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Microwave dielectric properties of high dielectric tunable - low permittivity $Ba_{0.5}Sr_{0.5}TiO_3$–$Mg_2(Ti_{0.95}Sn_{0.05})O_4$ composite ceramics

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Abstract

$Ba_{0.5}Sr_{0.5}TiO_3$–$Mg_2(Ti_{0.95}Sn_{0.05})O_4$ composite ceramics have been synthesized by the solid-state reaction. Phase structure, microstructure and microwave dielectric properties have been systematically characterized. The permittivity is tailored to a certain extent with the addition of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$. Both X-ray diffraction (XRD) and back electric image (BEI) analysis show the co-existence of two-phase structures of ABO_3 perovskite and A_2BO_4 spinel structure. A high dielectric tunablity can be obtained and a high Q value can be achieved at microwave frequency. The composition 30 wt.%$Ba_{0.5}Sr_{0.5}TiO_3$–70 wt.%$Mg_2(Ti_{0.95}Sn_{0.05})O_4$ exhibits good dielectric properties with ε of 79, Q of 152 (at 2.997 GHz) and T of 15.8% (30 kV/cm & 10 kHz) at room temperature, which make it a promising candidate for tunable microwave device applications in the wireless communication system.

Keywords: B. Composites; C. Dielectric properties; D. $BaTiO_3$ and titanates; Tunable

1. Introduction

The critical parameters of materials for microwave designs are low permittivity, low dielectric loss tangent, and high dielectric tunability. These requirements are ''contradictory'' in pure ferroelectrics. In order to overcome the drawbacks, a number of nonferroelectric materials with low permittivity and low loss such as MgO, Mg_2SiO_4 [1–3], are added into the BST composites to dilute the permittivity and suppress the dielectric loss. However, the dielectric tunability is reduced. For example, the experiments of BST-based composites with Mg_2SiO_4 and MgO have been reported to obtain low permittivity downward to 126.82 and 116.86, respectively. Nevertheless, the tunability was reduced to less than 10% [2,3]. Besides this, some others reported the materials with comparatively low losses at microwave frequencies and a high tunability but with a high permittivity. There are few studies that possess low permittivity, high tunability and low loss tangent simultaneously. Our previous study indicated 30 wt.% $Ba_{0.5}Sr_{0.5}TiO_3$–70 wt.% Mg_2TiO_4 composite ceramics exhibit a dielectric tunability ~16.4% (at 30 kV/cm) versus a permittivity ~87 and a Q value ~88 (at 3.040 GHz). Based on this result, we attempt to improve the microwave dielectric properties meanwhile do not deteriorate the tunability by adding $Mg_2(Ti_{0.95}Sn_{0.05})O_4$, which has a similar structure with Mg_2TiO_4, into BST matrix.

The $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ microwave dielectric material [4] with low permittivity ($\varepsilon \sim 15.57$) and high quality factor ($Q \times f \sim 318{,}000$@10.8 GHz) introduced to form composites with $Ba_{0.5}Sr_{0.5}TiO_3$. $(1-x)Ba_{0.5}Sr_{0.5}TiO_3$ (BST)–$xMg_2(Ti_{0.95}Sn_{0.05})O_4$(MTSO) ($x$ = 50, 60, 70, 80 wt.%) composite ceramics are fabricated via the conventional solid-state reaction method. Phase structure, microstructure and microwave dielectric properties have been investigated. The BST–MTSO composite ceramics demonstrate improved properties and breakthrough the ''contradictory'' in satisfying simultaneously low loss tangent and higher tunability versus lower permittivity.

2. Experimental

xMTSO–$(1-x)$BST (x = 0, 50, 60, 70, 80 wt.%) composite ceramics were prepared by the conventional solid-state reaction route. High purity $BaCO_3$ (99.8%), $SrCO_3$ (99.0%), TiO_2 (99.9%), MgO (99.9%) and SnO_2 (99.99%) were used as starting materials. BST and MTSO were synthesized at 1200 °C

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and 1260 °C, respectively. Then two powders were mixed by ball milling with zirconia media in ethanol for 24 h and consequently dried. The dried powders, mixed with 8 wt.% polyvinyl alcohol, were pressed into disk-shaped pellets. The green pellets were burned out to remove the solvent as well as the binder and then sintering at 1360–1420 °C in air for 4 h.

Phase identification of the sintered ceramics was conducted using XRD (Bruker D8 Advanced, Germany) with Cu Kα radiation. Backscattered electron image (BEI, JSM EMP-800) was used to characterize their microstructures. Temperature dependent permittivity (ε) and loss tangent ($\tan\delta$) of the composite ceramics samples were measured using an Agilent 4980A precision LCR meter (Agilent, Palo Alto, CA). Room temperature permittivity versus DC bias voltage was measured at 10 kHz by a Keithley model 2410 (Cleveland, OH) high voltage source coupled with TH2816A LCR meter (Changzhou, China). The samples' permittivity and loss in the range of microwave frequencies were measured using the resonance method [5] with a vector network analyzer (Agilent E5071C).

3. Results and discussion

The typical XRD patterns of sintered samples are shown in Fig. 1. A cubic paraelectric BST and a face-centered-cubic spinel structure MTSO are observed. It implies there are no obvious chemical reactions among BST and MTSO during the BST–MTSO preparation process, and both phases are well preserved in the final composite ceramics. The shift of diffraction peaks is observed with the addition of MTSO content due to the difference ions radii among Mg^{2+} (0.117 nm), Ba^{2+} (0.161 nm), Sr^{2+} (0.158 nm) and Ti^{4+} (0.0605 nm), Sn^{4+} (0.069 nm) [6], but it does not shift to lower angles with continues increase of MTSO content from 50 wt.% to 80 wt.%. As we know the Mg^{2+} ions initially enter into the A sites of perovskite structure and consequently occupied the B sites when the Mg^{2+} concentration exceeds 5 mol% in the BST and up to the solubility limit (~15 at.%) [7]. The concentration of MTSO (~55.95 at.%) preponderates over the solubility limit of Mg in BST, as a result, the diffraction peak positions do not change when the content of MTSO increases from 50 to 80 wt.%.

BEI micrographs of the composite ceramics are presented in Fig. 2. Two phases were obviously observed. As an illustration, EDS spectra of the sample (d) are also presented in Fig. 2(b). The EDS results reveal the light grains with flocculent structure contain Ba, Sr, Ti, O and Mg and the edgily dark grains with dense structure contained Mg, Ti, O, Sn and Ba, Sr (Au act as surface electrode material). This implies formation of a complex solid solution due to the incorporation of foreign ions in each phase. Therefore, it is confirmed the light grains are mainly BST marked as "A" and the dark grains are mainly MTSO marked as "B". The BST grain size of composite ceramics is much smaller than that of undoped BST ceramics (not shown in here). The result reveals the attendance of MTSO acts as a grain growth inhibiter, which has a significant effect on size reduction. It could be explained MTSO phase lie in the grain boundaries of BST and hinders the ions diffusion, which warps the BST grains and inhibits the grain growth [2].

The temperature dependences of the dielectric permittivity and loss tangent measured at 10 kHz for all composite ceramics are shown in Fig. 3. Broadened and suppressed dielectric peaks and shifts of Curie temperature T_C are observed with increasing of the MTSO content. The dielectric permittivity is effectively reduced from 2035 to 44 at 10 kHz and room temperature. We

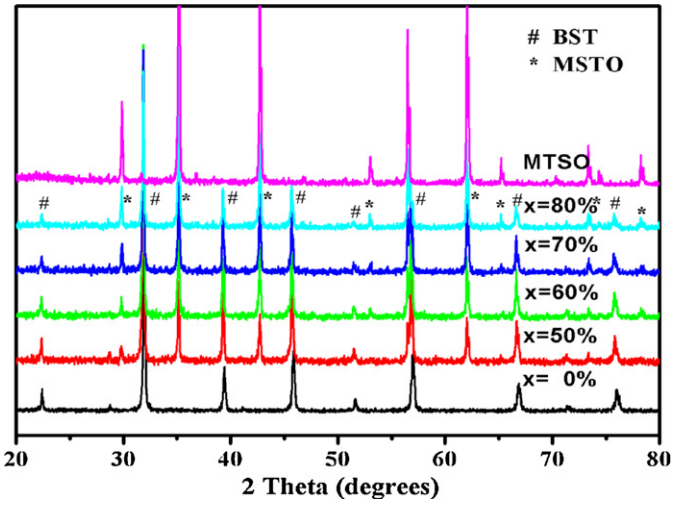

Fig. 1. XRD patterns of the $x Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$(1-x)Ba_{0.5}Sr_{0.5}TiO_3$ (x = 0, 50, 60, 70, 80 wt.%) composite ceramics.

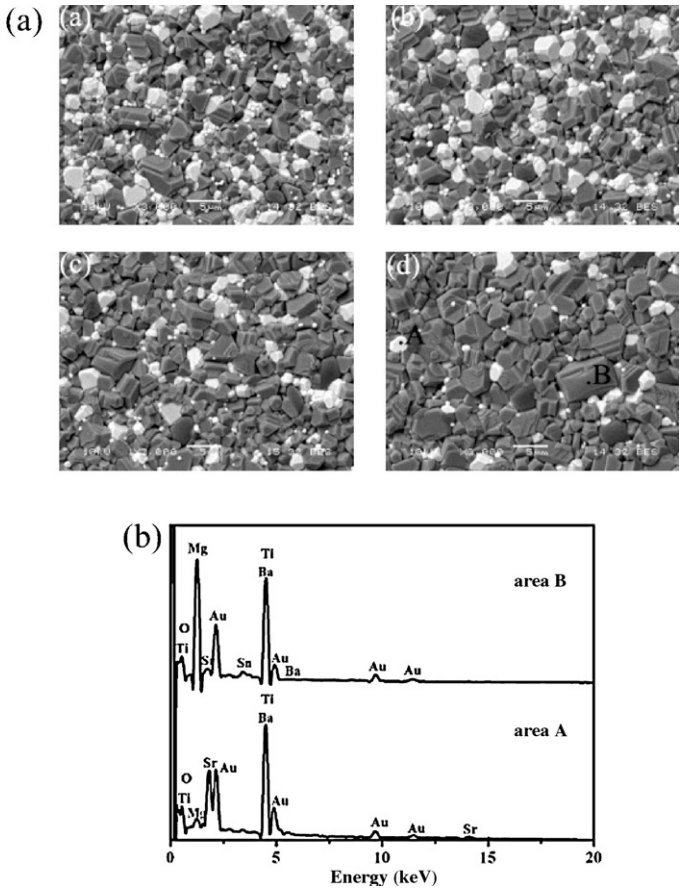

Fig. 2. BES micrographs of the $x Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$(1-x)Ba_{0.5}Sr_{0.5}TiO_3$ composite ceramics: (a) x = 50, (b) x = 60, (c) x = 70 and (d) x = 80 wt.%.

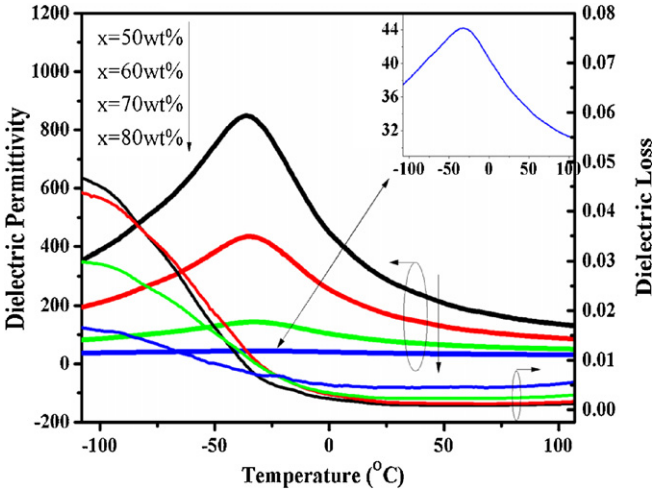

Fig. 3. Temperature dependences of dielectric permittivity and loss tangent of the xMg$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$–(1 − x)Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (x = 0, 50, 60, 70, 80 wt.%) composite ceramics at 10 kHz.

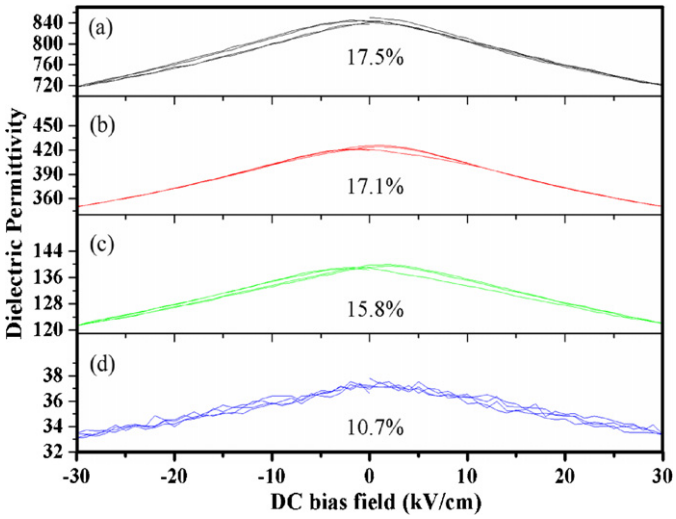

Fig. 4. DC bias field dependences of dielectric permittivity of the xMg$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$–(1 − x)Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (x = 0, 50, 60, 70, 80 wt.%) composite ceramics measured at 10 kHz and room temperature.

regard the main reason for the suppression of the permittivity peak is MTSO dielectrics introduced to BST can dilute the ferroelectricity. The dielectric loss increases slightly at room temperature but is still below 0.5%. This may due to the substitution of Mg^{2+} for Ti^{4+}, which induces the oxygen vacancies and increases the conduction loss [8]. The T_C of 50 wt.% MTSO–50 wt.% BST is decreased compared with pure BST, which caused by the deterioration of the ferroelectric long-range order due to the replacement of Ti^{4+} by Mg^{2+} [9] that is similar to other reported data [10]. As the content of Mg^{2+} ion has reached its solid solubility, further increasing of Mg^{2+} does not lower the T_C point continuously. Moreover, T_C is observed to shift slightly to higher temperature with increasing MTSO content from 50 wt.% to 80 wt.%. The internal stress decreases as the grain size increases and leads to the shift of T_C to higher temperature [2]. So we regard the diffusion of Mg^{2+}, together with the change of grain size, brought on the fluctuation of T_C.

Fig. 4 shows the tunability of BST–MSTO composite ceramics. The dielectric properties of samples and calculated tunabilities are summarized in Table 1. The permittivity of composite ceramics is availably reduced but still keeps relatively high tunability. The tunability of composition 30 wt.% BST–70 wt.%MTSO is still 15.8% whereas the permittivity decreases to 144 at 10 kHz and 20 °C. When the MTSO content is 80 wt.%, the tunability keeps more than 10.7%, but the permittivity decreases to 38. This result implies the continuously connected chains of Ti–O–Ti bonds and the interactions of Ti^{4+} ions of BST–MTSO composite ceramics are not weakened as observed in the composition of Ba$_{1-x}$Sr$_x$TiO$_3$–MgO and Ba$_{1-x}$Sr$_x$TiO$_3$–Mg$_2$SiO$_4$ [2,3]. As pointed out above, it is beneficial to decrease the permittivity and ensure comparatively high tunability for the development of tunable microwave devices.

Table 1 shows the results of the dielectric properties at microwave frequency and room temperature of (1 − x)BST–xMTSO composite ceramics. The Q values of all composite ceramics are above 120. The decrease of dielectric permittivity from low frequency to microwave frequency band is claimed to

Table 1
Microwave and low frequency dielectric properties of the xMg$_2$(Ti$_{0.95}$Sn$_{0.05}$)O$_4$–(1 − x)Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ and xMg$_2$TiO$_4$–(1 − x)Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (x = 0, 50, 60, 70, 80 wt.%) composite ceramics sintered at 1360–1420 °C for 4 h.

	x	Dielectric properties (at 10 kHz)				Microwave properties		
		T_C (°C)	At about 20 °C		Tunability (%) at 30 kV/cm bias	Resonant frequency (GHz)	ε (at resonant frequency)	Q (1/tanδ)
			ε	tanδ				
	0	−26.0	2035	0.0010	23.5	1.130	1611	424
MTSO	50	−36.2	849	0.0012	17.5	1.527	302	232
	60	−35.1	434	0.0017	17.1	1.953	169	195
	70	−33.1	144	0.0024	15.8	2.997	79	152
	80	−32.5	38	0.0044	10.7	4.431	30	121
MTO	50	−28.9	417	0.0006	18.4	1.838	354	131
	60	−25.7	224	0.0014	18.1	2.060	191	115
	70	−25.5	98	0.0026	16.4	3.040	87	88
	80	−25.0	44	0.0049	10.8	4.928	33	68

due to the origin of the different mechanisms, i.e., space charges, dipole and ionic polarization [11]. The dielectric loss of the composite ceramics at microwave frequencies is higher than that at low frequencies (under 1 MHz), which can be attributed to the ferroelectric relaxor behavior of the composite ceramics [12]. The dielectric relaxation is closely related to the microstructure, defects, and chemical bonds. It should be noticed the resonant frequency also increase with MTSO additive, which own to the influence of intrinsic loss [13].

The corresponding parameters of $Ba_{0.5}Sr_{0.5}TiO_3$–Mg_2TiO_4(BST–MTO) are also presented in Table 1 for comparison. Compared to the BST–MTO composite, BST–MTSO has a lower permittivity, lower dielectric loss tangent at microwave frequency and comparative tunablity. The tunability of BST–MTSO is slightly less than that of BST–MTO. This is probably related to the presence of residual polar clusters as a result of the addition of Sn [11]. It should worth notice the Q value is greatly improved in BST–MTSO composite ceramics.

4. Conclusions

$Ba_{0.5}Sr_{0.5}TiO_3$–$Mg_2(Ti_{0.95}Sn_{0.05})O_4$ composite ceramics have been synthesized by the solid-state reaction route. The introduction of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ resulted in a reduction in grain growth of the composite ceramics. Compact and uniform ceramics were obtained. Meanwhile outstanding microwave dielectric properties have achieved. It is noteworthy the sample of 30 wt.% $Ba_{0.5}Sr_{0.5}TiO_3$–70 wt.% $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ has a Q value of 152 (at ∼2.997 GHz), a tunability of ∼15.8% (at 30 kV/cm biasing) and a permittivity of ∼79, which suggest it is a suitable material for electrically tunable microwave devices.

Acknowledgments

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