Structure and microwave dielectric properties of CaSmAlO₄–CaTiO₃–Sm₀.₉Nd₀.₁AlO₃ ceramics with medium to high permittivity

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The CaSmAlO₄-doped 0.84CaTiO₃–0.16Sm₀.₉Nd₀.₁AlO₃ ceramics with permittivity around 62 were prepared using a conventional solid-state reaction method. The relationship between their structures and microwave dielectric properties was explored by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. A suitable amount of CaSmAlO₄ addition is beneficial for improving the $Q\times f$ value and tuning $\tau_r$ concurrently. However, excess amount of CaSmAlO₄ generated secondary phase and deteriorated the $Q\times f$ value. The 0.5 mol% CaSmAlO₄-doped 0.84CaTiO₃–0.16Sm₀.₉Nd₀.₁AlO₃ ceramics exhibited the best performance of $\varepsilon_r = 62.3$, $Q\times f = 38400$ GHz and $\tau_r = -4.49$ ppm/°C sintered at 1400 °C for 6 h. Although the temperature stability needs to be made better, the CaSmAlO₄-doped 0.84CaTiO₃–0.16Sm₀.₉Nd₀.₁AlO₃ ceramics pave the way to develop a promising candidate for 5G dielectric resonators with medium-high permittivity (60 < $\varepsilon_r < 70$).

Key-words: Microwave dielectric properties, CaTiO₃ solid solutions, Medium-high permittivity, Dielectric resonator

1. Introduction

With the advance of wireless communication technology, microwave dielectric ceramics have played a critical role in a diverse range of applications including filters, dielectric resonators, duplexers and antennas.¹⁻³ Generally speaking, excellent microwave dielectric ceramics are considered to perform three key properties to satisfy the requirement of market applications, namely, (1) a reasonable dielectric constant ($\varepsilon_r$, a criterion to judge to what extent the size of devices can be reduced), (2) a high quality factor ($Q\times f$ value, to ensure prominent frequency selectivity) and (3) a near-zero temperature coefficient of the resonator frequency ($\tau_r$, which represents reliable thermal stability). For better minimization and integration of devices, $\varepsilon_r$ is expected to be as high as possible within a specific frequency range. A great many dielectric materials have been investigated and they exhibit outstanding properties in the middle-permittivity group ($\varepsilon_r = 25–50$), such as Ti-rich compositions BaTiO₃, Ba₂Ti₆O₁₆, Ba-based complex perovskite compound Ba(Zn₁₂/₇Nb₂/₇)O₃, 0.7CaTiO₃–0.3NdAlO₃ solid solution, Ruddlesden–Popper compound Sr₂TiO₄ and so forth.⁴⁻¹⁰ In the high permittivity group, Ba₆₋₃xLnₓ₊₂Ta₁₋ₓO₃₄ (Ln = Nd, Sm, La) ceramics have been extensively explored due to their high permittivity ($\varepsilon_r > 80$) and high $Q\times f$ value.¹¹,¹² However, when it comes to dielectric ceramics with a medium-high permittivity ($\varepsilon_r = 50–80$), high $Q\times f$ and near-zero $\tau_r$ are hardly obtained simultaneously. Related studies have been up to date reported in materials including CoTiNb₂O₈, Ba₄.₂–Sm₀.₂Ti₁₈O₅₄, BiVO₄, and CaTiO₃(Al₁/₂Ta₁/₂)O₃, which we have listed in Table 1 to compare their properties. Obviously, due to either high dielectric loss or undesirable temperature stability, it is essential to search for a well-qualified medium-high-permittivity dielectric material, especially during the era of transition from 4G to 5G in digital communication.

As mentioned above, $x$CaTiO₃–(1 − $x$)LnAlO₃ (Ln = La, Sm, Nd) solid solutions are well known as one member of the middle-permittivity family, of which the dielectric constant fluctuates regularly with the composition $x$. For 0.84CaTiO₃–0.16Sm₀.₉Nd₀.₁AlO₃ (CTSA), a relatively high permittivity of 65 and high $Q\times f$ value more than 25000 GHz was reported,¹¹,¹² which has the potential to be employed as a medium-high permittivity material. However, the temperature stability of this system ($\tau_r = -54$ ppm/°C) is not good enough.

CaSmAlO₄ ceramics with a K₂NiF₄ structure have a low permittivity of 19, high $Q\times f$ value of 54600 GHz and negative $\tau_f$ of −14.9 ppm/°C sintered at 1450 °C.¹³ It might be feasible to tune the temperature coefficient of the resonator frequency of CTSA ceramics by doping suitable amount of CaSmAlO₄ ceramics that have the opposite temperature stability. Therefore, the additive CaSmAlO₄ was utilized in CTSA ceramics in an effort to modify their...
microwave dielectric properties in this work. The effect of CaSmAlO4 addition on microwave dielectric properties and structure evolution was investigated.

2. Experimental procedure

CaSmAlO4-doped CTSA ceramics were prepared using a conventional solid-state reaction process. Starting materials included CaCO3, TiO2, Sm2O3, Al2O3 and Nd2O3 with high-purity (99.9%). Firstly, CaTiO3 and Sm0.9Nd0.1AlO3 were synthesized following their stoichiometric compositions individually. After ball milled for 24 h, those well-blended powders were respectively dried and calcined at 1170 °C for 3 h. Then in the light of the formula 0.84CaTiO3-0.16Sm0.9Nd0.1AlO3 + x mol % CaSmAlO4 (x = 0, 0.25, 0.5, 0.75), mixed powders comprised of CaTiO3, Sm0.9Nd0.1AlO3, CaCO3, Sm2O3 and Al2O3 were ball milled for 12 h and went through a calcination of 1250 °C for 2.5 h again. Afterwards powders were ground with 5 wt% PVA and then pressed into 10 mm diameter, 5–6 mm thick pellets at 200 MPa. The pellets were finally sintered at different temperatures from 1360 to 1400 °C for 6 h in air.

The crystal structures of samples were investigated using an X-ray diffraction (XRD) instrument (D/max 2500, Rigaku, Japan). Raman spectra were collected using a Raman spectrometer (LabRAM HR800, HORIBA Jobin-Yvon Ltd., France). The microstructures of specimens were observed using a scanning electron microscope (SEM) (JSM-7001F, JEOL, Japan). The bulk density of the sintered samples was measured by Archimedes method. The microwave dielectric properties of the ceramic specimens were evaluated using a network analyzer (HP8720ES, Hewlett-Packard, USA) connected to a temperature chamber. The dielectric constants were measured by the Hakki-Poole equation, in the range of observation. In addition, several superlattice reflections are found in XRD patterns, which result from the octahedral distortion in the orthorhombic perovskite structure, that is, in-phase and anti-phase octahedral tilting.

3. Results and discussion

Figure 1 shows the XRD patterns of CTSA ceramics with various amounts of CaSmAlO4 sintered at 1375 °C. All patterns display a typical orthorhombic perovskite structure, in accordance with the standard pattern of pure CaTiO3 (JCPDS #82-0228). No secondary phase peaks are detected within the entire doping concentration range. Lattice parameters for each sample are listed in Table 2. Because the ionic radius of both A and B site in CaSmAlO4 is smaller than that of CTSA at the same compositions, the lattice constant a, b and c axes decrease linearly with the doping amount x, which is in agreement with Vegard’s law. It indicates that CaSmAlO4-doped CTSA ceramics form solid solutions in the range of observation. In addition, several superlattice reflections are found in XRD patterns, which result from the octahedral distortion in the orthorhombic perovskite structure, that is, in-phase and anti-phase octahedral tilting.

Figure 2 demonstrates the Raman spectra of CTSA ceramics with various amounts of CaSmAlO4 sintered at 1375 °C. For the range of 100–1000 cm⁻¹, eight bands are depicted at 156, 218, 243, 286, 340, 475, 508 and

| Table 1. Microwave dielectric properties of ceramic materials with medium-high permittivity reported |
|-----------------------------------------------|
| Material                  | Sintering Temperature (°C) | εr | Q×f (GHz) | τf (ppm/°C) | Ref. |
| CaTiNbO4                 | 1150                        | 66.41 | 10153     | +25.56      | 13  |
| CaTiNbO4+2 wt%CuO       | 950                         | 61.45 | 15938     | +42.12      | 14  |
| Bi2(VO4)3                 | 1025                        | 65.1  | 15500     | -17.5       | 3   |
| Sr3Ti2O5                  | 1525                        | 63    | 84000     | +293        | 10  |
| BiVO4                    | 820                         | 68    | 80000     | -260        | 15, 18 |
| Ba4.2Nd9.2Ti18O54         | 1340                        | 68    | 11400     | -0.7        | 16  |
| Ba4.2Sm9.2Ti18O54         | 1340                        | 76.9  | 10120     | -22.7       | 17  |
| 0.6Sr0.5Ce0.5TiO3+0.4NdAlO3 | 1550                     | 72    | 12052     | +5          | 19  |
| Ca3Ti(Al1_xTi_x)2O9       | 1500                        | 65.4  | 20000     | +113        | 20  |

Fig. 1. XRD patterns of CTSA ceramics doped with x mol % CaSmAlO4 demonstrating superstructure reflections associated with: anti-parallel A-site cations displacement (●), in-phase octahedral tilting (◆) and anti-phase octahedral tilting (▲).

| Table 2. Lattice parameter and unit-cell volume of CTSA ceramics doped with x mol % CaSmAlO4 |
|-----------------------------------------------|
| x (mol %) | a (Å) | b (Å) | c (Å) | V (Å³)   |
| 0         | 5.3721 | 5.4216 | 7.6273 | 222.15   |
| 0.25      | 5.3713 | 5.4186 | 7.6272 | 221.99   |
| 0.5       | 5.3708 | 5.4211 | 7.6262 | 222.04   |
| 0.75      | 5.3682 | 5.4195 | 7.6230 | 221.78   |

Figure 2: Raman spectra of CTSA ceramics with various amounts of CaSmAlO4.
788 cm\(^{-1}\), which are in consistent with the reports of Levin\(^{26}\) and Zheng.\(^{27}\) The band at 156 cm\(^{-1}\), similarly observed in Ca–TiO\(_3\) lattice mode,\(^{28}\) is attributed to the motion of A-site ions. The bands between 200 and 340 cm\(^{-1}\) are ascribed to the rotation of the oxygen cage.\(^{29}\)

The bands located at 475 and 508 cm\(^{-1}\) correspond to bending or internal vibrations of oxygen octahedral, which are in agreement with the report on CaTiO\(_3\)–NdAlO\(_3\) system.\(^{30}\) The broad mode at 788 cm\(^{-1}\) originates from the octahedral tilting, usually marked as \(A_{1g}\) mode. Known as a signal of short-rang ordering at B-site ions, \(A_{1g}\) mode always appears in simple solid CaTiO\(_3\)-based compounds as well as complex perovskites.\(^{26,27,31,32}\) With the variation of CaSmAlO\(_4\) amount, there is little change in the Raman shifts of all the bands discussed above. Nevertheless the CaSmAlO\(_4\) content clearly affects the width and height of the \(A_{1g}\) mode. The sharpness and intensity of the Raman lines were used to measure the degree of short-range ordering in the structure. Hence we calculated the full width at half-maximum (FWHM) of the 788 cm\(^{-1}\) band using Lorentz function fitting and plotted the result as an inset of Fig. 2. It reveals that the FWHM narrows when more CaSmAlO\(_4\) is doped, implying the Al/Ti short range order in B-site lattice is improved as more CaSmAlO\(_4\) added. Owing to the fact that a growing number of Al atoms contributed from CaSmAlO\(_4\) additive are occupying Ti lattice in CTSA ceramics, it is more likely to generate a locally ordered structure in CTSA ceramics.

**Figure 3** illustrates the SEM micrographs of the CTSA ceramics containing various amounts of CaSmAlO\(_4\) sintered at 1375 °C. All the samples possess relatively dense microstructure with low porosity. Large grains with a size approximately 9.5 \(\mu m\) are achieved and the grain size increases slightly with increasing CaSmAlO\(_4\) amount. However, for the sample with \(x = 0.75\), needle-shaped grains show up, which present as a dark phase (marked as A) in the backscattered electron micrograph [Fig. 3(d)].

We utilized energy dispersion spectrum (EDS) to determine the constitution of phase A and the white parent phase (marked as B). EDS results shown in Fig. 3(e) suggests that phase A contains more Al elements than phase B. According to the result of the elemental atomic analysis listed in **Table 3**, the ratio of Ca/Al element in the secondary phase is about 1:1. A small amount of Ti and Sm elements observed in phase A are supposed to be the concentration of the matrix, considering the relatively large analysis region of EDS. As elucidated by Jacar\(^{29}\) in CaTiO\(_3\)–NdAlO\(_3\) system, the reason why a secondary phase is formed might be that the diffusion rate of Al is slower than that of Sm element during the sintering reaction, which brought about the deposition of excess Al along the grain boundary. Because the content of the calcium aluminum phase is lower than the resolution of the XRD instrument, it is not detected in XRD analysis.

**Figure 4** depicts the bulk density of CaSmAlO\(_4\)-doped CTSA ceramics sintered at various temperatures. For each fixed composition of CaSmAlO\(_4\) addition, bulk densities

![Fig. 2. Raman spectra of CTSA ceramics doped with x mol% CaSmAlO\(_4\).](image)

![Fig. 3. SEM micrographs of CTSA ceramics added with x mol% CaSmAlO\(_4\) sintered at 1375 °C: (a) x = 0; (b) x = 0.25; (c) x = 0.5; (d) x = 0.75, backscattered electron image; (e) EDS analysis for A and B phases.](image)

**Table 3.** EDS results of the areas in Fig. 3(e)

| Area | O | Al | Ca | Ti | Nd | Sm |
|------|---|----|----|----|----|----|
| A    | 71.26 | 13.23 | 12.96 | 2.04 | 0 | 0.51 |
| B    | 60.93 | 2.92 | 16.33 | 16.59 | 0.55 | 2.68 |
are not significantly affected by sintering temperature variation. However, the bulk density increases slightly with increasing amount of CaSmAlO₄, mainly related to the larger theoretical density of CaSmAlO₄ (5.73 g/cm³) than that of 0.84CaTiO₃·0.16Sm0.9Nd0.1AlO₃ (4.50 g/cm³). Since all bulk densities are above 4.41 g/cm³, the relative densities are more than 97.5%, implying that all specimens are of high densification.

Figure 5 gives the microwave dielectric properties of CTSA ceramics sintered at different temperatures as a function of CaSmAlO₄ addition x. The permittivity, εᵣ, varies linearly and decreases from 65 to 62 with the increase of x value. In general, εᵣ hinges on both densification and ionic polarizability at microwave frequencies, and it correlates positively with B-site ionic polarizability. The effect of densification herein can be ignored because all samples possess high relative density. Thus polarizability should be the dominant factor in determining permittivity. The total polarizability in volume is diluted when Ti ions are substituted by Al ions with smaller polarizability (Ti: 2.93 Å³, Al: 0.79 Å³) that derived from CaSmAlO₄ additives. Correspondingly, permittivity decreases with increasing x. Q×f values increase with increasing amount of CaSmAlO₄ addition until they reach the maximum (38400 GHz) when x = 0.50. Then a deterioration of the Q×f value is observed at the point of x = 0.75. The Q×f value is raised a little at an elevated sintering temperature as well. The dielectric loss is sensitive to extrinsic factors, such as the microstructure, secondary phase, grain size, density and B-site ordering. As a result, the improvement of the short-range order confirmed from Raman spectra analysis favors to enhance the Q×f value when CaSmAlO₄ was doped in CTSA ceramics. Given that the dielectric loss decreases with increasing grain size, which has been proved in several microwave materials systems, higher Q×f values also benefit from the growth of grains. However, the presence of calcium aluminum phase in the sample with 0.75 mol % dopant should be the main reason to degrade the Q×f values. It is worth noting that the Q×f values (more than 35000 GHz) are superior to the limited reports of dielectric ceramics with dielectric constant around 60 to 70.

The variation of the τᵣ value agrees with the dependence of εᵣ on x, and it is improved from +55.4 to +48.4 ppm/°C with 0.75 mol % CaSmAlO₄ additives, which is ascribed to the negative τᵣ value of CaSmAlO₄. Despite that τᵣ value is still far from zero in this work, CaSmAlO₄ is favorable to enhance the temperature stability of CTSA ceramics.

4. Conclusions

The CaSmAlO₄-doped CTSA ceramics, with a medium-high permittivity around 62 to 65, have been prepared via a solid-state reaction process. The as-sintered ceramics formed a solid solution with an orthorhombic perovskite structure within a minor doping amount of CaSmAlO₄. The addition of CaSmAlO₄ contributes to a promotion in short-range ordering and grain growth, which led to an increase in Q×f value. The dielectric constant and τᵣ value are declined simultaneously due to the dilution of polarizability. However, a secondary phase appears as the dopant amount ascended, which is harmful to Q×f value. An optimal combination of microwave dielectric properties is achieved when the amount of CaSmAlO₄ is 0.5 mol %: εᵣ = 62.3, Q×f = 38400 GHz and τᵣ = +49.5 ppm/°C sintered at 1400 °C for 6h. This result might
open up the possibility of novel high-performance microwave dielectric materials with $60 < \varepsilon_r < 70$ that can meet the demand of base station technologies for 5G telecommunication.

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