ceram Int 2017, 43: 1682–1687.

[277] Fang ZX, Tang B, Yuan Y, et al. Structure and microwave dielectric properties of the Li2/3(1−x)Mg1/3Sn2/3−xO3 (0 ≤ x ≤ 0.4) ceramics. J Am Ceram Soc 2018, 101: 252–264.

[278] Xie TY, Zhang LZ, Ren HS, et al. A novel temperature-stable and low-loss microwave dielectric using Ca4Sr1−xTiO2-modified Li2Mg3TiO6 ceramics. J Mater Sci: Mater Electron 2017, 28: 13705–13709.

[279] Zhou HF, Tan XH, Huang J, et al. Sintering behavior, phase evolution and microwave dielectric properties of thermally stable Li4O−3MgO−mTi2O2 ceramics (1 ≤ m ≤ 6). Ceram Int 2017, 43: 3688–3692.

[280] Pan HL, Xing CF, Jiang XS, et al. Characterization on low loss dielectric Li3MgTiO3 ceramics based on chemical bond theory at microwave frequency. J Alloys Compd 2016, 688: 416–421.

[281] Bi JX, Niu YJ, Wu HT. Li2Mg3Ti2O7: A novel low-loss microwave dielectric ceramic for LTCC applications. Ceram Int 2017, 43: 7522–7530.

[282] Pan HL, Cheng L, Wu HT. Relationships between crystal structure and microwave dielectric properties of Li2(Mg1−xCo2x)3Ti5O14 (0 ≤ x ≤ 0.4) ceramics. Ceram Int 2017, 43: 15018–15026.

[283] Fu ZF, Liu P, Ma JL, et al. Novel series of ultra-low loss microwave dielectric ceramics: Li2Mg1−xSnxO3 (B = Ti, Sn, Zr). J Eur Ceram Soc 2016, 36: 625–629.

[284] Bi JX, Xing CF, Yang CH, et al. Phase composition, microstructure and microwave dielectric properties of rock salt structured Li2Zn4O7–MgO ceramics. J Eur Ceram Soc 2018, 38: 3840–3846.

[285] Liu LT, Wang LG, Du JL, et al. Effects of (Mg1/3Sb2/3)+ substitutions on the sintering behaviors and microwave
dielectric properties of Li$_3$Mg$_2$Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$O$_6$ ceramics. J Alloys Compd 2021, 865: 158942.

[286] Shi XL, Zhang HW, Zhang DN, et al. Effect of zirconium deficiency on structure characteristics, morphology and microwave dielectric properties of Li$_3$Mg$_2$Zr$_{1-x}$O$_x$ ceramics. Ceram Int 2021, 47: 12567–12573.

[287] Wang G, Zhang DN, Gan GW, et al. Synthesis, crystal structure and low loss of Li$_3$Mg$_2$NbO$_6$ ceramics by reaction sintering process. Ceram Int 2019, 45: 19766–19770.

[288] Xing CF, Bi JX, Wu HT. Effect of Co-substitution on microwave dielectric properties of Li$_3$(Mg$_{1−x}$Co$_x$)$_2$NbO$_6$ (0.00 ≤ x ≤ 0.10) ceramics. J Alloys Compd 2017, 719: 58–62.

[289] Zhang P, Liu L, Xiao M, et al. A novel temperature stable and high Q microwave dielectric ceramic in Li$_3$(Mg$_{1−x}$Mn$_x$)$_2$NbO$_6$ system. J Mater Sci: Mater Electron 2017, 28: 12220–12225.

[290] Zhang P, Sun KX, Xiao M, et al. Crystal structure, densification, and microwave dielectric properties of Li$_3$Mg$_2$(Nb$_{1−x}$Mo$_x$)$_2$O$_6$ (0 ≤ x ≤ 0.08) ceramics. J Am Ceram Soc 2019, 102: 4127–4135.

[291] Wang G, Zhang DN, Huang X, et al. Crystal structure and enhanced microwave dielectric properties of Ta$^{5+}$ substituted Li$_3$Mg$_2$NbO$_6$ ceramics. J Am Ceram Soc 2020, 103: 214–223.

[292] Pei CJ, Li Y, Hou CD, et al. Sintering behavior and microwave dielectric properties of Y$^{3+}$ substituted Li$_3$Mg$_2$SbO$_6$ ceramics. J Mater Sci: Mater Electron 2019, 30: 14495–14499.

[293] Pei CJ, Tan JJ, Li Y, et al. Effect of Sb-site nonstoichiometry on the structure and microwave dielectric properties of Li$_3$Mg$_2$Sb$_{1−x}$O$_6$ ceramics. J Adv Ceram 2020, 9: 588–594.

[294] Li H, Zhang PC, Chen XQ, et al. Effect of Zn$^{2+}$ substitution for Mg$^{2+}$ in Li$_3$Mg$_2$SbO$_6$ and the impact on the bond characteristics and microwave dielectric properties. J Alloys Compd 2020, 832: 155043.

[295] Zhang P, Hao MM, Mao XR, et al. Effects of W$^{6+}$ substitution on crystal structure and microwave dielectric properties of Li$_3$Mg$_2$NbO$_6$ ceramics. Ceram Int 2020, 46: 21336–21342.

[296] Wang G, Zhang DN, Li J, et al. Crystal structure, bond energy, Raman spectra, and microwave dielectric properties of Ti-doped Li$_3$Mg$_2$NbO$_6$ ceramics. J Am Ceram Soc 2020, 103: 4321–4332.

[297] Zhang P, Sun KX, Mao XR, et al. Crystal structures and high microwave dielectric properties in Li$^+$/Ti$^{4+}$ ions co-doped Li$_3$Mg$_2$NbO$_6$ ceramics. Ceram Int 2020, 46: 8097–8101.

[298] Zhang P, Hao MM, Xiao M. Microwave dielectric properties of Li$_3$Mg$_2$NbO$_6$-based ceramics with (M,W$_{1−y}$)$_3$O$_6$ (M = Li$^+$, Mg$^{2+}$, Al$^{3+}$, Ti$^{4+}$) substitutions at Nb$^{5+}$ sites. J Alloys Compd 2021, 853: 157386.

[299] Wang G, Zhang HW, Huang X, et al. Crystal structure and enhanced microwave dielectric properties of non-stoichiometric Li$_3$Mg$_2$,NbO$_6$ ceramics. Mater Lett 2019, 235: 84–87.

[300] Chu X, Gan L, Ren SQ, et al. Low-loss and temperature-stable (1−x)Li$_3$TiO$_3$−xLi$_3$Mg$_2$NbO$_6$ microwave dielectric ceramics. Ceram Int 2020, 46: 8413–8419.

[301] Zhang X, Tang B, Fang ZX, et al. Structural evolution and microwave dielectric properties of a novel Li$_3$Mg$_2$Sb$_{1−x}$Ti$_x$O$_6$ system with a rock salt structure. Inorg Chem Front 2018, 5: 3113–3125.

[302] Zhang X, Zhang X, Fang ZX, et al. Effects of lattice evolution and ordering on the microwave dielectric properties of tin-modified Li$_3$Mg$_2$O$_6$-based ceramics. J Phys Chem C 2020, 124: 22069–22081.

[303] Qin F, Zhang S, Zuoz RZ. Ultralow-loss and thermally stable Li$_3$Mg$_{12}$Nb$_{12}$O$_{36}$ microwave dielectric ceramics. J Mater Sci: Mater Electron 2020, 31: 5567–5572.

[304] Li L, Chen XM. Frequency-dependent Qf value of low-loss Ba$_2$Ti$_6$O$_{15}$ ceramics at microwave frequencies. Ceram Int 2012, 38: 6831–6835.

[305] Huang XL, Song Y, Wang FP. Microwave dielectric properties of BaTi$_4$O$_9$–BaSm$_2$Ti$_4$O$_{12}$ composite ceramics. J Ceram Soc Japan 2013, 121: 880–883.

[306] Yang QH, Luo T, Yu T, et al. Improvement of microwave dielectric properties of Ba$_2$Ti$_6$O$_{15}$ ceramics using [Zn$_{10}$Nb$_{25}$]$^{4+}$ substitution for Ti$^{4+}$. J Mater Sci: Mater Electron 2020, 31: 15184–15191.

[307] Jawahar IN, Mohanan P, Sebastian MT. A$_3$B$_4$O$_{15}$ (A = Ba, Sr, Mg, Ca, Zn; B = Nb, Ta) microwave dielectric ceramics. Mater Lett 2003, 57: 4043–4048.

[308] Zheng JJ, Yang YK, Wu HT, et al. Structure, infrared spectra and microwave dielectric properties of the novel Eu$_2$TiO$_3$ ceramics. J Am Ceram Soc 2020, 103: 4333–4341.

[309] Niu H, Gou HY, Ewing RC, et al. First-principles investigation of structural, elastic and electronic properties of lanthanide titanate oxides Ln$_2$TiO$_5$. MRS Online Proc Libr 2011, 1298: 85–90.

[310] Ohsato H. Science of tungstenbronze-type like Ba$_{6+3x}$R$_{2+3x}$Ti$_9$O$_{34}$ (R = rare earth) microwave dielectric solid solutions. J Eur Ceram Soc 2001, 21: 2703–2711.

[311] Suvorov D, Valant M, Kolar D. The role of dopants in tailoring the microwave properties of Ba$_{6+3x}$R$_{2+3x}$Ti$_9$O$_{34}$ R = (La–Gd) Ceramics. J Mater Sci 1997, 32: 6483–6488.

[312] Snashall AL, Norén L, Liu Y, et al. Phase analysis and microwave dielectric properties of BaO–Nd$_2$O$_3$–5TiO$_2$ composite ceramics using variable size TiO$_2$ reagents. Ceram Int 2012, 38: S153–S157.

[313] Yao XG, Lin HX, Zhao XY, et al. Effects of Al$_2$O$_3$ addition on the microstructure and microwave dielectric properties of Ba$_6$Nd$_{13}$Ti$_9$O$_{34}$ ceramics. Ceram Int 2012, 38: 6723–6728.

[314] Chen HT, Xiong Z, Yuan Y, et al. Dependence of microwave dielectric properties on site substitution in Ba$_{1.25}$Nd$_{0.5}$Ti$_9$O$_{34}$ ceramic. J Mater Sci: Mater Electron
[315] Setasuwon P, Freer R, Azough F, et al. (Ba1−xPbx)1−yNd3+yTi18−xSnO44 and (Ba1−xSr)xNd3+yTi18−xSnO44 microwave dielectric ceramics: Effect of Pb and Sr substitution on dielectric properties. *Br Ceram Trans* 2002, 101: 237–241.

[316] Muhammad R, Iqbal Y, Rambo CR. Characterization of Ba4(1−x)ZnO−xNd2O3−4TiO2 ceramics. *J Adv Ceram* 2017, 6(1): 10951–10957.

[317] Huang BY, Wang ZF, Chen T, et al. Microstructure and microwave dielectric properties of Ba4(1−x)ZnO−xNd2O3−4TiO2 (x = 0, 0.25, 0.5, 1, 1.5, 2) ceramics. *J Mater Sci: Mater Electron* 2015, 26: 3375–3379.

[318] Guo X, Tang B, Chen HT, et al. Microwave dielectric properties and microstructure of (Ba0.9Nd0.1)x(Nd0.2Sn0.8)3Ti18−xO44 ceramics. *J Mater Sci: Mater Electron* 2015, 26: 6182–6188.

[319] Guo X, Tang B, Liu JQ, et al. Microwave dielectric properties and microstructure of Ba2−xNd4+yTi18−yCr12−2yNb23O34 ceramics. *J Alloys Compd* 2015, 646: 512–516.

[320] An SB, Jiang J, Wang JZ, et al. Microwave dielectric property modification of Ba4Nd3+yTi18−yO44 ceramics by the substitution of (Al0.95Nd0.05)4+y for Ti4+y and the addition of NdAlO3. *Ceram Int* 2020, 46: 3960–3967.

[321] Xiong Z, Tang B, Fang ZX, et al. Crystal structure, Raman spectroscopy and microwave dielectric properties of Ba4(1−x)Nd3+yTi18−y(Al12−2yNb23)O34 ceramics. *J Alloys Compd* 2017, 723: 580–588.

[322] Zhou LL, Zhou HQ, Shao H, et al. Microstructure and microwave dielectric properties of Ba0.8−xSm2+yTi18−yO44 ceramics with various Ba0.8Sm1.8−xTi0.8O44 additions. *J Rare Earths* 2012, 30: 142–145.

[323] Xu Y, Fu RL, Agathopoulos S, et al. Synthesis and microwave dielectric properties of BaO−SmO2−5TiO2 ceramics with NdAlO3 additions. *Ceram Int* 2016, 42: 14573–14580.

[324] Yao XG, Lin HX, Chen W, et al. Anti-reduction of Ti4+y in Ba4(1−x)Nd3+yTi18−yO44 ceramics by doping with MgO, Al2O3, and MnO2. *Ceram Int* 2012, 38: 3011–3016.

[325] Wang G, Fu QY, Shi H, et al. Novel thermally stable, high-quality factor Ba0.8(Pr0.6Sm0.4)3.2Ti18−xGd4+yO44 microwave dielectric ceramics. *J Am Ceram Soc* 2020, 103: 2520–2527.

[326] Wang G, Fu QY, Guo PJ, et al. A/B-site cosubstituted Ba3Pr2+yTi18−yO44 microwave dielectric ceramics with temperature stable and high Q in a wide range. *Ceram Int* 2020, 46: 11474–11483.

[327] Roth RS, Rawn CJ, Lindsay CG, et al. Phase equilibria and crystal chemistry of the binary and ternary barium polyanitane and crystallography of the barium zinc polyanitane. *J Solid State Chem* 1993, 104: 99–118.

[328] Tang B, Yu SQ, Chen HT, et al. The influence of Cu substitution on the microwave dielectric properties of BaZn2Ti4O13 ceramics. *J Alloys Compd* 2013, 551: 463–467.

[329] Yu SQ, Tang B, Zhang SR, et al. Temperature stable high-Q microwave dielectric ceramics in (1−x)BaTiO3−xBaZn2Ti4O13 system. *Mater Lett* 2012, 67: 293–295.

[330] Yu SQ, Tang B, Zhang X, et al. Improved high-Q microwave dielectric ceramics in CuO-doped BaTiO3–BaZn2Ti4O13 system. *J Am Ceram Soc* 2012, 95: 1939–1943.

[331] Yu SQ, Zhang SR, Tang B, et al. Microwave dielectric properties of BaO−2(1−x)ZnO−xNd2O3−4TiO2 (x = 0–1.0) ceramics. *Ceram Int* 2012, 38: 613–618.

[332] Yang YY, Kyzhzhubek T, Genevois C, et al. Ba3CoNb24−yTa2O48 eight-layer shifted hexagonal perovskite ceramics with spontaneous Ta4+ ordering and near-zero τf. *Inorg Chem* 2019, 58: 10974–10982.

[333] Sanoj MA, Reshmi CP, Sreena KP, et al. Sinterability and microwave dielectric properties of nano structured 0.95MgTiO3−0.05CaTiO3 synthesised by top down and bottom up approaches. *J Alloys Compd* 2011, 509: 3089–3095.

[334] Rajput SS, Keshri S. Structural, vibrational and microwave dielectric properties of (1−x)Mg0.95Co0.05TiO3−xCo0.8Sn0.2TiO3 ceramic composites. *J Alloys Compd* 2013, 581: 223–229.

[335] Rajput SS, Keshri S, Gupta VR. Microwave dielectric properties of (1−x)Mg0.95Zn0.05TiO3−xCo0.8La0.8/3TiO3 ceramic composites. *J Alloys Compd* 2013, 552: 219–226.

[336] Huang JB, Yang B, Yu CY, et al. Microwave and terahertz dielectric properties of MgTiO3–CaTiO3 ceramics. *Mater Lett* 2015, 138: 225–227.

[337] Hsu CH, Chang CH. A temperature-stable and high-Q microwave dielectric ceramic of the MgTiO3–(Ca0.8Sr0.2)(Zr0.1Ti0.9)O3 system. *Ceram Int* 2015, 41: 6965–6969.

[338] Li LX, Li S, Tian T, et al. Microwave dielectric properties of (1−x)Mg0.95TiO3−xCo0.8Sn0.2TiO3 ceramic system. *J Mater Sci: Mater Electron* 2016, 27: 1286–1292.

[339] Chen CY, Wang ZF, et al. Microwave dielectric properties of novel (1−x)MgTiO3−xCa0.05Sn0.95TiO3 ceramics. *J Mater Sci: Mater Electron* 2020, 31: 13696–13703.

[340] Hou GH, Wang ZH, Zhang F. Sintering behavior and microwave dielectric properties of (1−x)CaTiO3−xLaAlO3 ceramics. *J Rare Earths* 2011, 29: 160–163.

[341] Liang F, Ni M, Wu LZ, et al. Microwave dielectric properties and crystal structures of 0.7CaTiO3−0.3[La,Nd1−x]AlO3 ceramics. *J Alloys Compd* 2013, 568: 11–15.

[342] Li LX, Gao ZD, Liu YR, et al. Influence of LaAlO3 additive to MgTiO3–CaTiO3 ceramics on sintering behavior and microwave dielectric properties. *Mater Lett* 2015, 140: 5–8.

[343] Li LX, Li S, Lyu XS, et al. LaAlO3 doped (Mg0.95Zn0.05)TiO3–CaTiO3 ceramic system with

www.springer.com/journal/40145
ultra-high-$Q$ and temperature-stable characterization. *J Mater Sci: Mater Electron* 2015, **26**: 5871–5876.

[344] Zhang LZ, Lin HX, Zhao XY, et al. Investigation on microwave dielectric properties and microstructures of $(1-x)$LaAlO$_3$-$Ca_0.8Sr_0.2TiO$_3$ ceramics. *J Alloys Compd* 2015, **649**: 254–260.

[345] Dou ZM, Jiang J, Wang G, et al. Effect of Ga$^{3+}$ substitution on the microwave dielectric properties of 0.67CaTiO$_3$–0.33LaAlO$_3$ ceramics. *Ceram Int* 2016, **42**: 6743–6748.

[346] Wang MH, Liahuf CT, Lin SM, et al. Sintering behaviors, microstructure, and microwave dielectric properties of CaTiO$_3$–LaAlO$_3$ ceramics sintered at medium temperatures with the additives of H$_2$BO$_3$–Li$_2$CO$_3$. *J Mater Sci: Mater Electron* 2020, **31**: 14879–14885.

[347] Niu ST, Jiang J, Wang JZ, et al. The sintering behavior and microwave dielectric properties of 0.67CaTiO$_3$–0.33LaAlO$_3$ ceramics sintered at medium temperatures with the additives of H$_2$BO$_3$–Li$_2$CO$_3$. *J Mater Sci: Mater Electron* 2020, **31**: 14879–14885.

[348] Wang SF, Wang YR, Hsu JC. Densification, microstructural evolution, and dielectric properties of CaTiO$_3$–LaAlO$_3$ ceramics using CuO/B$_2$O$_3$ additions. *Materials* 2019, **12**: 4187.

[349] Feteira A, Iddles D, Price T, et al. Effect of bond valence on the vibrational modes of A-site ions and microwave dielectric properties of CaTiO$_3$–SrMgAlO$_3$ ceramics. *J Mater Sci: Mater Electron* 2012, **23**: 4662–4668.

[350] Chen JH, Hsu YF, et al. Composite dielectrics with a near-zero temperature coefficient at microwave frequency. *J Mater Sci: Mater Electron* 2016, **27**: 11110–11117.

[351] Yang XY, Zhang CY, Wu HY, et al. Effect of Ga$^{3+}$ substitution added CaTiO$_3$–SmAlO$_3$ ceramics prepared by reaction sintering method. *Ceram Int* 2021, **47**: 3741–3746.

[352] Yang XY, Zhang CY, Wu HY, et al. Structure and microwave dielectric properties of CaSmAlO$_3$–CaTiO$_3$–Sm$_{0.9}$Nd$_{0.1}$AlO$_3$ ceramics with medium to high permittivity. *J Ceram Soc Jpn* 2020, **128**: 756–760.

[353] Zhang LX, Gan L, Cheng HY, et al. Crystal structure, Raman spectra analysis and microwave dielectric properties optimization of (Ca$_0.65$Li$_0.35$)$_3$O$_3$ TiO$_3$ ceramics doped with SmAlO$_3$. *J Alloys Compd* 2020, **817**: 152708.

[354] Chen YC, You HM. Tuning the microwave dielectric properties of Zn$_2$SnO$_4$ ceramics by adding Ca$_0.8$Sr$_0.2$TiO$_3$. *Ceram Int* 2015, **41**: 9521–9526.

[355] Huang CL, Chien YH, Shih CF, et al. Crystal structure and dielectric properties of $x$CaTiO$_3$–$y$(Nd$_{1/3}$Ca$_{2/3}$)$_{1/2}$TiO$_3$ at the microwave frequency. *Mater Res Bull* 2015, **63**: 1–5.

[356] Reda AE, Ibrahim DM, Aziz DAA. Microwave dielectric properties of $x$CaTiO$_3$–$y$(Nd$_{1/3}$Ca$_{2/3}$)$_{1/2}$TiO$_3$ ceramics. *J Ceram Sci Tech* 2016, **7**: 243–248.

[357] Lin SH, Chen YB. Structure and characterization of B$_2$O$_3$ modified $y$Nd$_{0.65}$CaTiO$_3$–(1–$y$)Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics with a near-zero temperature coefficient at microwave frequency. *Ceram Int* 2017, **43**: 2368–2371.

[358] Yang SW, Liang BL, Liu CH, et al. Microwave sintering and microwave dielectric properties of $(1-x)$Ca$_{0.8}$La$_{0.2}$TiO$_3$–Nd$_{0.65}$CaTiO$_3$ ceramics. *Materials* 2021, **14**: 438.
permittivity \( (\varepsilon_{\text{max}} \sim 487) \). *J Adv Ceram* 2019, **803**: 850–859.

[372] Zhou XJ, Zhou HF, Luan XW, *et al.* Structure and dielectric properties of novel series of 3CaO–RE2O5–2WO3 (RE = La, Nd and Sm) microwave ceramics and the adjustment of \( \tau_f \) value. *J Mater Sci: Mater Electron* 2020, **31**: 14953–14960.

[373] Zhang XH, Chang N, Zhang J, *et al.* Low-loss \((1-x)\text{B}_{60}\text{Sr}_{10}\text{La}_{10}\text{Ti}_{15-x}\text{CaTiO}_{3}\) microwave dielectric ceramics with medium permittivity. *J Adv Ceram* 2020, **819**: 153011.

[374] Zhou XJ, Wang KG, Hu S, *et al.* Preparation, structure and microwave dielectric properties of novel \( \text{La}_2\text{MgGeO}_6 \) ceramics with hexagonal structure and adjustment of its \( \tau_f \) value. *Ceram Int* 2021, **47**: 7773–7789.

[375] Hsu CH, Chang CH. Microwave dielectric properties of \( \text{(Ca}_x\text{Sr}_{1-x})_{(\text{Sn},\text{Ti})_{1-x}}\text{O}_3 \) ceramics. *Mater Sci Eng: B* 2013, **178**: 354–357.

[376] Ravi GA, Azough F, Freer R. Structure and microwave dielectric properties of \( \text{Ca}_x\text{Ti}_{1-x}\text{Al}_{2x-3}\text{Ga}_{x}\text{O}_3 \) ceramics. *Adv Appl Ceram* 2012, **111**: 398–403.

[377] Lowndes R, Azough F, Cernik R, *et al.* Structures and microwave dielectric properties of \( \text{Ca}_{1-y}\text{Nd}_{2y}\text{TiO}_3 \) ceramics. *J Eur Ceram Soc* 2012, **32**: 3791–3799.

[378] Li JM, Qiu T. Microwave sintering of \( \text{Ca}_0\text{La}_{0.2667}\text{TiO}_3 \) microwave dielectric ceramics. *Int J Miner Metall Mater* 2012, **19**: 245–251.

[379] Iqbal Y, Muhammad R. Phase, microstructure and microwave dielectric properties of \( \text{Nb} \) and \( \text{Ga} \) doped \( \text{Ca}_0\text{La}_{0.2667}\text{TiO}_3 \) ceramics. *J Mater Sci: Mater Electron* 2015, **26**: 10119–10122.

[380] Zhou CR, Chen GH, Cen ZY, *et al.* Structure and microwave dielectric characteristics of lithium-excess \( \text{Ca}_{0.35}\text{Li}_{0.25}\text{Nd}_{0.35}\text{TiO}_3 \) ceramics. *Mater Res Bull* 2013, **48**: 4924–4929.

[381] Hsu CH, Tsai PS, Tseng CF, *et al.* Microwave dielectric properties of \( \text{Ca}_{0.4}\text{Mg}_{0.6}\text{Sn}_2\text{TiO}_5 \) ceramics. *J Adv Ceram Compd* 2014, **582**: 355–359.

[382] Muhammad R, Iqbal Y. Microwave dielectric properties of \( \text{Ca}_{1-x}\text{(Nd}_{0.5}\text{Ga}_{0.5})\text{O}_3 \) ceramics. *Mater Lett* 2015, **153**: 121–123.

[383] Xu Y, Fu RL, Agathopoulos S, *et al.* Sintering behavior, microstructure, and microwave dielectric properties of \( \text{Ca}_{0.68}\text{Ti}_{0.68}\text{Sm}_{0.32}\text{Al}_{0.31}\text{O}_3 \) ceramics. *Ceram Int* 2016, **42**: 19036–19041.

[384] Xu Y, Fu RL, Zhao P, *et al.* Sintering behavior, microwave dielectric properties of \( \text{Ca}_{0.66}\text{Ti}_{0.66}\text{Nd}_{0.26}\text{Al}_{0.13}\text{O}_3 \) ceramics revealed by microstructure and Raman scattering. *J Adv Ceram Compd* 2019, **785**: 335–342.

[385] Chen GH, Chen JS, Kang XL, *et al.* Structural and microwave dielectric properties of new \( \text{CaTi}_{1-x}\text{(Al}_{0.6}\text{Nb}_{0.4})\text{O}_3 \) thermally stable ceramics. *J Adv Ceram Compd* 2016, **675**: 301–305.

[386] Hameed I, Liu XQ, Li L, *et al.* Structure evolution and improved microwave dielectric characteristics in \( \text{CaTi}_{1-x}\text{(Al}_{0.6}\text{Nb}_{0.4})\text{O}_3 \) ceramics. *J Adv Ceram Compd* 2020, **845**: 155435.

[387] Yan YX, Li ZM, Zhang ML, *et al.* Preparation and microwave dielectric properties of \( \text{Ca}_0\text{La}_{0.8}\text{Sn}_{0.15}\text{Ti}_{1-x}\text{O}_3 \) ceramics. *Ceram Int* 2017, **43**: 8534–8537.

[388] Wang XH, Mu ML, Jiang H, *et al.* Investigation on structure and microwave dielectric properties of novel high dielectric constant \( \text{Ca}_{1-x}\text{Ce}_{x}\text{TiO}_3 \) ceramics sintered in nitrogen atmosphere. *J Mater Sci: Mater Electron* 2019, **30**: 1591–1599.

[389] Liu S, Tang B, Zhou MK, *et al.* Microwave dielectric characteristics of high permittivity \( \text{Ca}_{0.35}\text{Li}_{0.2}\text{Nd}_{0.35}\text{Ti}_{3-x}\text{(Zn}_{0.1}\text{Ti}_{0.2})\text{O}_3 \) ceramics \((x = 0.00–0.12)\). *Ceram Int* 2019, **45**: 8600–8606.

[390] Xiong Z, Tang B, Luo FC, *et al.* Characterization of structure, chemical bond and microwave dielectric properties in \( \text{Ca}_0\text{La}_{0.178}\text{TiO}_3 \) ceramic substituted by chromium for titanium. *J Adv Ceram Compd* 2020, **835**: 155249.

[391] Shi L, Peng R, Zhang HW, *et al.* Effects of Magnesium–tungsten co-substitution on crystal structure and microwave dielectric properties of \( \text{CaTi}_{1-x}\text{(Mg}_{0.5}\text{W}_{1-x})\text{O}_3 \) ceramics. *Ceram Int* 2021, **47**: 3354–3360.

[392] Zaman A, Uddin S, Mehbub N, *et al.* Structural investigation and improvement of microwave dielectric properties in \( \text{Ca}(\text{H},\text{Ti}_{1-x})\text{O}_3 \) ceramics. *Phys Scr* 2020, **96**: 025701.

[393] Hu P, Jiao H, Wang CH, *et al.* Influence of thermal treatments on the low frequency conductivity and microwave dielectric loss of \( \text{CaTiO}_3 \) ceramics. *Mater Sci Eng: B* 2011, **176**: 401–405.

[394] Hsu CH, Chang CH. Microwave dielectric properties of new \( \text{(Ca}_0\text{Sr}_{0.2})\text{Sn}_3\text{O}_7 \) ceramics. *Ceram Int* 2012, **38**: 4411–4413.

[395] Chen YC, Chen KC, Wu CY. Microwave dielectric properties of \((1-x)\text{Nd}_{1-x}\text{Ba}_{0.5}\text{Sn}_{0.5}\text{O}_3 \) \((0.0\leq x\leq 0.12)\) ceramic. *J Mater Sci: Mater Electron* 2012, **24**: 819–826.

[396] Shi F, Fu GG, Xiao EC, *et al.* Lattice vibrational characteristics and dielectric properties of pure phase \( \text{CaTiO}_3 \) ceramic. *J Mater Sci: Mater Electron* 2020, **31**: 18070–18076.

[397] Tian CL, Yue ZX, Zhou YY. Microwave dielectric properties of \( \text{BaTi}_{1-x}\text{(Ga}_{0.5}\text{Al}_{0.5})\text{O}_3 \) \((0.0\leq x\leq 0.12)\) perovskite ceramics. *Mater Res Bull* 2013, **48**: 455–460.

[398] Liu F, Yuan CL, Liu XY, *et al.* Effects of structural characteristics on microwave dielectric properties of \((\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Nd}_{0.5})\text{Ti}_{0.5}\text{Ge}_{0.5}\text{O}_3 \) ceramics. *Mater Res Bull* 2015, **70**: 678–683.

[399] Parida S, Rout SK, Subramanian V, *et al.* Structural, microwave dielectric properties and dielectric resonator antenna studies of \( \text{Sr}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 \) ceramics. *J Adv Ceram Compd* 2012, **528**: 126–134.

[400] Wang JY, Zhou H, Liu JT, *et al.* Microstructure and dielectric tunable properties of \( \text{SrO}(\text{Sr}_{1-x}\text{Ba})\text{TiO}_3 \) in microwave ceramics. *Ceram Int* 2012, **38**: 3503–3507.

www.springer.com/journal/40145
[401] Zhang MW, Zhai JW, Shen B, et al. Microwave dielectric properties of low loss and highly tunable Ba$_x$Sr$_{1-x}$Ti$_2$O$_5$ ceramics. J Mater Res 2012, 27: 910–914.

[402] Zhang JJ, Zhai JW, Wang JY. Structural and dielectric tunable properties of Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$ microsized ceramics. Sci China Technol Sci 2012, 55: 610–615.

[403] Tang LJ, Zhai JW, Shen B, et al. Property optimization of Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$–BaMoO$_4$ composite ceramics for tunable microwave applications. Ceram Int 2012, 38: 4967–4971.

[404] Tang LJ, Zhai JW, Zhang JJ, et al. Microwave dielectric properties of tunable Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$ and scheelite AMoO$_3$ (A = Ba, Sr) composite ceramics. J Alloys Compd 2013, 551: 556–561.

[405] Tang LJ, Wang JW, Zhai JW, et al. Dielectric tunable properties of Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$–MgMoO$_4$ composite ceramics for microwave applications. J Mater Sci: Mater Electron 2013, 24: 2576–2580.

[406] Jiang HT, Zhai JW, Zhang MW, et al. Enhanced microwave dielectric properties of Ba$_{0.8}$Sr$_{0.2}$Ti$_2$O$_5$–Zr$_{0.2}$Sn$_{0.8}$TiO$_4$ composite ceramics. J Mater Sci 2012, 47: 2617–2623.

[407] Zhang QW, Zhai JW, Ben QQ, et al. Enhanced microwave dielectric properties of Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$ ceramics doping by metal Fe powders. J Appl Phys 2012, 112: 104104.

[408] He YY, Zhao JY, Xu YB, et al. Microstructures and dielectric tunable properties of Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$–MgO–Mg$_2$TiO$_4$ composite ceramics. J Mater Sci 2013, 24: 2372–2378.

[409] He YY, Zhao JY, Xu YB, et al. Anomalous correlation between dielectric constant and tunability in (Ba,Sr)Ti$_2$O$_5$–MgO–Mg$_2$SiO$_4$ composite ceramics. J Am Ceram Soc 2013, 96: 1203–1208.

[410] Liu D, Pu YP, Shi X. Effects of Bi$_2$O$_3$ and Cr$_2$Ti$_2$O$_5$ co-doping on dielectric properties in BaTiO$_3$-based ceramics. Vacuum 2012, 86: 1568–1571.

[411] Hu GX, Gao F, Liu LL, et al. Microstructure and dielectric properties of highly tunable Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$–MgO–Al$_2$O$_3$/ZnO composite. J Alloys Compd 2012, 518: 44–50.

[412] Jiang K, Zhang JZ, Yu WL, et al. Manganese doping effects on interband electronic transitions, lattice vibrations, and dielectric functions of perovskite-type Ba$_x$Sr$_{0.5}$Ti$_2$O$_5$ ferroelectric ceramics. Appl Phys A 2012, 106: 877–884.

[413] Tseng CF, Lu SC. Microwave dielectric properties of (Ba$_{0.5}$Mg$_{0.5}$)(A$_{0.05}$Ti$_{0.95}$)O$_3$ (A = Zr, Sn) ceramics. Ferroelectrics 2013, 451: 76–83.

[414] Liu F, Liu XY, Yuan CL, et al. Microstructures and microwave dielectric properties of (1–x)(Sr$_x$Na$_{0.5}$La$_{0.5}$)TiO$_3$–xLnAlO$_3$ (Ln = Sm, Nd) ceramic systems. J Eur Ceram Soc 2015, 35: 2091–2098.

[415] Xie WT, Jiang QX, Cao QL, et al. Effect of ZnO/WO$_3$ additives on sintering behavior and microwave dielectric properties of (Sr,Ca)TiO$_3$–(Sm,Nd)AlO$_3$ ceramics. J Mater Sci: Mater Electron 2018, 29: 9745–9750.

[416] Singh J, Bahel S. Structural and dielectric properties of (Ba,Mg)$_{1-x}$(Tb$_{0.5}$Sr$_{0.5}$)$_x$O$_3$ (x = 0.025, 0.05, 0.075 and 0.1) solid solutions. J Mater Sci: Mater Electron 2019, 30: 6500–6506.

[417] Ma PP, Liu XQ, Zhang FQ, et al. Sr(Ga$_{0.5}$Nb$_{0.5}$)$_3$Ti$_4$O$_9$ low-loss microwave dielectric ceramics with medium dielectric constant. J Am Ceram Soc 2015, 98: 2534–2540.

[418] Qu JJ, Liu F, Yuan CL, et al. Microwave dielectric properties of 0.2SrTiO$_3$–0.8Ca$_{0.6}$Nd$_{0.3}$Ti$_1$Al$_2$O$_7$ ceramics. Mater Sci Eng B 2015, 191: 15–20.

[419] Singh J, Bahel S. Synthesis and characterization of temperature stable low-loss (1–x)Mg(Ti$_{0.95}$Sn$_{0.05}$)O$_3$–xBaTiO$_3$ (0 ≤ x ≤ 0.1) ceramics for microwave applications. J Mater Sci 2021, 56: 10947–10964.

[420] Ullah B, Lei W, Cao QS, et al. Structure and microwave dielectric behavior of A-site-doped Sr$_{0.6}$Ce$_{0.4}$TiO$_3$ ceramics system. J Am Ceram Soc 2016, 99: 3286–3292.

[421] Tian CL, Yue ZX, Meng SQ, et al. Structures and microwave dielectric properties of BaTi$_1$–(Co$_{0.05}$W$_{0.95}$)O$_3$ (x = 0.40–0.90) perovskite ceramics. J Am Ceram Soc 2012, 95: 1645–1650.

[422] Tian CL, Yue ZX, Zhou YY, et al. Crystal structures and microwave dielectric properties of Zn, W co-substituted BaTiO$_3$ perovskite ceramics. J Solid State Chem 2013, 197: 242–247.

[423] Lin YJ, Wang SF, Chen SH, et al. Microwave dielectric properties of (Ba$_{1-x}$Sr)$_x$(Mg$_{0.5}$W$_{0.5}$)O$_3$ ceramics. Ceram Int 2015, 41: 8931–8935.

[424] Chen YC, Syu RY. Dielectric properties of Ba$_2$Mg$_{0.95}$Zn$_{0.05}$W$_2$O$_5$ ceramics at microwave frequency. J Mater Sci: Mater Electron 2016, 27: 6979–6984.

[425] Biao JJ, Wu JY. Structure and microwave dielectric properties of B-site deficient double perovskite–Ba$_x$(Mg$_{1–x}$Y$_x$)$_2$TiO$_4$ ceramics. Ceram Int 2016, 42: 3290–3295.

[426] Ullah B, Lei W, Wang XW, et al. Structure instability and high microwave dielectric permittivity of nonstoichiometric (Sr$_{0.6}$Ce$_{0.4}$)$_x$Nd$_{1–x}$Ti$_3$O$_9$Mg$_2$O$_3$ system for wireless communication. J Matieriomics 2021, 7: 25–33.

[427] Hu X, Huang XJ, Chen YH, et al. Phase evolution and microwave dielectric properties of SrTiO$_3$ added ZnAl$_2$O$_4$–Zn$_2$SiO$_4$–SiO$_2$ ceramics. Ceram Int 2020, 46: 7050–7054.

[428] Liu F, Qu JJ, Yan HG, et al. Study on phase structures and compositions, microstructures, and dielectric characteristics of (1–x)NdGaO$_3$–Bi$_2$O$_3$–Nd$_2$O$_3$ microwave ceramic systems. Ceram Int 2020, 46: 16185–16195.

[429] Jin X, Guo QH, Bian JJ. Structure and dielectric properties of A-site-deficient perovskite Nd$_{1–x}$M$_x$NdBO$_3$ (M = Li, Ag, 0 ≤ x ≤ 0.20) ceramics. J Mater Sci 2012, 47: 6015–6024.

[430] Xiao M, Zhang QQ, Jia CR. The microstructure and properties of Ag(Nb$_{0.5}$Ta$_{0.5}$)$_2$–(Mn$_{0.3}$W$_{0.7}$)O$_3$ ceramic system. J Wuhan Univ Technol Mater Sci Ed 2012, 27:
735–739.

[431] Peng Y, Li LX, Cao LF, et al. Correlation between crystal structure and properties of ultra-high dielectric constant ceramics xSrCoO3–(1–x)Bi2O3–Ag(Nb,Ta)O3. J Electroceramics 2012, 28: 209–213.

[432] Saleem M, Iqbal Y, Qin S, et al. Phase, microstructure and microwave dielectric properties of A-site deficient (La,Nd)2/3TiO3 perovskite ceramics. Mater Sci Pol 2015, 33: 126–130.

[433] Zhang MM, Li LX, Xia WS, et al. Structure and properties analysis for MgTiO3 and (Mg0.95Mn0.05)TiO3 (M = Ni, Zn, Co and Mn) microwave dielectric materials. J Alloys Compd 2012, 537: 76–79.

[434] Gogoi P, Sharma P, Pamu D. Microwave and broadband dielectric properties of Ni substituted MgTiO3 ceramics. J Mater Sci: Mater Electron 2016, 27: 9052–9060.

[435] Gogoi P, Singh LR, Pamu D. Characterization of Zn doped MgTiO3 ceramics: An approach for RF capacitor applications. J Mater Sci: Mater Electron 2017, 28: 11712–11721.

[436] Lin SH, Chen YB. Low dielectric loss characteristics of [(Mg1−xZnx)(0.5Co0.5)O]1.02TiO3.02 ceramics at microwave frequencies. J Mater Sci: Mater Electron 2017, 28: 4154–4160.

[437] Li LX, Ding X, Liao QW. Structure and properties analysis for low-loss (Mg1−xCo)xTiO3 microwave dielectric materials prepared by reaction-sintering method. Ceram Int 2012, 38: 1937–1941.

[438] Gangwar RK, Singh SP, Choudhary M, et al. Microwave dielectric properties of (Zn1−xMgx)TiO3 (ZMT) ceramics for dielectric resonator antenna application. J Alloys Compd 2011, 509: 10195–10202.

[439] Yu HT, Xue XM, Xu GL. Correlation between Sn substitution for Ti and microwave dielectric properties of magnesium titanate ceramics. Int J Appl Ceram Technol 2013, 10: E186–E191.

[440] Santhosh Kumar T, Gogoi P, Perumal A, et al. Effect of cobalt doping on the structural, microstructure and microwave dielectric properties of MgTiO3 ceramics prepared by semi alkoxide precursor method. J Am Ceram Soc 2014, 97: 1054–1059.

[441] Gong ZJ, Wang ZF, Wang LX, et al. Microwave dielectric properties of high-Q Mg(Sn,Ti)xO3 ceramics. Electron Mater Lett 2013, 9: 331–335.

[442] Jia XB, Xu Y, Zhao P, et al. Structural dependence of microwave dielectric properties in ilmenite-type MgTi1−xNb2O5 solid solutions by Rietveld refinement and Raman spectra. Ceram Int 2021, 47: 4820–4830.

[443] Wu HT, Jiang YS, Cui YJ, et al. Improvements in the sintering behavior and microwave dielectric properties of geikielite-type MgTiO3 ceramics. J Electron Mater 2013, 42: 445–451.

[444] Wang HP, Yang QH, Li DH, et al. Sintering behavior and microwave dielectric properties of MgTiO3 ceramics doped with B2O3 by sol–gel method. J Mater Sci Technol 2012, 28: 751–755.

[445] Tseng CF, Lu SC. Influence of SrTiO3 modification on dielectric properties of Mg(Zr0.05Ti0.95)O3 ceramics at microwave frequency. Mater Sci Eng: B 2013, 178: 358–362.

[446] Yu HT, Cheng JL, Zhang WB, et al. Microwave dielectric properties of Mg(Zr0.05Ti0.95)O3–SrTiO3 ceramics. J Mater Sci: Mater Electron 2012, 23: 572–575.

[447] Xue XM, Yu HT, Xu GL. Phase composition and microwave dielectric properties of Mg-excess MgTiO3 ceramics. J Mater Sci: Mater Electron 2013, 24: 1287–1291.

[448] Huang CL, Huang SH. Low-loss microwave dielectric ceramics in the (Co1−xZnx)TiO3 (x = 0–0.1) system. J Alloys Compd 2012, 515: 8–11.

[449] Liou YC, Yang SL, Chu SY. Effects of MgO and Mg(OH)2 on phase formation and properties of strontium-doped MgTiO3 microwave dielectric ceramics. J Alloys Compd 2013, 576: 161–169.

[450] Li H, Tang B, Li YX, et al. Effects of Mg2.05Si0.45 addition on phase structure and microwave properties of MgTiO3–CaTiO3 ceramic system. Mater Lett 2015, 145: 30–33.

[451] Tang B, Li YX, Li H, et al. Structure and microwave dielectric properties of (Zn0.1Co0.9)Ti1−xSnxO3 ceramics. J Mater Sci: Mater Electron 2015, 26: 2795–2799.

[452] Huang XP, Liu F, Yuan CL, et al. Microstructures and microwave dielectric properties of Mg1−xTi3n+1 ceramics with ultralow dielectric loss. Mater Lett 2016, 185: 432–435.

[453] Chen CY, Peng ZJ, Xie LZ, et al. Effects of adding B2O3 on microwave dielectric properties of 0.9625MgTiO3–0.0375(Ca0.5Sr0.5)TiO3 composite ceramics. Int J Appl Ceram Technol 2020, 17: 2545–2552.

[454] Yu T, Luo T, Yang QH, et al. Ultra-high quality factor of Mg6Ti5O16-based microwave dielectric ceramics with temperature stability. J Mater Sci: Mater Electron 2021, 32: 2547–2556.

[455] Chen KC, Chen YC, Chen MD. Microwave dielectric properties of Mg1.9(Nb2)3Sn4O12 ceramics. Ferroelectr Lett Sect 2012, 39: 1–7.

[456] Bhuyan RK, Kumar TS, Pamu D, et al. Structural and microwave dielectric properties of Mg5Ti6O14 ceramics synthesized by mechanical method. Int J Appl Ceram Technol 2013, 10: E18–E24.

[457] Bhuyan RK, Kumar TS, Goswami D, et al. Liquid phase effect of La2O3 and V2O5 on microwave dielectric properties of Mg5Ti6O14 ceramics. J Electroceramics 2013, 31: 48–54.

[458] Bhuyan RK, Kumar TS, Goswami D, et al. Enhanced densification and microwave dielectric properties of Mg5Ti6O14 ceramics added with CeO2 nanoparticles. Mater Sci Eng: B 2013, 178: 471–476.
frequency. *J Eur Ceram Soc* 2012, **32**: 2365–2371.

[460] Chen YB. Dielectric properties and crystal structure of Mg2TiO4 ceramics substituting Mg2+ with Zn2+ and Co2+. *J Alloys Compd* 2012, **513**: 481–486.

[461] Cheng L, Liu P, Qu SX, *et al*. Microwave dielectric properties of Mg3TiO4 ceramics synthesized via high energy ball milling method. *J Alloys Compd* 2015, **623**: 238–242.

[462] Lyu XS, Li LX, Sun H, *et al*. A novel low-loss spinel microwave dielectric ceramic Co2ZnTiO4. *J Mater Sci: Mater Electron* 2015, **26**: 8663–8666.

[463] Li H, Tang B, Li YX, *et al*. Relationships between Sn substitution for Ti and microwave dielectric properties of Mg3(Ti1–xSnx)O4 ceramics system. *J Mater Sci: Mater Electron* 2015, **26**: 571–577.

[464] Chen YC, Syu RY. Enhancement quality factor of ZnNiTiO4 microwave ceramics by substituting Ti4+ with Sn4+. *J Mater Sci: Mater Electron* 2017, **28**: 673–678.

[465] Chen YC, Syu RY. Elucidating the microstructures and microwave dielectric properties of ZnNiTiO4 ceramics. *J Mater Sci: Mater Electron* 2016, **27**: 8356–8362.

[466] Li H, Xiang R, Chen XQ, *et al*. Intrinsic dielectric behavior of Mg2TiO4 spinel ceramic. *Ceram Int* 2020, **46**: 4235–4239.

[467] Xiang R, Li H, Zhang PC, *et al*. Crystal structure and microwave properties of Mg2Ti1–Ga4x3O4 (0.05 ≤ x ≤ 0.13) ceramics. *Ceram Int* 2021, **47**: 8447–8452.

[468] Fang ZX, Tang B, Li YX, *et al*. Microstructures and microwave dielectric properties of Na0.2Nd0.2Sm0.1Ti1–xSnxO3 ceramics (x = 0.00 to 0.50). *J Electron Mater* 2015, **44**: 4236–4242.

[469] Zhou L, Tang B, Zhang SR. Influence of Sn-substitution on microstructure and microwave dielectric properties of Na1–xNd1+2/3Ti0.7O3 ceramics. *J Mater Sci: Mater Electron* 2015, **26**: 424–428.

[470] Fang ZX, Tang B, Si F, *et al*. Effects of Zr-substitution on microwave dielectric properties of Na0.5Nd0.5Sm0.1Ti1–xZr1/2xO3 ceramics (x = 0.00–0.30). *J Electron Mater* 2016, **45**: 5198–5205.

[471] Fang ZX, Tang B, Zhang SR. Microwave dielectric properties of Na1/2Sm1/2Ti1–x(Cr1/2Nb1/2)xO3 Ceramics (x = 0–0.025). *IOP Conf Ser: Mater Sci Eng* 2017, **170**: 012029.

[472] Gan L, An SB, Yuan SF, *et al*. Sintering characteristics and microwave dielectric properties of (1−x)Li2O·Sm2O3·TiO2−xNa2O·Sm2O3·TiO3 (x = 0.35 to 0.45) ceramics. *J Electron Mater* 2019, **48**: 3624–3630.

[473] Zhou YY, Tian CL, Meng SQ, *et al*. Structural transitions and microwave dielectric properties of Ba1.5Sr2.5Sn2O9 double perovskites. *J Am Ceram Soc* 2012, **95**: 1665–1670.

[474] Wu JY, Bian JJ. Structure stability and microwave dielectric properties of double perovskite ceramics–Ba0.5Mg1–xCaxW0.5 (0.0 ≤ x ≤ 0.15). *Ceram Int* 2012, **38**: 3217–3225.

[475] Chen YC, Wang YN, Syu RY. Effect of sintering temperature on microstructures and microwave dielectric properties of Ba2MgWO6 ceramics. *J Mater Sci: Mater Electron* 2016, **27**: 4259–4264.

[476] Diao CL, Wang CH, Luo NN, *et al*. First-principle calculation and assignment for vibrational spectra of Ba(Mg1/2W1/2)O3 microwave dielectric ceramic. *J Am Ceram Soc* 2013, **96**: 2898–2905.

[477] Li L, Zhang W, Chen XM, *et al*. Dielectric properties of CaCu3Ti4O12, Ba(Fe1/2Nb1/2)O3, and Sr(Fe1/2Nb1/2)O3 giant permittivity ceramics at microwave frequencies. *J Appl Phys* 2012, **111**: 064108.

[478] Tay KW, Fu YP, Huang JF, *et al*. Effect of Bi2O3 and Ba2O3 additives on the sintering temperature, microstructure, and microwave dielectric properties for Sm(Mg0.5Ti0.5)O3 ceramics. *Ceram Int* 2011, **37**: 1025–1031.

[479] Chen YB. New microwave dielectric material system of Nd(Mg1/2Ti1/2)O3–SnTiO3 in the microwave frequency range. *J Alloys Compd* 2011, **509**: 2285–2288.

[480] Chen YC. Improving microwave dielectric properties of La2+0.5Sr0.5–(Mg0.5Sn0.5)O3 ceramics with CuO additive. *Curr Appl Phys* 2012, **12**: 483–488.

[481] Hsu CH, Chang CH. Microwave dielectric properties of Nd(Zn1/2Ti1/2)O3 ceramics with V2O5 additives. *J Mater Eng Perform* 2013, **22**: 312–315.

[482] Chen YY, Chen YC, Liu HX, *et al*. Effect of Sm substitution on microwave dielectric properties of Nd(Mg0.5Sn0.5)O3 ceramics. *J Mater Sci: Mater Electron* 2013, **24**: 4600–4606.

[483] Chen YC, Yao SL, Wu CY. Microwave dielectric properties and microstructures of Nd(Mg0.5Co0.5)O3 ceramics. *J Mater Sci: Mater Electron* 2012, **23**: 1320–1326.

[484] Wang YN. Enhancing the microwave dielectric properties of Nd(Mg0.5Sn0.5)O3 ceramics by substituting Nd3+ with Ca2+. *J Mater Sci: Mater Electron* 2013, **24**: 4510–4515.

[485] Chen YC, Wu CY. Effect of Sr substitution on microwave dielectric properties of Nd(Mg0.5Sn0.5)O3 ceramics. *Ceram Int* 2013, **39**: 1877–1883.

[486] Chen YC, Weng MZ, Chen YY. Influence of Ba2+ substitution on the microwave dielectric properties of Nd(Mg0.5Sn0.5)O3 ceramics. *J Mater Sci: Mater Electron* 2013, **24**: 2970–2975.

[487] Chen YC, Chen YY, Yao SL. Improved microwave dielectric properties of Nd(Mg0.5Sn0.5)O3 ceramics with Ni2+ substituting. *J Mater Sci: Mater Electron* 2013, **24**: 1150–1157.

[488] Chen YC, Chang KC, Yao SL. Improved microwave dielectric properties of Nd(Mg0.5Sn0.5)O3 ceramics by substituting Mg2+ with Zn2+. *Ceram Int* 2012, **38**: 5377–5383.

[489] Chen YC, Tsai RJ, Wu CY. Microwave dielectric properties and microstructures of Nd(Mg0.5Sn0.5–x, Ti)O3 ceramics. *Ceram Int* 2012, **38**: 2927–2934.
[490] Chen YC, Chang KC, Tsai DY. A hybrid dielectric resonator antenna based upon novel complex perovskite microwave ceramic. Ceram Int 2013, 39: 3043–3048.

[491] Li JM, Qi T. Microwave dielectric properties of Nd[(Zn1−xCo)x]0.5TiO3 ceramics. J Adv Ceram 2012, 28: 2597–2600.

[492] Li JM, Fan CG, Cheng ZX, et al. Influence of Zn nonstoichiometry on the phase structure, microstructure and microwave dielectric properties of Nd(Zn0.5Ta0.5)O3 ceramics. J Alloys Compd 2019, 793: 385–392.

[493] Cao ZK, Xiao EC, Li XH, et al. Lattice vibrational characteristics, crystal structures and dielectric properties of non-stoichiometric Nd1−x(Mg0.5Sn0.5)O3 ceramics. J Materiomics 2020, 6: 476–484.

[494] Shi F, Xiao EC, Chen GH, et al. Lattice vibrational characteristics and structures–properties relationships of non-stoichiometric Nd[0.8Sr0.2]TiO3 ceramics. Appl Phys A 2020, 126: 1–14.

[495] Chen YC, Wang YN, Lee WC. Microstructures and microwave dielectric properties of La1−xB4(Mg0.5Sn0.5)O3 ceramics. J Eur Ceram Soc 2013, 33: 3126–3131.

[496] Chen YC. Improved microwave dielectric properties of La(Mg0.5Sn0.5)O3 ceramics with Sr2+ doping. J Adv Ceram 2013, 2: 041501.

[497] Wang YN, Chen MD. Improved microwave dielectric properties of La(Mg0.5Sn0.5)O3 ceramic with Ba2+ substitution. J Mater Sci: Mater Electron 2013, 24: 3730–3735.

[498] Remya GR, Dhwajam DB, Thomas JK, et al. Dielectric and optical properties of ZnO and Eu2O3 doped Pb0.75Y0.25TaO3 ceramic. J Mater Sci: Mater Electron 2013, 24: 370–375.

[499] Chen YY, Chen YC, Chen MD. Tuning the microwave dielectric properties of La(Mg0.5Sn0.5)O3 by introducing Ca0.5Sr2Ta2O7. J Mater Sci: Mater Electron 2013, 24: 3126–3131.

[500] Tseng CF, Huang CC. Microwave dielectric properties of (1−x)Nd(Co0.62Ti1−x)O3−x(Ca0.5Sn0.5)TiO3 composite ceramics. J Mater Sci 2012, 47: 3982–3988.

[501] Wang YN, Chen MD. Improved microwave dielectric properties of La(Mg0.5Sn0.5)O3 ceramic with Sr2+ Substitution. Ferroelectr Lett Sect 2013, 40: 121–129.

[502] Li JM, Qi T. Microwave dielectric properties of (1−x)Ca0.5La0.5xTi2O5−x(CatSn0.5Nb0.5)O3 ceramics. Ceram Int 2012, 38: 4331–4335.

[503] Fan J, Zhao Q, Du K, et al. Lattice structure and microwave dielectric properties of La[Al1−x(0.5Mg0.5)3]xO3 (x = 0–0.2)-based ceramics. J Am Ceram Soc 2020, 103: 3231–3237.

[504] Yang HC, Zhang SR, Yang HY, et al. Vibrational spectroscopic and crystal chemical analyses of double perovskite Y2MgTiO4 microwave dielectric ceramics. J Am Ceram Soc 2020, 103: 1121–1130.

[505] Chen CT, Huang CY, Lin YM, et al. Structure and microwave dielectric property relations in Barium cobalt magnesium niobate ceramics. Jpn J Appl Phys 2011, 50: 091503.

[506] Wang SF, Wang YR, Liu CY, et al. Microwave dielectric properties of multi-ions Ba(Zn,Ta)O3-based perovskite ceramics. Ceram Int 2012, 38: 1127–1132.

[507] Ning PF, Li LX, Zhang P, et al. Raman scattering, electronic structure and microwave dielectric properties of Ba[Mg1−xZnx]3Ta2O9 ceramics. Ceram Int 2012, 38: 1391–1398.

[508] Chen CT, Huang CY, Lin HJ, et al. Effect of small amount of cobalt substitution on structure and microwave dielectric properties of Barium magnesium niobate ceramics. J Eur Ceram Soc 2012, 32: 2373–2380.

[509] Sun TL, Li L, Mao MM, et al. Effects of postdensification annealing on microwave dielectric properties of Ba[Mg1−xCo]3Ta2O9 ceramics. Int J Adv Ceram Technol 2013, 10: E210–E218.

[510] Ma PP, Yi L, Liu XQ, et al. Effects of postdensification annealing upon microstructures and microwave dielectric characteristics in Ba(Co0.6xZnx)3Ta2O9 ceramics. J Am Ceram Soc 2013, 96: 3417–3424.

[511] Ma PP, Yi L, Liu XQ, et al. Effects of Mg substitution on order/disorder transition, microstructure, and microwave dielectric characteristics of Ba(Co0.6yZny)3Ta2O9 complex perovskite ceramics. J Am Ceram Soc 2013, 96: 1795–1800.

[512] Diao CL, Shi F. Effect of sintering temperature on dielectric properties, vibrational modes and crystal structures of Ba[(Mg1−xZnx)3]0.5Ta2/3O3 ceramics. J Mater Sci 2012, 47: 5438–5445.

[513] Wang J, Lu WZ, Lei W. Effects of Ba deficiency on ion ordering, grain growth, and microwave dielectric properties of Ba1−xZnxTa2/3O3 ceramics. Jpn J Appl Phys 2012, 51: 041501.

[514] Diao CL, Shi F. Correlation among dielectric properties, vibrational modes, and crystal structures in Ba[Sn1−xNi0.3]O3 solid solutions. J Phys Chem C 2012, 116: 6852–6858.

[515] Shi F, Diao CL. Evaluation of dielectric properties, vibration modes, and crystal structures in Ba[(Zn1−xNi0.3)3]O3 ceramics. Metall Mater Trans A 2013, 44: 381–387.

[516] Fu MS, Ni L, Chen XM. Abnormal variation of microwave dielectric properties in A/B site co-substituted (Ca1−aLa2+a)0.5(Mg0.5Ta0.5)3−yTi4yO13 complex perovskite ceramics. J Eur Ceram Soc 2013, 33: 813–823.

[517] Sun TL, Mao MM, Chen XM. Structure and microwave dielectric properties of Ba[(Mg1−xNi)x]3Nb2/3O9 ceramics. Mater Res Bull 2015, 72: 291–298.

[518] Sindam B, James Raju KC. Influence of sintering temperature on microwave dielectric properties, structure and lattice modes of Ba(Zn1−xTa2/3)3O9 resonators. J Mater Sci: Mater Electron 2015, 26: 3997–4004.

[519] Sun TL, Zhao YF, Chen XM. Improvement of microwave dielectric properties for BaNi1/2Nb1/2:0.3O3 ceramics by
Zr-substitution. *Ceram Int* 2015, 41: 5872–5880.

[520] Sun TL, Chen XM. Tailoring the order-disorder transition and microwave dielectric properties of Ba[(Ni0.6Zn0.4)1/3Nb2/3]O3 ceramics by Mg-substitution. *Mater Chem Phys* 2015, 165: 142–149.

[521] Wang ZF, Huang BY, Wang LX, et al. Low loss (Ba1−xSr0.5)x(Mn1−yCo2/3)O3 solid solution: Phase evolution, microstructure and microwave dielectric properties. *J Mater Sci Mater Electron* 2015, 26: 4273–4279.

[522] Zhou XH, Zhang YQ, Yang XS, et al. Effects of Y2O3 substitution on microwave dielectric properties of Ba(Co0.9Zn0.1)1−xNb2/3O3 ceramics. *J Mater Sci Mater Electron* 2015, 26: 7683–7689.

[523] Zhang YQ, Zhou XH, Yang XS, et al. Effects of Y2O3/CoO co-doping on microwave dielectric properties of Ba(Co0.9Zn0.1)1−xNb2/3O3 ceramics. *J Alloys Compd* 2016, 679: 247–253.

[524] Rodrigues JEFS, Castro PJ, Pizani PS, et al. Structural ordering and dielectric properties of Ba5CaNb2O9-based microwave ceramics. *Ceram Int* 2016, 42: 18087–18093.

[525] Ni LZ, Li LX, Du MK. Ultra-high-Q and wide temperature stable Ba(Mg1/3Ta2/3)O3 microwave dielectric ceramic for 5G power waveguide window. *Microwave Ceramics* 2020, 844: 156106.

[526] Jinga SI, Stoleriu S, Busuioc C. Microwave dielectric properties of Ba(ZnMn)1/3Ta2/3O3 ceramics doped with NbO3, MnO2 or V2O5. *Mater Res Bull* 2012, 47: 3713–3718.

[527] Wang ZF, Huang BY, Wang LX, et al. Sintering characteristics and microwave dielectric properties of Ba(Co0.9Zn0.1)1−xNb2/3O3. *J Mater Sci Mater Electron* 2015, 26: 1107–1112.

[528] Tang B, Fang ZX, Li YX, et al. Microwave dielectric properties of Ba(Co0.56Y0.08Zn0.39)1−xNb2/3O3 (x = 0.004 ~ 0.008) ceramics. *J Mater Sci Mater Electron* 2015, 26: 6585–6591.

[529] Sindam B, James Raju KC. Microwave dielectric properties of Ba(Zn1/3Ta2/3)O3 for application in high power waveguide window. *Eur Phys J B* 2016, 89: 92.

[530] Peng S, Xu JM, Li H. Microstructure and microwave dielectric properties of Ba[(Mg1/3,Zn1/3)1/3Ta2/3]O3 solid solution ceramics. *J Mater Sci Mater Electron* 2020, 31: 20423–20430.

[531] Peng S, Wu MQ, Xu JM, et al. Effect of La2O3 addition on the microwave dielectric properties of Ba(Mg1/3Ta2/3)O3 ceramics. *J Mater Sci Mater Electron* 2017, 28: 3349–3355.

[532] Peng S, Xu JM, Li F. Influence of Ca2+ substitution for Ba2+ on the crystal structure and microwave dielectric properties of Ba1−xCa(Mg1/3Ta2/3)O3 ceramics. *J Mater Sci Mater Electron* 2020, 31: 15822–15828.

[533] Peng S, Wu MQ, Xu JM, et al. Microwave dielectric properties of Ba(Mg1/3−xSn1/3Ta2/3−xZr2/3)O3 (x = 0–0.25) ceramics. *J Mater Sci Mater Electron* 2017, 28: 174–179.

[534] Ni LZ, Li LX, Du MK, et al. Wide temperature stable Ba(Mg,Ta2/3)O3 microwave dielectric ceramics with ultra-high-Q applied for 5G dielectric filter. *Ceram Int* 2021, 47: 1034–1039.

[535] Guevarra J, van Smaalen S, Rotiroti N, et al. Crystal structure of Ca3NbO17. *J Solid State Chem* 2005, 178: 2934–2941.

[536] Joseph T, Anjana PS, Letourneau S, et al. Structure and microwave dielectric properties of Ca3A2TiO7 (A = Nb, Ta) ceramics. *Mater Chem Phys* 2010, 121: 77–82.

[537] Manan A, Iqbal Y. Influence of Sm substitution on the phase, microstructure and microwave dielectric properties of SrLa4Ti5O17. *J Mater Sci Mater Electron* 2011, 22: 1848–1854.

[538] Iqbal Y, Manan A, Reaney IM. Low loss Sr1−xCa4La2Ti5O17 microwave dielectric ceramics. *Mater Res Bull* 2011, 46: 1092–1096.

[539] Iqbal Y, Manan A. Phase, microstructure and microwave dielectric properties of Zr-doped SrLa4Ti5−xZr2O7. *J Mater Sci Mater Electron* 2012, 23: 536–541.

[540] Li CC, Wei XY, Yan HX, et al. Microwave dielectric properties of CaO−La2O3−Nb2O5−TiO2 ceramics. *J Mater Sci Mater Electron* 2013, 24: 1947–1954.

[541] Li CC, Wei XY, Yan HX, et al. Microwave dielectric properties of La3Ti2TaO11 ceramics with perovskite-like layered structure. *J Eur Ceram Soc* 2012, 32: 4015–4020.

[542] Manan A, Reaney IM. The effect of processing conditions on the phase, microstructure and dielectric properties of SrCa4Nb2TiO17 and Ca3Nb2TiO7 microwave ceramics. *Mater Sci Pol* 2012, 30: 98–104.

[543] Iqbal Y, Muhammad R. Phase, microstructure, and microwave dielectric properties of NaCa1−xSr,xNb2O7 (x = 0 to 4) ceramics. *J Electron Mater* 2013, 42: 452–457.

[544] Muhammad R, Iqbal Y. Preparation and characterization of K-substituted NaCa4Nb2O7 microwave dielectric ceramics. *J Mater Sci Mater Electron* 2013, 24: 2322–2326.

[545] Rejini R, Subodh G, Sebastian MT. Ca3La2Ti3O17: A novel low loss dielectric ceramics in the CaO−La2O3−TiO2 system. *J Mater Sci Mater Electron* 2008, 19: 1153–1155.

[546] Chen GH, Di JC, Xu HR, et al. Microwave dielectric properties of NaCa1−xSr,xNb2O7 (x = 0 to 4) ceramics. *J Am Ceram Soc* 2012, 95: 1394–1397.

[547] Di JC, Chen GH, Hou MZ, et al. Low loss and middle permittivity of (1−x)CaLa2Ti5O17−xNdAlO3 dielectric resonators with near-zero temperature coefficient of the resonant frequency. *J Mater Sci* 2012, 47: 2271–2277.

[548] Chen GH, Di JC, Li M, et al. Synthesis, microstructure and microwave dielectric properties of Ca4−xMg2xLa2Ti5O17 ceramics. *J Mater Sci Mater Electron* 2012, 23: 746–752.

[549] Fang L, Li CC, Peng XY, et al. Microwave dielectric properties of SrLa4Ti5−xMg2/3Nb2/3O17 ceramics. *J Am Ceram Soc* 2010, 93: 1884–1887.

[550] Fang L, Li CC, Peng XY, et al. Two novel A2B2O7-type microwave ceramics with high-Q and near-zero τ. *J Mater Res* 2010, 25: 1239–1242.
Fan XC, John A, Thomas JK, et al. Structural, spectroscopic and dielectric investigations on Ba$_2$Zn$_{0.5}$Nb$_{0.5}$O$_3$ microwave ceramics. *Mater Res Bull* 2010, **45**: 1389–1395.

Suresh MK, John A, Thomas JK, et al. Structural analysis and properties of thermally stable Ba$_2$Mg$_x$Nb$_{0.5}$O$_3$ microwave ceramics. *J Alloys Compd* 2011, **509**: 2401–2406.

Solomon S, Suresh MK, Thomas JK, et al. Synthesis, structural analysis and dielectric properties of Ba$_2$(Mg$_1$,Zn$_2$)Nb$_{0.5}$O$_3$ hexagonal perovskites. *Ceram Int* 2012, **38**: 6487–6494.

Fang L, Su CX, Wei ZH, et al. Phase structure, band gap and microwave dielectric properties of Ba$_4$Ti$_3$Nb$_{4-x}$Sb$_x$O$_{24}$ ceramics. *Ceram Int* 2013, **39**: 579–583.

Tian CL, Yue ZX, Zhou YY. Microstructures and microwave dielectric properties of Ba$_4$LiNb$_3$O$_{12-}$BaWO$_4$ composite ceramics. *Mater Sci Eng: B* 2013, **178**: 178–182.

Zhou HF, Liu XB, Chen XL, et al. Ba$_3$LiNb$_3$O$_{12}$: Phase evolution, microstructure and optimized microwave dielectric properties. *Mater Lett* 2013, **96**: 199–202.

Tang Y, Fang WS, Fang L, et al. Phase transformation and microwave dielectric properties of Ba$_4$LiTa$_3$O$_{12}$, *Ceram Int* 2015, **41**: 6653–6656.

Liao W, Fang L, Xiang F, et al. Effect of Sb$^{5+}$ substitution on the dielectric properties of Ba$_4$LiTa$_3$O$_{12}$ ceramics. *J Mater Sci: Mater Electron* 2013, **24**: 272–276.

Fang L, Liao W, Wu MX, et al. Microwave dielectric properties of Ba$_4$LiNb$_{3-x}$Sb$_x$O$_{24}$ (x = 0–3) ceramics. *Mater Lett* 2012, **76**: 73–76.

Fang L, Wu MX, Liu QW, et al. High ε and low loss microwave dielectric ceramics Ba$_4$LiNb$_{3-x}$Ta$_x$O$_{24}$. *Mater Chem Phys* 2015, **163**: 599–603.

Wang KG, Zhou HF, Luan XW, et al. Microwave dielectric properties of Li$_2$SmTa$_2$O$_7$ ceramics with A-site deficient perovskite structure. *Mater Lett* 2020, **274**: 128020.

Fan XC, Chen XM, Liu XQ. Structural dependence of microwave dielectric properties of Sr$_3$RAIO$_4$ (R = Sm, Nd, La) ceramics: Crystal structure refinement and infrared reflectivity study. *Chem Mater* 2008, **20**: 4092–4098.

Fan XC, Mao MM, Chen XM. Microstructures and microwave dielectric properties of the CaSmAlO$_4$-based ceramics. *J Adv Ceram* 2008, **91**: 2917–2922.

Yuan HX, Chen XM, Mao MM. Structure and microwave dielectric characteristics of Ca$_{1-x}$Nd$_x$Al$_{1-x}$Ti$_2$O$_4$ ceramics. *J Am Ceram Soc* 2009, **92**: 2286–2290.

Mao MM, Fan XC, Chen XM. Effect of A-site ionic radius on the structure and microwave dielectric characteristics of Sr$_1-x$Sm$_x$Al$_{1-x}$Ti$_2$O$_4$ ceramics. *Int J Appl Ceram Technol* 2010, **7**: E156–E162.

Zhang C, Yi L, Chen XM. Improvement of microwave dielectric characteristics in SrNdAlO$_4$ ceramics by Ca-substitution. *Ceram Int* 2014, **40**: 6077–6082.

Xiao Y, Chen XM, Liu XQ. Microstructures and microwave dielectric characteristics of CaRAIO$_4$ (R = Nd, Sm, Y) ceramics with tetragonal K$_2$NiF$_4$ structure. *J Am Ceram Soc* 2004, **87**: 2143–2146.

Mao MM, Chen XM. Infrared reflectivity spectra and microwave dielectric properties of (Sr$_3-x$Ca$_x$)SmAlO$_4$ (0 ≤ x ≤ 1) ceramics. *Int J Appl Ceram Technol* 2011, **8**: 1023–1030.

Mao MM, Chen XM, Liu XQ. Structure and microwave dielectric properties of solid solution SrLaAl$_2$O$_4$–SrTiO$_3$ system. *J Am Ceram Soc* 2011, **94**: 3948–3952.

Mao MM, Liu XQ, Chen XM. Structural evolution and its effects on dielectric loss in Sr$_{1-x}$Sm$_x$Al$_2$Ti$_4$O$_{14}$ microwave dielectric ceramics. *J Am Ceram Soc* 2011, **94**: 2506–2511.

Liu B, Yi L, Liu XQ, et al. Structure and microwave dielectric properties of SrSmAlO$_4$–Sr$_2$TiO$_3$ solid solutions. *J Electroceramics* 2015, **34**: 114–121.

Liu B, Li L, Liu XQ, et al. Structural evolution of SrLaAl$_{1-x}$(Zn$_{0.5}$Ti$_{0.5}$)$_x$O$_4$ ceramics and effects on their microwave dielectric properties. *J Mater Chem C* 2016, **4**: 4684–4691.

Ren GR, Zhu JY, Li L, et al. SrLa(R$_x$Zn$_{1-x}$)$_3$O$_4$ (R = Mg, Zn) microwave dielectric ceramics with complex K$_2$NiF$_4$-type layered perovskite structure. *J Am Ceram Soc* 2017, **100**: 2582–2589.

Yan H, Chen GY, Li L, et al. Microwave dielectric properties of SrLa[Ga$_n$(Mg$_{0.5}$Ti$_{0.5}$)$_{3-n}$]O$_4$ and SrLa[Ga$_n$(Zn$_{0.5}$Ti$_{0.5}$)$_{3-n}$]O$_4$ (x = 0.2–0.8) ceramics. *Int J Appl Ceram Technol* 2020, **17**: 790–796.

Manan A, Ullah R, Iqbal Y, et al. Tailoring the microwave dielectric properties of Sr$_0.6$Ca$_{0.4}$LaAlO$_4$ ceramic by TiO$_2$ addition. *J Aust Ceram Soc* 2020, **56**: 1013–1019.

Liu B, Li L, Liu XQ, et al. Sr$_{1-x}$Ti$_2$O$_{4+1}$ (x = 1, 2) microwave dielectric ceramics with medium dielectric constant and ultra-low dielectric loss. *J Am Ceram Soc* 2017, **100**: 496–500.

Yuan ZQ, Liu B, Liu XQ, et al. Structure and microwave dielectric characteristics of Sr(La$_{1-x}$Sm$_x$)$_3$AlO$_4$ ceramics. *RSC Adv* 2016, **6**: 96229–96236.

Liu B, Liu XQ, Chen XM. Sr$_2$LaAlTiO$_4$: A new Ruddlesden–Popper compound with excellent microwave dielectric properties. *J Mater Chem C* 2016, **4**: 1720–1726.

Yi L, Li L, Liu XQ, et al. Structure evolution and enhanced microwave dielectric characteristics of (Sr$_{1-x}$Ca$_x$)La$_2$AlO$_4$ ceramics. *J Am Ceram Soc* 2014, **97**: 3531–3536.

Yi L, Liu XQ, Li L, et al. Sr$_2$LaAlO$_3$ (Ln = La, Nd, Sm) microwave dielectric ceramic new materials. *Int J Appl Ceram Technol* 2013, **10**: E177–E185.

Dias A, Viegas JL, Moreira RL. Synthesis and μ-Raman scattering of Ruddlesden–Popper ceramics Sr$_2$Ta$_2$O$_7$ and Sr$_2$LaAlTiO$_4$. *J Alloys Compd* 2017, **725**: 77–83.

Hameed I, Liu B, Li L, et al. (Sr$_{1-x}$Ca$_x$)$_2$TiO$_4$ microwave
dielectric ceramics with R-P structure ($x = 0–0.15$). *Int J Appl Ceram Technol* 2019, 16: 2040–2046.

[583] Liu B, Huang YH, Song KX, et al. Structural evolution and microwave dielectric properties in Sr$_2$(Ti$_{1-x}$Sn$_x$)O$_4$ ceramics. *J Eur Ceram Soc* 2018, 38: 3833–3839.

[584] Hameed I, Wu SY, Li L, et al. Structure and microwave dielectric characteristics of Sr$_2$[Ti$_{1-x}$[(Al$_{0.5}$Nb$_{0.5}$)$_x$]O$_4$ ($x \leq 0.50$) ceramics. *J Am Ceram Soc* 2019, 102: 6137–6146.

[585] Xie MQ, Song XQ, Du K, et al. Improved microwave dielectric properties of the (Sr$_{1.3-x}$La$_x$)Ti$_{1-x}$Ce$_x$O$_4$ ceramics. *J Mater Sci: Mater Electron* 2020, 31: 13541–13548.

[586] Dai QL, Zuo RZ. A novel ultralow-loss Sr$_2$CeO$_4$ microwave dielectric ceramic and its property modification. *J Eur Ceram Soc* 2019, 39: 1132–1136.

[587] Wang Y, Tang TL, Li MX, et al. Ce$_{0.75}$Y$_{0.25}$O$_{1.875}$: New temperature-stable microwave dielectric ceramics with high Q values for microwave application. *Ceram Int* 2020, 46: 6984–6986.

[588] Ullah A, Liu HX, Manan A, et al. Microwave dielectric properties of Bi$_2$(La$_{0.5}$Ti$_{1.5}$)O$_6$–TiO$_2$-based ceramics for 5G cellular base station resonator application. *Ceram Int* 2021, 47: 8416–8423.

[589] Wang ZJ, Chen Y. Structures and microwave dielectric properties of Ti-doped CeO$_2$ ceramics with a near-zero temperature coefficient of resonant frequency. *J Alloys Compd* 2021, 854: 157270.

[590] Du C, Guo HH, Zhou D, et al. Dielectric resonator antennas based on high quality factor MgAl$_2$O$_4$ transparent dielectric ceramics. *J Mater Chem C* 2020, 8: 14880–14885.

[591] Qin TY, Zhong CW, Qin Y, et al. The structure evolution and microwave dielectric properties of MgAl$_2$–(Mg$_{0.5}$Ti$_{0.5}$)$_2$O$_3$ solid solutions. *Ceram Int* 2020, 46: 19046–19051.

[592] Liu B, Song KX. Vibrational spectroscopy and microwave dielectric properties of two novel Ca$_{3}$Ln$_2$W$_6$O$_{12}$ (Ln = La, Sm) tungstate ceramics. *Mater Res Bull* 2021, 133: 111022.

[593] Hu S, Zhou HF, Zhou XJ, et al. Phase structure, sintering behaviour and microwave dielectric properties of Ln$_2$MoO$_6$ (Ln = La and Y) ceramics. *Ceram Int* 2020, 46: 24552–24556.

[594] Kim E, Huang K, Jegelka S, et al. Virtual screening of inorganic materials synthesis parameters with deep learning. *npj Comput Mater* 2017, 3: 53.

[595] Raccuglia P, Elbert KC, Adler PDF, et al. Machine-learning-assisted materials discovery using failed experiments. *Nature* 2016, 533: 73–76.

[596] Weng BC, Song ZL, Zhu RL, et al. Simple descriptor derived from symbolic regression accelerating the discovery of new perovskite catalysts. *Nat Commun* 2020, 11: 3513.

[597] Kim C, Pilania G, Ramprasad R. Machine learning assisted predictions of intrinsic dielectric breakdown strength of ABX$_3$ perovskites. *J Phys Chem C* 2016, 120: 14575–14580.

[598] Xue D, Balachandran PV, Yuan R, et al. Accelerated search for BaTiO$_3$-based piezoelectrics with vertical morphotropic phase boundary using Bayesian learning. *PNAS* 2016, 113: 13301–13306.

[599] Sun YT, Bai HY, Li MZ, et al. Machine learning approach for prediction and understanding of glass-forming ability. *J Phys Chem Lett* 2017, 8: 3434–3439.

[600] Kim C, Pilania G, Ramprasad R. From organized high-throughput data to phenomenological theory using machine learning: The example of dielectric breakdown. *Chem Mater* 2016, 28: 1304–1311.

[601] Qin JC, Liu ZF, Ma MS, et al. Machine learning approaches for permittivity prediction and rational design of microwave dielectric ceramics. *J Materiomics* 2021, https://doi.org/10.1016/j.jmat.2021.02.012.

[602] Qin J, Liu Z, Ma M, et al. Structure and microwave dielectric properties of gillespite-type ACuSi$_4$O$_{10}$ (A = Ca, Sr, Ba) ceramics and quantitative prediction of the $Q \times f$ value via machine learning. *ACS Appl Mater Interfaces* 2021, 13: 17817–17826.

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