Sc modification induced short-range ordering in ZnGa$_2$O$_4$ spinel leading to high microwave dielectric performance

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Abstract

Sc$^{3+}$ (0,0.1,0.3,0.5,0.7mol%) modified ZnGa$_2$O$_4$ (abbreviated Sc-ZGO) ceramics were synthesized by solid-state method. The relationship between microwave dielectric performance and bonds vibration of Sc-ZGO as a function of Sc$^{3+}$ modification has been systematically investigated. With Sc$^{3+}$ modification, the $\varepsilon_r$ of Sc-ZGO ceramics keeps steady (~10). While the $\tau_f$ of Sc-ZGO shows linear correlation with Sc$^{3+}$ concentration increasing from -71ppm/℃ to -39ppm/℃, and the $Q\times f$ value climbs up to a maximum value (5Sc-ZGO) and then ramp down. 5Sc-ZGO sintered at 1350℃ for 2 h exhibits the best microwave dielectric properties with $\varepsilon_r = 9.9$, $Q\times f = 124,147$ GHz, $\tan\delta = 7.98\times 10^{-5}$, and $\tau_f = -56$ ppm/℃ (@9.9 GHz). $Q\times f$ value of Sc modified ZGO increased by almost 45% compared with normal spinel ZnGa$_2$O$_4$ ceramics. The enhancement of $\tau_f$ and $Q\times f$ on Sc modified ZnGa$_2$O$_4$ can be attributed to higher densification, however, further Raman and FT-IR analysis elucidated that short-range cation ordering degree is another governing factor. The influence of Sc$^{3+}$ modification on ZnGa$_2$O$_4$ bonds vibration has been discussed in detail.

Keywords

ZnGa$_2$O$_4$; spinel; Sc$^{3+}$ modification; bond vibration; microwave dielectric materials

Introduction

Spinel-type compounds AB$_2$O$_4$ have been extremely investigated in science and technical fields such as phosphor [1-2], catalysts [3-4], semiconductors [5-6], superconductors [7-8] and microwave dielectric materials [9-12]. Among these applications, microwave dielectric materials in high frequency (5G) is one of the most important applications with wide investigations. The framework of Spinel-type compounds has close packed tetrahedral (AO$_4$ or BO$_4$) and octahedral (BO$_6$ or AO$_6$). This type of crystal structure has a great variability because of variety cation selections,
and possibilities in cation ordering such as common spinel (AB₂O₄), inverse spinel (B(AB)O₄) and mixed-type spinel. So far, spinel structured ceramics for high frequency application include M₂SnO₄ [13-14], M₂SiO₄ [15-16], MAI₂O₄ (M=Zn, Mg) [17-18] and MGₐ₂O₄ (M = Zn, Mg) [19-23].

However, the development and application of stannate are limited by large negative τᵣ and low Q×f. As for silicate, it is difficult to prepare because of their sensitivity to synthesis conditions. Although the quality factor of aluminate can exceed 60,000 GHz, its sintering temperature is relatively high as well as silicate. Cause most of the spinel ceramics need high sintering temperature for about 1600°C. Considering environment friendly materials, explorations in lower sintering temperature by materials design and composition engineering are increased. Compared with M₂SnO₄, M₂SiO₄ and MAI₂O₄ (M=Zn, Mg), MGₐ₂O₄ have good microwave dielectric properties, lower sintering temperature and a wide sintering temperature region. Therefore, MGₐ₂O₄ (M=Zn,Mg) materials are promising candidates for high frequency (5G) applications.

For MGₐ₂O₄ (M=Zn, Mg) materials, ZnGa₂O₄ is a normal spinel and MGₐ₂O₄ is a mixed-type spinel. Thus, the crystal structure of MgGa₂O₄ is more complexed than the former one and the mixed proportion varied with synthesis conditions which brings more difficulties to reveal relationships among synthesis conditions, modification, crystal structure and microwave dielectric properties. Hence, ZnGa₂O₄ with normal spinel structure got our attention. It is reported that ZnGa₂O₄ possesses lower sintering temperature (1400°C), large sintering range (1300°C - 1500°C) with excellent dielectric performance (εᵣ = 9.8, Q×f = 83,000 GHz, τᵣ = -71 ppm/°C) [10]. However, relatively large negative τᵣ (-71 ppm/°C), and the relatively large tanδ (19×10⁻⁵) are the two difficulties in the application of ZnGa₂O₄ microwave dielectric ceramics.

For microwave dielectric materials possessing high density and good crystallinity, the initial temperature coefficient at resonant frequency (τᵣ) can be got through formula 1 as follows [24]:

$$\tau_r = -\left(\frac{1}{2}\tau_e + \frac{1}{2}\tau_{μ} + α_L\right)$$

(1)

Thus, the permittivity coefficient (τₑ), permeability coefficient (τμ), coefficient of thermal expansion (αL) are three considerable factors to influence the τᵣ. That means adjusting τₑ, τμ, and αL can obtain near zero τᵣ. In our previous study, TiO₂ was applied to form TiO₂-ZnGa₂O₄ composite ceramics to adjust τₑ and through this method near zero τᵣ was obtained at 0.1TiO₂-0.9ZnGa₂O₄ [19]. Another study applied Mn to modified the τₑ of ZnGa₂O₄ and it successfully shift τᵣ from -71ppm/°C to -12ppm/°C [20].

To achieve a high signal noise ratio to ensure transmission quality, resonators should possess higher Q×f. 1/Q is the total loss (tanδ) and can be figured out through formula 2 [25]. 1/Qᵣ, 1/Qₓ, 1/Qᵣ, 1/Qₓₑ, and 1/Qₓₑ are related to dielectric, conductor, radiation and external power loss, respectively.

$$\frac{1}{Q} = \frac{1}{Q_ᵣ} + \frac{1}{Qₓ} + \frac{1}{Qᵣ} + \frac{1}{Qₓₑ}$$

(2)

Classically, materials with close packed, ordered structure, high density, good crystallinity and fine morphology possess low dielectric loss because of lower vibration
loss, grain boundary and impurity loss. In our previous study, Cr$^{3+}$ doped ZnGa$_2$O$_4$ obtain excellent microwave dielectric properties due to the higher density and higher short-range cation ordering [21]. Cu$^{2+}$ was also applied to form Cu-ZGO solid solutions and obtain mixed spinel structure, the higher density and higher short-range cation ordering contribute to the higher $Q\times f$ [22-23].

Rare earth (RE) elements possess special atomic structure, physical and chemical properties which is mainly caused by their 4f electron configuration. The special structure of RE elements which leads to special optical, electrical, magnetic and thermal properties. And the application of RE elements in many ceramic materials has made great progress. Thus, RE modification have been applied extensively to control microstructures, crystal structures and dielectric properties, especially in piezoelectric ceramics and microwave dielectric ceramics like PZT [26], Ca/BaO-Ln$_2$O$_3$-TiO$_2$ [27] and CaO-Ln$_2$O$_3$-TiO$_2$-Li$_2$O [28]. The most used RE elements are Nd, Y, Sm and Ce, however, Sc has not yet been studied in this respect.

Based on the above discussion, Sc modified ZnGa$_2$O$_4$ (abbreviated Sc-ZGO) were designed to achieve higher $Q\times f$ and near zero $\tau_f$. As a result, we obtain a low $\varepsilon_r$ of 10 at 13GHz, sintered at 1350°C for 2 h which is lower than most of spinel ceramics without sintering additives. The microwave dielectric performance of Sc-ZGO, demonstrating low dielectric loss, and a near zero $\tau_f$ was achieved. Thus, it can provide guidance on the enhancement of spinel-type microwave dielectric ceramics properties.

**Materials and Methods**

**Sample preparation**

Solid state reactions were adopted to prepare Sc-ZGO with Sc content range from 0.1mol to 0.7mol%, using analytical grade Sc$_2$O$_3$, Ga$_2$O$_3$, and ZnO. According to the Sc-ZGO chemical formula, Sc$_2$O$_3$, Ga$_2$O$_3$, and ZnO were weighted and ball milled in polyethylene jars for one day with ethanol. These mixtures were dried at 80°C for one day and then calcined at 1000°C for 2 h. The green ceramics pellets with diameter~13 mm and thickness ~6 mm, was obtained under an uniaxial pressure ~75 MPa for 1min, and then sintered at 1300-1450°C for 4 h in high-temperature electric furnace (KSX4-16, Allfine, Wuxi, China).

**Characterization**

The micromorphology of Sc-ZGO was detected by a scanning electron microscope (SEM) (Hitachi SU8010, Japan). Archimedes’ method was applied to measure the density of the given samples. Phase composition and evolution of Sc modified ZnGa$_2$O$_4$ ceramics were identified via X-ray diffraction (XRD) (Rigaku Cu, RigakuD/Max 2500, Japan) and Raman spectroscopy (Raman) (HR800, Horiba Labram, 514 nm He-Cd laser, 20mW laser power). The high resolution TEM (HRTEM) images and selected-area electron diffraction (SAED) patterns were achieved at 200 kV using a transmission electron microscope (JEM-2100, JEOL). X-ray photoelectron spectrometer (XPS) (ESCALAB 250, Thermo Fisher, UK) was employed to collect XPS data to reveal elements chemical status in Sc-ZGO and the X-ray source was Al-Kα. Microwave dielectric performance, including $\varepsilon_r$, tan$\delta$, $f$ and $\tau_f$, were measured using the cavity
resonator method [29] via a Lightwave Component Analyzer (Hewlett Packard 8703A, 1550 nm/130 MHz to 20 GHz). A NICOLET 5700 FT-IR spectrometer (Thermo, America) were applied to get the Fourier transform infrared (FT-IR) spectrum.

**Results and Discussion**

**Microstructure of Sc-ZGO ceramics**

Fig. 1 (a) Relative density of Sc-ZGO, SEM images of Sc-ZGO sintered at 1350 °C for 2 h and (b-e) are 1Cr-ZGO, 3Cr-ZGO, 5Cr-ZGO, and 7Cr-ZGO, respectively. (f) EDS of 5Sc-ZGO.

The microstructures and relative density of Sc-ZGO ceramics sintered at 1350°C for 2 hours are shown in Fig. 1(a-e), and Fig. 1(f) shown the EDS spectrum of 5Sc-ZGO. As the Sc modification content increasing, the average size varied slightly, however, the relative density is different. It first increased with increasing Sc³⁺ content from 0.1-0.7mol% and achieved the highest density at 5Sc-ZGO, then decreased at 7Sc-ZGO. Thus, Sc³⁺ modification also improves the densification of ZnGa₂O₄. A relative density of 97% is reachable with Sc³⁺ content ranging from 0-0.7mol%.

**Crystal structure and cation distribution**
The XRD patterns of Sc-ZGO ceramics with Sc\(^{3+}\) modification content ranging from 0-0.7 mol% are shown in Fig. 2(a). Fig. 2(b) is the enlarged XRD patterns at 2θ=35.2-36.0. All the samples can be indexed as pure spinel structured ZnGa\(_2\)O\(_4\) (JCPDS card no. 86-0413). Due to the Sc modification, the main diffraction peak (~35.6°) shifts to higher diffraction degree which reveals lattice contraction in the Sc-ZGO crystals.

Fig. 2(c) shows an exemplar HRTEM image together with the SAED pattern in the inset, taken from 5Sc-ZGO. The lattice spacing is 0.48 nm which corresponds to the spacing between the (111) planes of spinel structured ZnGa\(_2\)O\(_4\). SAED pattern can provide further insight into the ceramic crystal structure. It can be indexed as a spinel structure with Face-Centered Cubic symmetry and a zone axis of [1 1 0]. The sharp diffraction spots in the SAED pattern, indicating Sc-ZGO possesses good crystallinity.

Confirming by previous XRD analysis, the higher Sc\(^{3+}\) concentration means the larger lattice contraction. This indicates that Sc-ZGO is a solid solution in the range from 0.1-0.7 mol% of Sc\(^{3+}\). Therefore, Sc\(^{3+}\) entered into ZnGa\(_2\)O\(_4\) structure which exhibited in Fig. 2(d).
Fig. 3 XPS spectra of the middle part of ZnGa$_2$O$_4$ sintered at 1350°C for 2 h, (a) full spectra, (b) Ga, (c) O, (d) Zn.

XPS spectrum of 5Sc-ZGO sintered at 1350°C for 2 h are shown in Fig. 3. These 5 peaks, Ga 3d, Sc 2p, O 1s, Zn 2p and Ga 2p peaks can be clearly seen in the full XPS spectrum in Fig. 3(a). And the reflection peaks at 19.8eV, 530.5eV, and 1044eV binding energy in Fig. 3(c-d), are corresponding to Ga 3d, O 1s, and Zn 2p, respectively. These means Sc existed as trivalent state in Sc-ZGO, and Sc$^{3+}$ modification didn’t affect bond valence of ZnGa$_2$O$_4$.

**Microwave dielectric properties**

Fig. 4 Effect of Sc$^{3+}$ modification on the microwave dielectric properties of ZnGa$_2$O$_4$ sintered at 1350°C for 2 h. (a) quality factor ($Q\times f$) at various sintering temperatures, (b) temperature
coefficient at resonant frequency (τ), and (c) dielectric constant (ε).

The microwave dielectric properties of Sc-ZGO sintered at 1350°C for 2 h, have been investigated and the results are shown in Fig. 4. As is shown in Fig. 4(a), the Q×f values of Sc-ZGO are strongly depend on Sc³⁺ modification. It reaches the maximum value of 124,147 GHz at 5Sc-ZGO, and then decreased with Sc³⁺ modification. According to our previous study, the Q×f value of Sc-ZGO increased by almost 1.45 times compared with unmodified ZnGa₂O₄. Therefore, Sc³⁺ modification is an effective way to improve Q×f values of ZnGa₂O₄. As already shown in Fig. 1(a), the relative density of Sc-ZGO is increased with Sc³⁺ modification.

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$$
ε = \frac{3}{(1-bαₘ/V_m)}-2
$$

FT-IR and Raman analysis on the spinel structure

![FT-IR spectra of Sc-ZGO](image)

Fig. 5 (a) FT-IR spectra of Sc-ZGO, (b) the FT-IR peak positions and dielectric constant (ε) of the Cr-ZGO ceramics as a function of Sc content, sintered at 1350°C for 2 h.

FT-IR spectra of Sc-ZGO sintered at 1350°C for 2 h is exhibited in Fig. 5(a). Two absorption bands: 420 cm⁻¹ (labeled as PEAK1) and 570 cm⁻¹ (labeled as PEAK2) were observed. Both PEAK1 and PEAK2 are belongs to T₁u IR-active mode. These two T₁u modes are induced predominantly by the vibrations of the octahedral site [30]. Hence, FT-IR spectrum can reflect the octahedral distortion in Sc-ZGO crystal structure. The absorption bands shift to lower wave number with Sc³⁺ content increasing which can be observed in Fig. 5(b), both for PEAK1 (from 434cm⁻¹ to 420cm⁻¹) and PEAK2 (from 577cm⁻¹ to 573cm⁻¹). These two FT-IR peaks shift was sensitive to Sc³⁺ and shown linear correlation with Sc³⁺ concentration, which means FT-IR shift were caused by Sc modification. Cause FT-IR absorption demonstrate bond vibration, the linear correlation between Sc³⁺ modification and FT-IR shift reflects that Sc³⁺ modification effectively influence ZGO bond vibration.
Fig. 6 (a) Raman spectra of Cr$^{3+}$ modified ZnGa$_2$O$_4$. (b) FWHM value of the A$_{1g}$ mode and dielectric loss (tanδ), (c) FWHM value of the T$_{2g}$ mode and dielectric loss (tanδ), (d) A$_{1g}$ shift and T$_{2g}$ shift of Sc-ZGO ceramics as a function of Sc$^{3+}$ concentration, sintered at 1350°C for 2 h.

Fig. 6(a) exhibits the Raman spectrum of Sc-ZGO. Two peaks: T$_{2g}$ phonon mode at $\sim$607 cm$^{-1}$ and A$_{1g}$ phonon mode at $\sim$712 cm$^{-1}$ can be clearly seen which is consistent with ZnGa$_2$O$_4$ Raman characterization reported by Wiglus [31]. The two T$_{2g}$ and A$_{1g}$ phonon modes in Fig.6(a) are the first order Raman modes. T$_{2g}$ phonon mode is the breathing mode of the octahedral site, and A$_{1g}$ phonon mode is the stretching vibration in the tetrahedral site, respectively.

For perovskite materials, the full width at half maxima (FWHM) of Raman phonon mode is indicative of the short-range cation ordering and can be used to explain tanδ variety [22-35]. Perovskite materials with higher short-range cation ordering degree usually possess lower Raman FWHM and higher $Q\times f$. As perovskite and spinel materials have a similar crystal structure, it can be supposed that the tanδ of spinel structured materials has a correlation with Raman FWHM. The FWHM of the A$_{1g}$, T$_{2g}$ phonon modes and tanδ of Sc-ZGO have been compiled in Fig. 6(b-c). The Raman shifts of the A$_{1g}$ and T$_{2g}$ phonon modes, and $\varepsilon$, with increasing Sc$^{3+}$ modification is compiled in Fig. 6(d). As FT-IR shift discussed above, these two Raman modes shift was sensitive to Sc$^{3+}$ and shown linear relation with Sc$^{3+}$ content, which means Raman modes shift was caused by Sc$^{3+}$ modification. Cause Raman modes also demonstrate bond vibration, and have complementary relationship with FT-IR modes. The linear correlation between Sc$^{3+}$ modification and Raman modes shift reflects that Sc$^{3+}$ modification effectively influence ZGO bond vibration.

**Conclusions**

Sc-modified ZnGa$_2$O$_4$ with excellent microwave dielectric properties have been successfully synthesized. Due to the tiny modification concentration and ionic polarization, with the increase Sc$^{3+}$ content, $\varepsilon$ of Sc-ZGO ceramics keeps steady. The $Q\times f$ value of Sc-ZGO ceramics ramp up to a maximum at 0.5mol% Sc$^{3+}$ modification.
and then ramp down continuously. In the Sc$^{3+}$ content range from 0 to 0.5mol% it increased from 83,000 GHz to 124,147 GHz and then decreased to 109,366 GHz. The $\tau_f$ value of Sc-ZGO increased linearly with Sc$^{3+}$ concentration from -71ppm/°C to -39 ppm/°C. Great microwave dielectric performance was achieved in 5Sc-ZGO spinel ceramics sintered at 1350°C for 2h: $\varepsilon_r = 9.9$, $Q\times f = 124,147$ GHz, tanδ = 7.98×10$^{-5}$, and $\tau_f = -56$ ppm/°C. The higher densification do benefit the $Q\times f$. However, Raman and FT-IR analysis on Sc$^{3+}$ modified ZnGa$_2$O$_4$ further elucidated that when the relative density is much the same, the short-range cation ordering degree is the dominant factor to higher $Q\times f$. The Raman shift of A$_{1g}$ and T$_{2g}$ phonon modes and FT-IR shift further confirm bond vibration induced by Sc$^{3+}$ modification. The tanδ was found to follow closely with the FWHM of A$_{1g}$ and T$_{2g}$ modes which represents the short-range cation ordering degree. The maximum $Q\times f$ value for 5Cr-ZGO can be attributed to the highest short-range cation ordering degree and highest density, while the decrease of $Q\times f$ of 7Sc-ZGO can be ascribed to the decrease of short-range cation ordering degree and lower density.

**Conflicts of interest**

There are no conflicts to declare.

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