Effects of co-precipitation method on microwave dielectric properties of 0.7CaTiO₃-0.3SmAlO₃ ceramics

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Abstract
The effects of co-precipitation method on densification, microstructure, phase composition and dielectric properties of 0.7CaTiO₃–0.3SmAlO₃ ceramics (CTSA) have been studied. Compared with the traditional solid-phase method, the co-precipitation method effectively reduced the calcining temperature of CaTiO₃ powders and SmAlO₃ powders from 1250 to 900 °C and reduced the sintering temperature of CTSA ceramics from 1470 to 1380 °C. The sintering and dielectric properties were improved. In particular, the Q × f value was found to increase from 47 056 to 51 507 GHz and the τ_f reduced from +8.2 to +6.3 ppm °C. The CTSA ceramics, which were prepared by co-precipitation method sintered at 1380 °C for 3 h, possessed good and reasonable microwave dielectric properties: ε_r = 44.85, Q × f = 51 507 GHz (f = 6.45 GHz), τ_f = +6.3 ppm °C.

1. Introduction

Microwave dielectric materials play a significant role in modern society with a wide range of applications from terrestrial and satellite communication including software radio, GPS, and DBS TV to environmental monitoring via satellites [1, 2]. Generally, the microwave dielectric materials applied to the base stations of telecommunications are demanded to possess high quality factor (Q × f) for high power, high dielectric constants (ε_r) for miniaturization and low temperature coefficients of resonant frequency (τ_f) for frequency stability [3–5]. CaTiO₃ is known for its high ε_r (=160) and moderate Q × f (=3500 GHz) but its high positive τ_f (=+800 ppm °C) makes it hard to be extended in practical applications [6, 7]. SmAlO₃, a promising material, has a larger negative τ_f and is added to the CaTiO₃ system to adjust the τ_f to zero [8–10]. Low-loss CaTiO₃-based ceramics with a temperature-stable resonant frequency can be synthesized by aliovalent substitution of Ca²⁺ and Ti⁴⁺ ions with Sm³⁺ and Al³⁺, respectively [11,12]. The equimolar partial substitution leads to the formation of (1−x)CaTiO₃−xSmAlO₃ solid solutions. At x = 0.3, the ceramics exhibit prominent properties: ε_r = 45, Q × f = 42 000 GHz, τ_f ≈ 0 ppm °C−1 [12].

In the system of alkali-earth titanate-lanthanide aluminate, it is reported that single-phase ceramics are difficult to obtain because the second phase is easy to form within wide temperature rage [13, 14], and such unexpected impurity phase is pernicious to the microwave dielectric properties of ceramics. Jiang et al [15] have pointed out an effective way to solve this problem that they prepared 0.675CaTiO₃–0.325LaAlO₃ perovskite ceramics by conventional solid-state reaction through four reaction routes, during which the consequence of synthesis reacting materials affected the properties of the ceramics and the fourth route presented the most excellent properties. However, the traditional solid-state reaction method has disadvantages such as high-temperature conditions as well as large grain sizes, which have a negative impact on microwave dielectric properties [16]. What’s more, other researchers have also reported that co-precipitation might be a valid access to the referred cumbersome problem. In our previous work, the 0.7CaTiO₃–0.3SmAlO₃ ceramics, in which...
SmAlO₃ was prepared by co-precipitation method and CaTiO₃ by conventional solid-phase reaction method, presented dielectric properties of $\varepsilon_r = 44.95$, $Q \times f = 50.137\, \text{GHz} \, (f = 6.47\, \text{GHz})$, $\tau_f = +7.6\, \text{ppm}\, ^\circ\text{C}$ when sintered at 1410 $^\circ\text{C}$ [17].

The main work is to analyze the influence of different preparation method on the properties of CTSA ceramics. Mainly, the CaTiO₃ and SmAlO₃ powders were both prepared by co-precipitation method. In this experiment, the objective is to obtain microwave dielectric ceramics with better properties by co-precipitation method than that by conventional method.

2. Experimental materials and methods

2.1. Raw materials

The CaTiO₃ precursor (refers to precipitates: CaC₂O₄, Ti(OH)₄) and SmAlO₃ precursor (refers to precipitates: Sm(OH)₃, Al(OH)₃) were both prepared by co-precipitation method. CaCO₃ (99.8%), Sm₂O₃ (99.0%), Ti(C₂H₄O₄)₃ (98.0%), Al(NO₃)₃·9H₂O (99.0%), HNO₃ (65~68%), NH₃·aq (25~28%), H₂C₂O₄·2H₂O (99.0%), TiO₂ (99.0%), Al₂O₃ (99.0%) were used as raw materials. These materials were weighed respectively according to the stoichiometric ratio of 0.7CaTiO₃·0.3SmAlO₃.

2.2. Preparation of samples

The specific preparation method of 0.7CaTiO₃·0.3SmAlO₃ ceramics is given in figure 1. First of all, it’s the preparation process of SmAlO₃ precursor, Sm₂O₃ was dissolved in diluted HNO₃ and then mixed with Al(NO₃)₃·9H₂O in distilled water at a molar ratio of Sm: Al=1:1. Next, NH₃·aq was dripped into the solution slowly until the value of pH was adjusted to 7.5~8 in order to make the Al⁺³, Sm⁺³ precipitate absolutely, and then the resulting solution was stirred for 2 h to obtain the mixture 1. There followed the preparation of CaTiO₃ precursor, CaCO₃ was dissolved in diluted HNO₃ as solution 1. At the same time, the H₂C₂O₄·2H₂O and Ti(C₂H₄O₄)₃ were mixed according to the molar ratio of 2:1 in ethanol solution as solution 2. Then the two mentioned solutions were intermixed and NH₃·aq was slowly dripped into the new solution until the value of pH reached 5 in order to restrain the hydrolysis of Ca²⁺ to promote the combination of Ca²⁺ and C₂O₄²⁻ [18]. Afterwards, the final solution was stirred for 2 h to get the mixture 2. Finally, the two mixtures were matured at room temperature for 12 h to complete precipitation. After the precipitates formed, precursors were obtained through filtration, washing and drying. Eventually, CaTiO₃ and SmAlO₃ precursors were calcined in the range of 750°C~950°C at a rate of 2°C min⁻¹ for 3 h to obtain fine CaTiO₃ and SmAlO₃ powders.

The 0.7CaTiO₃·0.3SmAlO₃ mixed powders were prepared by mixing CaTiO₃ and SmAlO₃ powders through stoichiometry and subjected to ball-milling for 6 h in distilled water. After drying (80°C), the obtained fine powders were granulated with 8 wt% poly vinyl alcohol solution as binder and pressed into cylinder (Φ12 mm × 5 mm) sheets of green samples at 300 MPa. The pellets were pre-sintered at 600°C for 2 h in air at a heating rate of 2°C min⁻¹ to remove the PVA binder colloid. The pre-sintered samples were then sintered in air at a rate of 2°C min⁻¹ for 3 h at different temperatures. The sintering temperatures were 1320°C, 1350°C, 1380°C, 1410°C and 1440°C, respectively. For comparison, 0.7CaTiO₃·0.3SmAlO₃ ceramics were also prepared by traditional solid-state reaction method with the raw materials of CaCO₃, TiO₂, Sm₂O₃, and Al₂O₃. The above powders were mixed in a stoichiometric ratio and calcined at 1250°C for 3 h. Thereafter, the pellets were sintered at 1470°C for 3 h.

2.3. Characterization of samples

Thermal analysis consisting of thermo gravimetric (TG) as well as differential scanning calorimetry (DSC) was studied in the air (STA 449C, Netzsch, Germany). The crystalline phase composition analysis of the powders and sintered samples was investigated by x-ray diffraction (XRD, Rigaku, Cukα, Japan). The microstructures and morphology of surfaces were observed by field emission scanning electron microscopy (FESEM, SU8010, Hitachi, Japan). The bulk densities of the sintered bodies were tested by the Archimedeans method using distilled water as medium. The microwave dielectric properties of the sintered samples were identified with a network analyzer (AGILENT 8722ET) and studied with the improved method called Hakki-Coleman and Courtney [19]. The $\tau_f$ was obtained by formular (1):

$$\tau_f = \frac{f_{80} - f_{25}}{f_{80}(80 - 25)^{-1}} = \frac{f_{80} - f_{25}}{f_{80}(80 - 25)}$$

(1)

Where $f_{25}$ and $f_{80}$ are the resonant frequencies at temperatures of 25°C and 80°C, respectively.
3. Results and discussion

3.1. Weight loss

The TG - DSC curves of CaTiO₃ precursor were measured with a thermal analyzer, as shown in figure 2. The sample's total weight loss was around 54.8% and the reaction process consisted of three parts. In the first stage, the sample's weight loss was 18.1% when the temperature increased from 20°C to 240°C. An endothermic peak existed in the DSC curve near 200°C. This might be due to the evaporation of free water and crystal water. Then the second stage started from 240°C to 600°C with 25.3% weight loss. An exothermic peak appeared at around 462°C because the CO that was generated by the C₂O₄²⁻ decomposition easily reacts with O₂ under the air atmosphere. The last stage was in 600°C – 800°C, where the weight loss reached about 11.4%. At this point, an endothermic peak existed at about 754°C, which was due to the formation of CaTiO₃ by TiO₂ and CaO through solid-state reaction. However, the DSC curve changed to be above 0 when the temperature exceeds over 800°C, which could be possibly related to the appearance of a small amount of TiO₂ from amorphous phase to crystalline phase as the calcination temperature increased. The presence of TiO₂ was mainly due to the loss of...
Ca\textsuperscript{2+} within the process of washing and filtering precipitate, which resulted in a slight excess of TiO\textsubscript{2}. After the TG-DSC curves were analyzed, the calcining temperature of CaTiO\textsubscript{3} precursor was determined from 750 to 950 °C. Figure 3 exhibits the TG-DSC curves of SmAlO\textsubscript{3} precursor. The SmAlO\textsubscript{3} precursor was set to be calcined from 800 to 950 °C using the similar analytic procedure \cite{17}.

3.2. The phase compositions and microstructure

Figure 4 presents the XRD patterns of CaTiO\textsubscript{3} precursor which was calcined at 750 °C–950 °C for 3 h. It can be seen from the diagram that CaTiO\textsubscript{3} with perovskite structure (JCPDS Card No.42-0423) has been formed when precursor is heated above 750 °C for 3 h and the sequential increasing of calcining temperature strengthens intensities of diffraction peaks of CaTiO\textsubscript{3}, which illustrates that the main crystal phase is completely synthesized. In addition, when the calcination temperature was 850 °C or higher, a small amount of TiO\textsubscript{2} appeared, which might be associated with the transition of excessive TiO\textsubscript{2} from amorphous phase to crystalline phase \cite{20}.

Figure 5 illustrates the XRD patterns of CTSA ceramics sintered at different sintering temperatures with precursor calcined at 900 °C. All the samples show a homogenous phase of 0.7CaTiO\textsubscript{3}–0.3SmAlO\textsubscript{3} with orthorhombic-type perovskite structure (JCPDS Card No.42-0423). This illustrated that when the preparation process of CaTiO\textsubscript{3} powder changed, the system was still a solid solution system, and sintering temperature showed little influence on the phase of 0.7CaTiO\textsubscript{3}–0.3SmAlO\textsubscript{3} ceramics. The second phase rutile TiO\textsubscript{2} (ICSD-PDF #21–1276) was identified in figure 5. The peak occurred when diffraction angle (2θ) was approaching to 27.5. However, the peak strength was weak here, so it was almost invisible in figure 5. The appearance of TiO\textsubscript{2} might be due to the loss of calcium ions during washing \cite{18}.

The SEM photographs of the CTSA ceramics samples sintered at 1380 °C with different calcining temperatures were exhibited in figures 6(a)–(d), from which the evolution of grain growth could be observed.
Among them, when the calcination temperature was at 900 °C, figure 6(c) presented more uniform and compact microstructure. At this time, the crystal boundaries and grains were both more obvious than that of other calcination temperature. Figures 7(a)–(d) showed the SEM images of samples sintered at different temperatures when the calcining temperature was at 900 °C. With the increase of sintering temperature, the average grain size increased as well as pores gradually vanished. It is very pronounced that the samples sintered at 1380 °C have the uniform and dense microstructure with average grain size of 7 μm, which demonstrates that the sintering temperature could provide sufficient energy for the grain growth. When sintered at higher temperature, the samples distinctly exhibit grain abnormal growth, which probably brings about incremental dielectric loss of ceramics. Moreover, terraced-shaped grains that overlapped each other, emerged in all CTSA samples. These show that the complex microstructures can be formed by substituting Sm³⁺ for A-site, which is in conformity with Liu’s report [21]. In the figures 6 and 7, some secondary phase was observed as rutile TiO₂, and it was consistent with the characterization results of the figure 5.

3.3. Sintering properties and dielectric properties

The effect of calcination temperatures and sintering temperatures on the bulk density and dielectric constant εᵣ of CTSA ceramics are shown in figures 8 and 9. The change trend of the dielectric constant εᵣ was consistent with that of the bulk density. The bulk density increases first and then remains almost unchanged with the increase of the sintering temperature. Obviously, the maximum bulk density is about 4.81 g cm⁻³, which reaches the
theoretical density of 98.4% at the calcining temperature of 900 °C and sintering temperature of 1380 °C. And $\varepsilon_r$ increases to a maximum value and then they are saturated after the sintering temperature reaching 1380 °C. That is because dielectric constant $\varepsilon_r$ usually is relied on dipoles in unit cell volume as well as the ionic polarizability of the composition [22].

Figure 6. SEM images of CTSA ceramics sintered at 1380 °C with different calcining temperatures (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C.

Figure 7. SEM images of CTSA ceramics with precursor powders calcined at 900 °C and sintering temperatures: (a) 1350 °C, (b) 1380 °C, (c) 1410 °C, (d) 1440 °C.
Figure 10 illustrates the $Q \times f$ value of the CTSA ceramics with different sintering temperatures. As we all know, the $Q \times f$ values are generally influenced by a variety of factors such as lattice defects, lattice vibrational modes, second phases, internal stress, pores, crystallinity, impurities and cation order. Therefore, it is ordinarily hard to ascertain the key influencing parameters [23–25]. From an overall perspective, $Q \times f$ value increases initially and then basically remains unchanged with the sintering temperature increasing. The maximum $Q \times f$ value (51 507 GHz) of ceramics is obtained at the calcination temperature of 900 °C and sintering temperature of 1380 °C. These results suggest that proper calcination temperature and sintering temperature are favorable for improving the dielectric properties of ceramics. Generally speaking, the activity of powders is also affected by calcination temperature, so the calcination temperature is one of the key factors to obtain compact ceramics with good performance. Since the powders that have high activity are favorable for ceramics’ densification at lower temperature [26, 27]. So, the powder with highly active calcined at 900 °C reaches maximum density of 4.81 g cm$^{-3}$ when sintered at a relatively low temperature of 1380 °C. All factors are comprehensively taken into consideration, the CTSA ceramic samples sintered at 1380 °C with precursor calcined at 900 °C exhibit satisfying dielectric properties of $\varepsilon_r= 44.85$, $Q \times f = 51 507$ GHz ($f = 6.45$ GHz).

Table 1 summarizes the bulk densities and dielectric properties of CTSA ceramics which are prepared by two various methods. In fact, all the ceramic samples are obtained by solid state method at high temperature. The only distinction is that the preparation methods of powders are different, which results in different properties and homogeneity. Compared with conventional solid-state method, the co-precipitation method reduces the sintering temperature of CTSA ceramics by 90 °C as well as enhances the $Q \times f$ up to 51 507 GHz. The reason
should be that powders prepared by co-precipitation have active reactivity, which decreases pores and promotes the densification of ceramics. In a way, the result corroborates that the preparation method of CTSA ceramics really plays an important part in properties of CTSA ceramics just as Jiang et al’s report on 0.675CaTiO$_3$-0.325LaAlO$_3$ ceramics.

4. Conclusion

Features of densification, crystalline structure and microwave dielectric properties of CTSA samples are investigated systematically. In this study, CTSA ceramics are mainly prepared through co-precipitation method, meanwhile the conventional solid-phase method is also taken as comparison. And the co-precipitation method could not only reduce the sintering temperature but also improve dielectric properties. The $\varepsilon_r$ and $Q \times f$ of the sintered samples are largely depended on the growth of complex microstructure of single grain. The CTSA ceramics which are sintered at 1380 °C with precursor calcined at 900 °C present exceedingly good dielectric properties: $\varepsilon_r = 44.85$, $Q \times f = 51507$ GHz ($f = 6.45$ GHz), $\tau_f = +6.3$ ppm °C.

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