FULL PAPER

Structure and microwave dielectric properties of CaSmAlO_4 – CaTiO_3 – $\text{Sm}_{0.9}\text{Nd}_{0.1}\text{AlO}_3$ ceramics with medium to high permittivity

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The CaSmAlO_4 -doped 0.84CaTiO_3 – $0.16\text{Sm}_{0.9}\text{Nd}_{0.1}\text{AlO}_3$ 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 CaSmAlO_4 addition is beneficial for improving the $Q \times f$ value and tuning τ_f concurrently. However, excess amount of CaSmAlO_4 generated secondary phase and deteriorated the $Q \times f$ value. The 0.5 mol % CaSmAlO_4 -doped 0.84CaTiO_3 – $0.16\text{Sm}_{0.9}\text{Nd}_{0.1}\text{AlO}_3$ ceramics exhibited the best performance of $\epsilon_r = 62.3$, $Q \times f = 38400$ GHz and $\tau_f = +49.5$ ppm/°C sintered at 1400 °C for 6 h. Although the temperature stability needs to be made better, the CaSmAlO_4 -doped 0.84CaTiO_3 – $0.16\text{Sm}_{0.9}\text{Nd}_{0.1}\text{AlO}_3$ ceramics pave the way to develop a promising candidate for 5G dielectric resonators with medium-high permittivity ($60 < \epsilon_r < 70$).

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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 (ϵ_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 (τ_f , which represents reliable thermal stability). For better minimization and integration of devices, ϵ_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 ($\epsilon_r = 25$ –50), such as Ti-rich compositions BaTiO_4 , $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, Ba-based complex perovskite compound $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, 0.7CaTiO_3 – 0.3NdAlO_3 solid solution, Ruddlesden–Popper compound Sr_2TiO_4 and so forth.^{4)–10)} In the high permittivity group, $\text{Ba}_{6-3x}\text{Ln}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{La}$) ceramics have been extensively explored due to their high permittivity ($\epsilon_r > 80$) and high $Q \times f$ value.^{11),12)} However, when it

comes to dielectric ceramics with a medium-high permittivity ($\epsilon_r = 50$ –80), high $Q \times f$ and near-zero τ_f are hardly obtained simultaneously. Related studies have been up to date reported in materials including $\text{CoTiNb}_2\text{O}_8$, $\text{Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54}$, BiVO_4 , and $\text{CaTi}_{0.7}(\text{Al}_{1/2}\text{Ta}_{1/2})_{0.3}\text{O}_3$,^{3),13)–20)} 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, $x\text{CaTiO}_3$ – $(1-x)\text{LnAlO}_3$ ($\text{Ln} = \text{La}, \text{Sm}, \text{Nd}$) 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 0.84CaTiO_3 – $0.16\text{Sm}_{0.9}\text{Nd}_{0.1}\text{AlO}_3$ (CTSA), a relatively high permittivity of 65 and high $Q \times f$ value more than 25000 GHz was reported,^{21),22)} which has the potential to be employed as a medium-high permittivity material. However, the temperature stability of this system ($\tau_f = +54$ ppm/°C) is not good enough.

CaSmAlO_4 ceramics with a K_2NiF_4 structure have a low permittivity of 19, high $Q \times f$ value of 54600 GHz and negative τ_f of -14.9 ppm/°C sintered at 1450 °C.²³⁾ It might be feasible to tune the temperature coefficient of the resonator frequency of CTSA ceramics by doping suitable amount of CaSmAlO_4 ceramics that have the opposite temperature stability. Therefore, the additive CaSmAlO_4 was utilized in CTSA ceramics in an effort to modify their

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Table 1. Microwave dielectric properties of ceramic materials with medium-high permittivity reported

Material	Sintering Temperature (°C)	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	Ref.
CoTiNb ₂ O ₈	1150	66.41	10153	+25.56	13
CoTiNb ₂ O ₈ +2 wt %CuO	950	61.45	15938	+42.12	14
Bi ₂ (Li _{0.5} Ta _{1.5})O ₇	1025	65.1	15500	−17.5	3
Sr ₃ Ti ₂ O ₇	1525	63	84000	+293	10
BiVO ₄	820	68	8000	−260	15, 18
Ba _{4.2} Nd _{0.2} Ti _{1.8} O _{5.4} +10 wt %NdAlO ₃	1340	68	11400	−0.7	16
Ba _{4.2} Sm _{0.2} Ti _{1.8} O _{5.4} +0.2 wt %Al ₂ O ₃	1340	76.9	10120	−22.7	17
0.6(Sr _{0.5} Ce _{0.5})TiO _{3+δ} −0.4NdAlO ₃	1550	72	12052	+5	19
CaTi _{0.7} (Al _{1/2} Ta _{1/2}) _{0.3} O ₃	1500	65.4	20000	+113	20

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 Sm_{0.9}Nd_{0.1}AlO₃ 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 0.84CaTiO₃−0.16Sm_{0.9}Nd_{0.1}AlO₃ + *x* mol % CaSmAlO₄ (*x* = 0, 0.25, 0.5, 0.75), mixed powders comprised of CaTiO₃, Sm_{0.9}Nd_{0.1}AlO₃, 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-Coleman dielectric resonator method with the TE₀₁₁ mode and the unloaded quality factors were measured using the TE_{01δ} mode in the cavity method.^{24,25)} The τ_f values of the samples were obtained by the cavity method between 25 and 80 °C.

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

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

<i>x</i> (mol %)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
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

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 coordination number (Sm³⁺: 1.079 Å, Ca²⁺: 1.120 Å, CN = 8; Al³⁺: 0.535 Å, Ti⁴⁺: 0.605 Å, CN = 6), the lattice constant of *a* 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 tilting of [BO₆] octahedral as well as anti-parallel A-site cations displacement.

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

788 cm^{-1} , which are in consistent with the reports of Levin²⁶⁾ 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 $\text{CaTiO}_3\text{--NdAlO}_3$ 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-range 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

Fig. 2. Raman spectra of CTSA ceramics doped with x mol % 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 $9.5\mu\text{m}$ 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 Jacar⁹⁾ in $\text{CaTiO}_3\text{--NdAlO}_3$ 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

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

Area	Element Atom %					
	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

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.

Fig. 4. Bulk densities of CTSA ceramics doped with x mol % CaSmAlO_4 .

are not significantly affected by sintering temperature variation. However, the bulk density increases slightly with increasing amount of CaSmAlO_4 , mainly related to the larger theoretical density of CaSmAlO_4 (5.73 g/cm^3)²³ than that of $0.84\text{CaTiO}_3\text{--}0.16\text{Sm}_{0.9}\text{Nd}_{0.1}\text{AlO}_3$ (4.50 g/cm^3).²¹ Since all bulk densities are above 4.41 g/cm^3 , 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 CaSmAlO_4 addition x . The permittivity, ϵ_r , varies linearly and decreases from 65 to 62 with the increase of x value. In general, ϵ_r hinges on both densification and ionic polarizability at microwave frequencies, and it correlates positively with B-site ionic polarizability.^{1),33),34)} 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: $2.93 \text{ \AA}^3$, Al: $0.79 \text{ \AA}^3$)³⁵⁾ that derived from CaSmAlO_4 additives. Correspondingly, permittivity decreases with increasing x .

$Q \times f$ values increase with increasing amount of CaSmAlO_4 addition until they reach the maximum (38400 GHz) when $x = 0.50$. Then a deterioration of the $Q \times f$ value is observed at the point of $x = 0.75$. The $Q \times f$ 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 $Q \times f$ value when CaSmAlO_4 was doped in CTSA ceramics. Given that the dielectric loss decreases with increasing grain size, which has been proved in several microwave materials systems,^{36)–39)} higher $Q \times f$ 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 $Q \times f$ values. It is worth noting that the $Q \times f$ values (more than 35000 GHz) are superior to the limited reports of dielectric ceramics with dielectric constant around 60 to 70.

Fig. 5. Microwave dielectric properties of CTSA ceramics doped with x mol % CaSmAlO_4 .

The variation of the τ_f value agrees with the dependence of ϵ_r on x , and it is improved from +55.4 to +48.4 ppm/°C with 0.75 mol % CaSmAlO_4 additives, which is ascribed to the negative τ_f value of CaSmAlO_4 . Despite that τ_f value is still far from zero in this work, CaSmAlO_4 is favorable to enhance the temperature stability of CTSA ceramics.

4. Conclusions

The CaSmAlO_4 -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 CaSmAlO_4 . The addition of CaSmAlO_4 contributes to a promotion in short-range ordering and grain growth, which led to an increase in $Q \times f$ value. The dielectric constant and τ_f value are declined simultaneously due to the dilution of polarizability. However, a secondary phase appears as the dopant amount ascended, which is harmful to $Q \times f$ value. An optimal combination of microwave dielectric properties is achieved when the amount of CaSmAlO_4 is 0.5 mol %: $\epsilon_r = 62.3$, $Q \times f = 38400 \text{ GHz}$ and $\tau_f = +49.5 \text{ ppm/}^\circ\text{C}$ sintered at 1400°C for 6 h. 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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