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$ZnAl_2O_4$–TiO_2–$SrAl_2Si_2O_8$ low-permittivity microwave dielectric ceramics

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Abstract

$(1-x)(0.75ZnAl_2O_4–0.25TiO_2)–xSrAl_2Si_2O_8$ (abbreviated as $(1-x)$ZAT–xSAS) ceramics were prepared by the solid-state reaction. The effects of SAS content on shrinkage, phase compositions, microstructure and microwave dielectric properties were investigated. It shows that SAS with a rare negative shrinkage characteristic can effectively adjust the shrinkage of the $(1-x)$ZAT–xSAS ceramics to near-zero value. In addition, $ZnAl_2O_4$ spinel, TiO_2 rutile and $SrAl_2Si_2O_8$ monoclinic phases can coexist in the $(1-x)$ZAT–xSAS system, which is helpful to control the microwave dielectric properties and obtain a serial ε_r value from 3.56 to 12.20 by changing the phase composition. Therefore, $(1-x)$ZAT–xSAS could be a kind of zero-shrinkage and low-permittivity microwave dielectric ceramics for many potential applications in the future.

Keywords: Microwave dielectric ceramics; Zero-shrinkage; Low-permittivity

1. Introduction

At present, microwave dielectric ceramics with low permittivity have attracted much scientific attention and have been widely used as substrate materials in microstrip antennas, radome and integrate circuits. Low permittivity (ε_r) can not only minimize the cross coupling between conductors but also shorten the propagation delay time of electromagnetic signal, and high quality factor ($Q\cdot f$) can increase the frequency selectivity, while near-zero temperature coefficient of resonant frequency (τ_f) can ensure the stability of operating frequency against temperature changes [1]. In general, substrate materials should have low permittivity ($\varepsilon_r < 15$), high quality factor and near-zero temperature coefficient of resonant frequency. Furthermore, the serialization of permittivity redounds to selectivity of component materials, and near-zero shrinkage is contributive to the manufacture of large components with complex structures. Whereas, it is hard for single-component-system microwave dielectric ceramics to obtain above mentioned excellent properties simultaneously, therefore, multicomponent-system ceramics must be introduced [2,3].

In 2005, Surendran et al. [4] found that $ZnAl_2O_4$–TiO_2 spinel-based ceramics have high thermal coefficient and low thermal expansion coefficient, and these ceramics can be proposed as low permittivity microwave dielectric ceramics substrate materials which are of broad prospects in application. Then, the effects of sintering processes and TiO_2 additions on the sinterability, phase compositions and microwave dielectric properties of $(1-x)ZnAl_2O_4$–$xTiO_2$ ceramics were investigated by Lei and Lu et al. [5–7] systematically. They suggested that the optimal microwave dielectric properties can be achieved in $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x=0.21$) ceramics calcined at 1150 °C and sintered at 1500 °C for 3 h at a heating rate of 5 °C/min, with ε_r value of 11.6, $Q\cdot f$ value of 74,000 GHz (at about 6.5 GHz), and τ_f value of −0.4 ppm/°C.

Our recent work shows that after being calcined at 1150 °C and sintered at 1500 °C for 3 h, $SrAl_2Si_2O_8$ ceramics exhibit not only excellent microwave dielectric properties ($\varepsilon_r=3.56$, $Q\cdot f=14600$ GHz, $\tau_f=-30.32$ ppm/°C), but also a rare

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negative shrinkage of −4.4%. Therefore, by mixing $SrAl_2Si_2O_8$ and $ZnAl_2O_4$–TiO_2 with positive shrinkage, low permittivity microwave dielectric ceramics with near-zero shrinkage is expected.

On the basis of the logarithmic mixing rule [5], $0.75ZnAl_2O_4$–$0.25TiO_2$ ($\tau_f = +17.79$ ppm/°C) and $SrAl_2Si_2O_8$ ($\tau_f = -30.32$ ppm/°C) were mixed to achieve composite ceramics substrate materials with near-zero τ_f in this study. The effects of $SrAl_2Si_2O_8$ content on the shrinkage, phase compositions, microstructure and microwave dielectric properties of $(1-x)(0.75ZnAl_2O_4$–$0.25TiO_2)$–$xSrAl_2Si_2O_8$ ceramics were investigated.

2. Experimental procedure

Reagent grade ceramic powders ZnO, TiO_2, $SrCO_3$, Al_2O_3 and SiO_2 were used as raw materials. $0.75ZnAl_2O_4$–$0.25TiO_2$ and $SrAl_2Si_2O_8$ precursors were prepared using the following process, respectively. Stoichiometric starting powders according to the composition of $0.75ZnAl_2O_4$–$0.25TiO_2$ and $SrAl_2Si_2O_8$ were milled with agate balls in ethanol for 3 h at a speed of 360 rpm (rotation per minute). The ZAT and SAS slurry was dried and then calcined in air at 1150 °C and 1050 °C for 3 h, respectively. After milling and drying again, the calcined powders were uniaxially pressed into the samples under a pressure of 150 MPa. After being sintered at 1450–1575 °C for 3 h at a heating rate of 5 °C/min in air, these samples were cooled at a rate of 2 °C/min up to 1000 °C and then they were furnace cooled.

The crystalline phases were analyzed by means of the X-ray diffraction method using CuKα radiation (X'Pert PRO). The microstructure observation was performed by scanning electron microscope (SEM; Quanta 200). ε_r and unloaded $Q \cdot f$ value were measured in the TE_{011} mode by the Hakki and Coleman method [8] using an Agilent E8362B network analyzer and parallel silver boards. τ_f value in the temperature range of 20–80 °C was calculated by formula (1):

$$\tau_f = \frac{1}{f(T_0)} \frac{[f(T_1) - f(T_0)]}{T_1 - T_0} \quad (1)$$

where $f(T_1)$ and $f(T_0)$ represent the resonant frequency at T_1 (80 °C) and T_0 (20 °C), respectively. The shrinkage of the ceramics was calculated by formula (2):

$$shrinkage = \frac{D_G - D_S}{D_G} \times 100\% \quad (2)$$

where D_G and D_S represent the diameter of the cylindrical sample before and after the sintering procedure, respectively.

3. Results and discussion

Fig. 1 shows XRD patterns of $(1-x)$ZAT–xSAS ceramics sintered at densification temperature. It is observed that the $(1-x)$ZAT–xSAS sintered body includes $ZnAl_2O_4$ spinel, TiO_2 rutile and $SrAl_2Si_2O_8$ monoclinic phases.

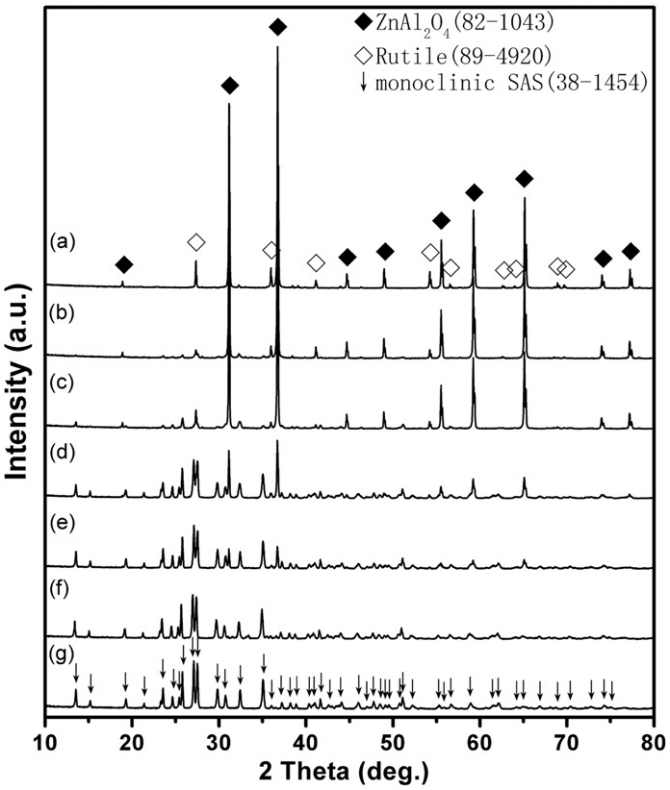

Fig. 1. XRD patterns of $(1-x)$ZAT–xSAS ceramics sintered at densification temperature: (a) $x=0.05$, 1500 °C; (b) $x=0.1$, 1500 °C; (c) $x=0.3$, 1550 °C; (d) $x=0.5$, 1550 °C; (e) $x=0.6$, 1550 °C; (f) $x=0.8$, 1575 °C; (g) $x=1.0$, 1575 °C.

As the x value increases, amounts of both $ZnAl_2O_4$ spinel phase and TiO_2 rutile phase decreases gradually and then disappears completely when x is equal to 1.0, as shown in Fig. 1(g), while that of $SrAl_2Si_2O_8$ monoclinic phase increases gradually. According to Ref. [5], in ZAT system, $ZnAl_2O_4$ and TiO_2 cannot form a solid-solution, and $ZnAl_2O_4$ spinel and TiO_2 rutile phases can be observed. When SAS is added to the ZAT system, there is no reaction between SAS and ZAT to form any new phase, as observed in Fig. 1. Compared with ZAT–$MgTiO_3$ system, ZAT–SAS system is more beneficial to tuning of τ_f to near-zero and serialization of permittivity. As in the former system, $MgTiO_3$ will easily react with TiO_2 in ZAT system to form $MgTi_2O_5$, which will weaken the adjusting capability of TiO_2 on ε_r and τ_f values [3].

Fig. 2 shows SEM micrographs of $(1-x)$ZAT–xSAS ceramics sintered at densification temperature. As seen in Fig. 2(a), two kinds of grains in different size appear in $(1-x)$ZAT–xSAS ($x=0.05$) sintered body. In our previous study, big grains are rutile phase which is easy to grow, and the small grains are $ZnAl_2O_4$ phase which are difficult to grow [5]. As the x value increases, rutile phase grains reduce rapidly and then vanish completely, while the variation of small equiaxed $ZnAl_2O_4$ grains located among rodlike SAS grains is inconspicuous, and average size of the SAS grains shows a variation tendency of initial

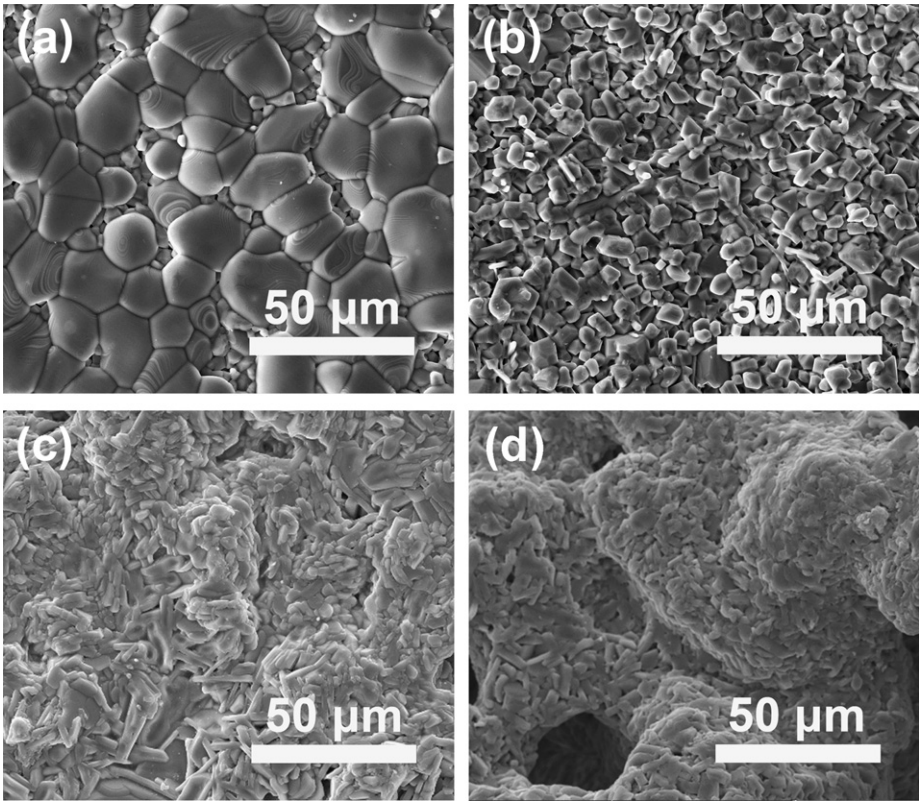

Fig. 2. SEM micrographs of $(1-x)$ZAT–xSAS ceramics at densification temperature: (a) $x=0.05$, 1500 °C; (b) $x=0.1$, 1500 °C; (c) $x=0.6$, 1550 °C; (d) $x=1.0$, 1575 °C.

Table 1
Shrinkage and microwave dielectric properties of $(1-x)$ZAT–xSAS ceramics.

x	T_{sint} (°C)	ε_r	$Q\cdot f$ (GHz)	τ_f (ppm/°C)	Shrinkage (%)
0	1500	12.20	68440	17.79	19.0
0.05	1500	10.02	13060	39.28	15.7
0.1	1500	8.11	26380	23.25	14.4
0.3	1550	7.32	27130	2.98	11.8
0.5	1550	6.64	27690	−19.28	9.1
0.56	1550	5.40	31710	−22.74	2.6
0.58	1550	4.79	32570	−23.19	−0.1
0.6	1550	4.18	35780	−27.05	−3.1
0.8	1575	3.99	35720	−22.39	−4.4
1.0	1575	3.56	14590	−30.32	−4.4

increase and then decrease. When x value is equal to 0.6, average size of the rodlike SAS grains reach to the maximum value, as shown in Fig. 2(c). As x reaches 1.0, size of SAS grains decreases, which leads to the increasing of the micropores in grain boundaries. Besides, some big micropores (see Fig. 2(d)) appear in the sintered body, and this microstructure determines rare negative shrinkage of SAS ceramics.

Table 1 shows shrinkage and microwave dielectric properties of the $(1-x)$ZAT–xSAS ceramics. It is known from Table 1 that, as the x value increases, shrinkage, ε_r and τ_f of $(1-x)$ZAT–xSAS all have a diminishing tendency. However, $Q\cdot f$ value rapidly reduces initially from 68440 GHz ($x=0$) to 13060 GHz ($x=0.05$), and then rises to 35780 GHz ($x=0.6$) slowly, finally drops to 14590 GHz ($x=1.0$).

ε_r and τ_f values of SAS ceramics are both lower than those of ZAT system. Therefore, according to the logarithmic mixing rule [5], both ε_r and τ_f values of $(1-x)$ZAT–xSAS ceramics exhibit decreasing tendency with the increase of x value. When x value is equal to 0.3, the composite ceramics reveals a near-zero τ_f value of 2.98 ppm/°C. As for the reasons why some singular points appeared in the variation of τ_f need further investigation.

When a small amount of SAS is added, $Q\cdot f$ value of the $(1-x)$ZAT–xSAS ceramics drops rapidly, which could result from the increase of the lattice defect and internal

stress caused by new second phase. As the x value increases further, ε_r reduces gradually, which leads to a decrease in total polarization and its loss, therefore quality factor of the system increases gradually. While x value is beyond 0.6, grain size of $(1-x)$ZAT–xSAS ceramics diminishes and micropores increase, which result in the increase of both weak-relative ion and polarization loss, and then the drop of the $Q \cdot f$ value [9].

Lots of micropores appear in SAS ceramics calcined at 1050 °C and sintered at 1575 °C for 3 h, respectively (see Fig. 2(d)). The sintered body reveals a rare negative shrinkage characteristic, and its shrinkage is −4.4%. As the increase of the SAS content, the effects of SAS phase on shrinkage of the sintered body during $(1-x)$ZAT–xSAS ceramics densification process become more and more magnificent, and the shrinkage decreases gradually. When x value is equal to 0.58, the shrinkage of the $(1-x)$ZAT–xSAS ceramics approaches to zero value (−0.1%).

4. Conclusions

(1). $(1-x)$ZAT–xSAS ceramics include $ZnAl_2O_4$-based spinel, TiO_2 rutile and $SrAl_2Si_2O_8$ monoclinic phases, and these three phases do not react with each other. By means of controlling the amount of different phases in the system, microwave dielectric properties of the composite ceramics can be tuned, and serialization of permittivity within the scope of 3.56–12.20 can be achieved. When x value is equal to 0.3, τ_f approximates to zero value.

(2). $SrAl_2Si_2O_8$ ceramics, calcined at 1050 °C and sintered at 1575 °C in air for 3 h respectively, exhibit a rare characteristic of negative shrinkage with −4.4%. While compounded with ZAT ceramics with positive shrinkage, $(1-x)$ZAT–xSAS microwave ceramics with continuous adjustable shrinkage can be synthesized. The shrinkage of this compound at $x=0.58$ is −0.1%.

Acknowledgments

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