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Microstructure and dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$–$MgAl_2O_4$ composite ceramics

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Abstract

$(1-x)Ba_{0.6}Sr_{0.4}TiO_3$–$xMgAl_2O_4$($x$ = 25, 30, 35 and 40 wt%) composite ceramics were prepared by conventional solid-state reaction method. The microstructures, dielectric properties and tunability of the composites have been investigated. The XRD patterns analysis reveals two crystalline phases, a cubic perovskite structure $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) and a spinel structure $MgAl_2O_4$ (MA). SEM observations show that the BST grains slightly dwindle and agglomerate with increasing amounts of MA. A dielectric peak with very strong frequency dispersion is observed at higher MA content, and the Curie temperature shifts to a higher temperature with increasing MA content. The ceramic sample with 30 wt% MA has the optimized properties: the dielectric constant is 1503, the dielectric loss is 0.003 at 10 kHz and 25 °C, the tunability is 23.63% under a dc electric field of 1.0 kV/mm, which is suitable for ferroelectric phase shifter.

Keywords: C. Dielectric properties; Barium strontium titanate; Composite ceramics; Frequency dispersion; Tunability

1. Introduction

Barium–strontium titanate, $Ba_{1-x}Sr_xTiO_3$(BST, $0 \leq x \leq 1$) has been investigated with considerable interest as a new dielectric material for tunable microwave application [1,2]. The large electrical field dependent dielectric constant can be used for tunable devices, such as tunable oscillators, phase shifters and varactors [3–5]. In phase shifters, it is desirable to have a low permittivity for good impedance matching, a low dielectric loss to minimize the insertion losses of devices, and a high dielectric tunability, which is the change of permittivity with dc field, for less power driving and high speed of phase shift. Meanwhile, the high sintering temperature of pure BST (1400 °C) is not preferable to the process costs and environment, and low-sintering-temperature materials are more readily applicable to low-temperature co-fired ceramics (LTCC) technology. Hence it is desirable to lower the dielectric constant and the sintering temperature of BST without deteriorating the tunability and dielectric loss [6].

To meet these requirements, non-ferroelectric materials with low dielectric constant and low dielectric loss have been employed as the secondary phase in the composite to improve the dielectric properties [7,8]. BST–MA composites have been synthesized and reported to demonstrate a significant reduction in dielectric constant and loss tangent compared with pure BST [9]. In this study, various amounts of MA were introduced to form composite ceramics with BST and the dielectric properties of the composites ceramics were investigated. The aim of the present study is to find a BST-based composite material system with moderate dielectric constant, low dissipation factor and moderate tunability and to systematically discuss the relaxor behavior of BST composite ceramics.

2. Experimental procedure

The conventional ceramic processing method was employed to prepare $Ba_{0.6}Sr_{0.4}TiO_3$–$MgAl_2O_4$ samples. $Ba_{0.6}Sr_{0.4}TiO_3$ powders were first prepared by the conventional solid-state reaction method: the starting raw materials, $BaCO_3$, $SrCO_3$, TiO_2 and CuO, V_2O_5 powders, were weighed according to the stoichiometry. The raw materials were then mixed together using alcohol and zirconia milling media for 12 h. After drying, the mixture was calcined at 1050 °C for 2 h in air. Meanwhile

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the $MgAl_2O_4$ powders were prepared in the same method with raw materials MgO and Al_2O_3 at a calcining temperature of 1050 °C. Then various amounts of $MgAl_2O_4$ (25, 30, 35 and 40 wt%) were added into the $Ba_{0.6}Sr_{0.4}TiO_3$ powder, remilled for 12 h and redried. The obtained powders were pulverized with 5 wt% polyvinyl alcohol (PVA) binder and pressed into disk-shaped pellets under 100 MPa. The green pellets of the composite ceramics were sintered at 1300 °C for 2 h in air. Silver paste was sintered on both sides of the samples at 500 °C for 15 min to form electrodes for the electrical measurements.

X-ray diffraction analysis (XRD, X'pert MPD PRO, Holland) with Cu Kα radiation was used for phase identification. A scanning electron microscope (SEM, JSM-5800, Japan) equipped with an energy-dispersive spectrometer (EDS) was used to characterize the microstructure and chemical component elements. The temperature dependence of dielectric constant and loss tangent was measured using a high-precision LCR meter (HP4284A) connected with a temperature controlled chamber. The microwave dielectric properties were analyzed using the Hakki–Coleman dielectric resonator method [10] by the network analyzer (HP8753E, Agilent, Palo Alto, CA) combining a resonating cavity.

The tunability of the material is determined by the following equation:

$$\text{Tunability} = \frac{\varepsilon_{(0)} - \varepsilon_{(\text{app})}}{\varepsilon_{(0)}} \times 100\% \qquad (1)$$

where $\varepsilon_{(0)}$ and $\varepsilon_{(\text{app})}$ are the dielectric constants under zero dc field and under the applied field, respectively.

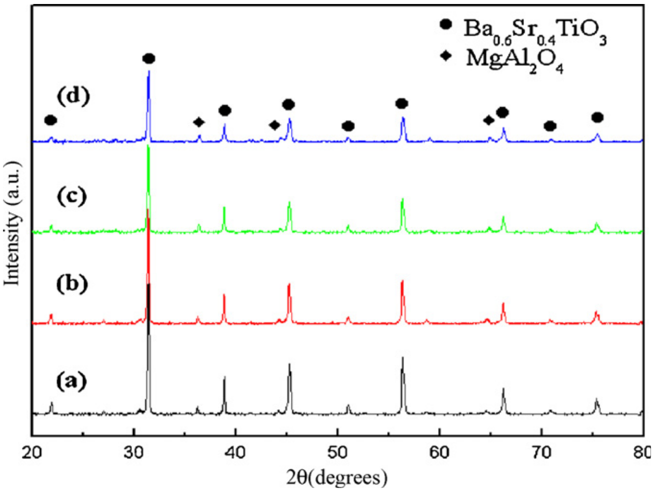


Fig. 1. X-ray diffraction patterns of $(1-x)$BST–xMA composite ceramics: (a) $x = 25\%$; (b) $x = 30\%$; (c) $x = 35\%$; (d) $x = 40\%$.

3. Results and discussion

The X-ray diffraction patterns of $(1-x)$BST–xMA composite ceramic samples are shown in Fig. 1. The main crystalline phases of all sintered samples are indexed to be a cubic perovskite BST phase and a faced-centered-cubic spinel MA phase without any other crystalline phase detected, which implies that no obvious chemical reaction occurs between BST and MA phase. The X-ray diffraction intensities of MA phase enhance gradually with increasing of MA content, while BST intensities reduce continuously. $I_{\text{MA}(311)}$ and $I_{\text{BST}(110)}$ are the largest XRD intensity for MA(3 1 1) peak and BST(1 1 0) peak.

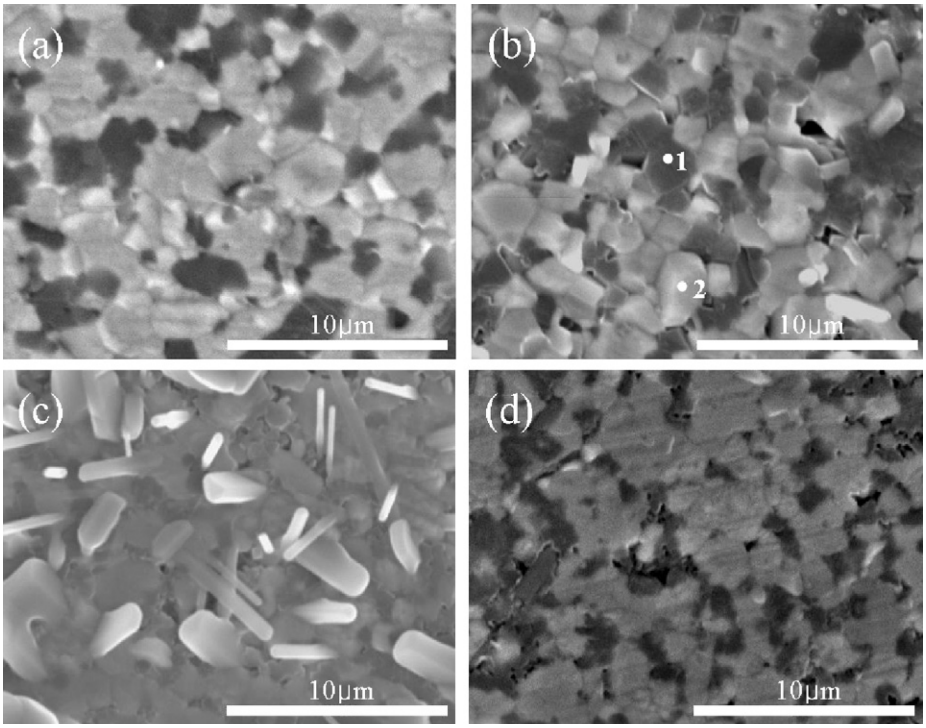
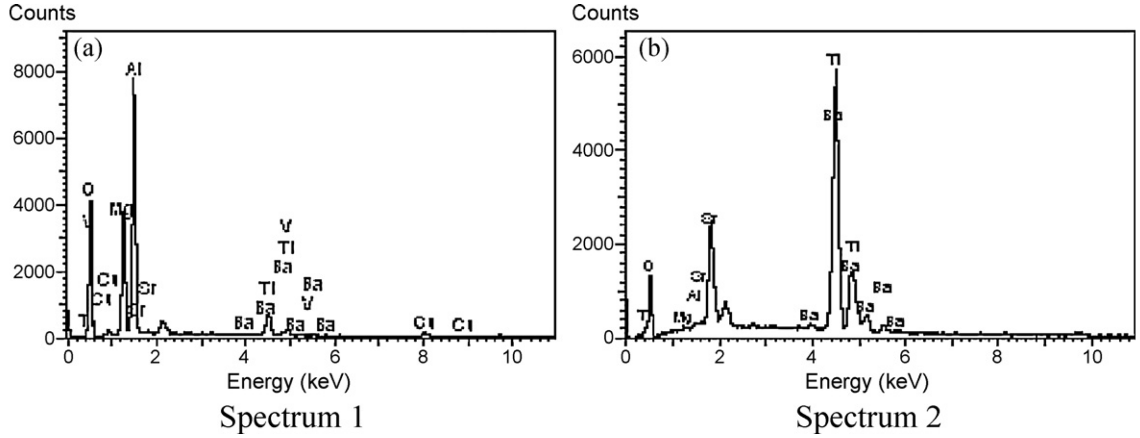


Fig. 2. SEM micrographs of $(1-x)$BST–xMA composite ceramic samples: (a) $x = 25\%$; (b) $x = 30\%$; (c) $x = 35\%$; (d) $x = 40\%$.



Spectrum 1 Spectrum 2

Fig. 3. EDS patterns of different microstructures in composite ceramics.

With increasing content of MA, the ratio of $I_{MA(311)}$ and $I_{BST(110)}$ increases. For example, The measured XRD intensity ratios of $I_{MA(311)}/I_{BST(110)}$ of samples are 0.055, 0.067, 0.087, 0.090, respectively.

The SEM micrographs of ceramic samples were shown in Fig. 2. It is very clear that two component phases are co-existed and the dense microstructures are observed. The energy dispersive spectroscopy (EDS) analysis (Fig. 3 and Table 1) were performed for sample doped with 30 wt% MA, it detected that the dark grain contained primarily Mg, Al, O and small amounts of Ba, Sr element, which means that the dark grain is spinel MA phase. The white grain contained primarily Ba, Sr, Ti, O and small amounts of Mg, Al element, which means that the white grain is perovskite BST phase. What's more, it indicated that the formation of complex solid solutions by the incorporation of foreign ions in each phase. As can be seen, with an increase of MA content, the MA grains grow larger and the BST grains slightly dwindle. At the same time, the BST grains markedly agglomerate, in accordance with Chen et al. [7] reported results.

The temperature dependence of the dielectric constant for $(1-x)$BST–xMA composite ceramics measured at the

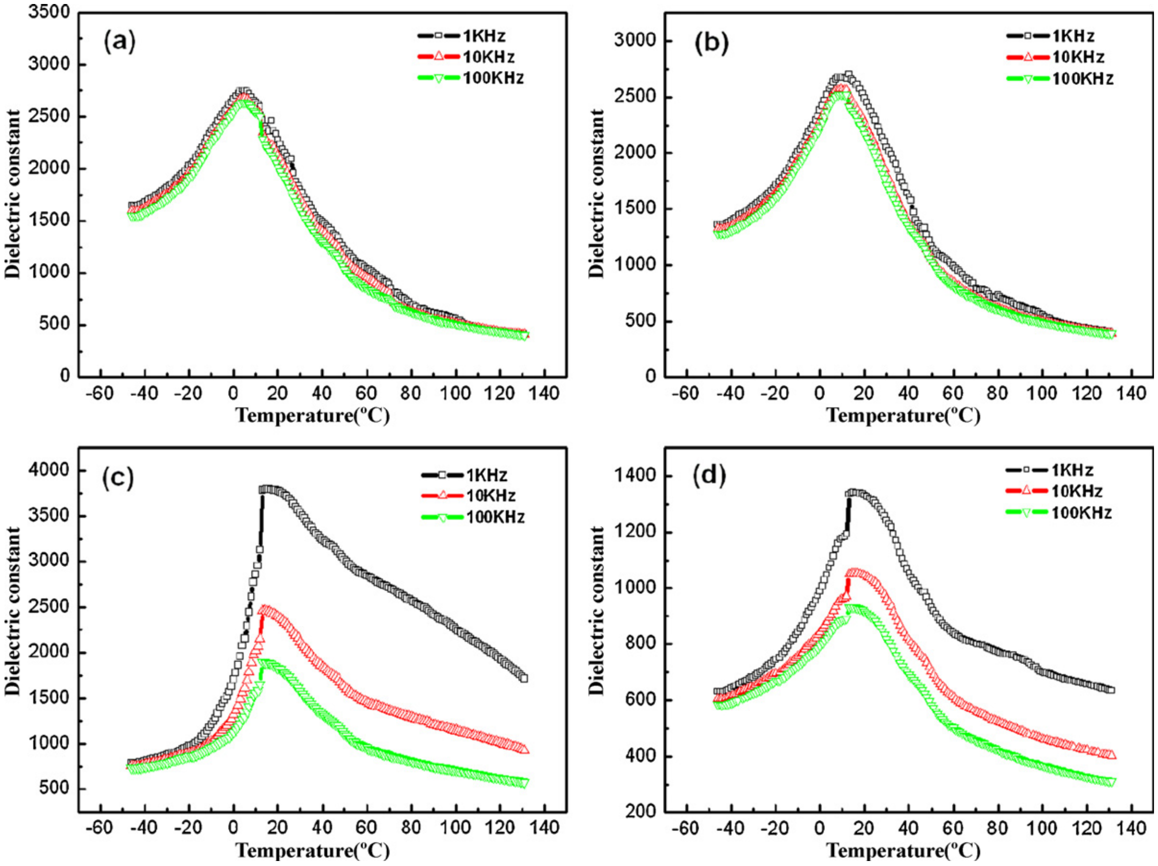


Fig. 4. The temperature dependence of the dielectric constant of $(1-x)$BST–xMA composite ceramics: (a) $x = 25\%$; (b) $x = 30\%$; (c) $x = 35\%$; (d) $x = 40\%$.

Table 1
EDS quantum analysis of different microstructures in composite ceramics.

Element/at.%	Spectrum 1	Spectrum 2
O	52.02	49.89
Mg	14.15	0.40
Al	29.65	0.64
Ti	2.44	27.11
V	0.20	–
Cu	1.09	–
Sr	0.21	9.87
Ba	0.24	12.09
Total	100.00	100.00

frequencies varying from 1 kHz to 100 kHz are displayed in Fig. 4. The dielectric peaks of composite ceramics are suppressed and broadened with the increase of the MA content. This could result from the dilution of the ferroelectricity [11] and the pinching of phase transition [12]. The T_C is obviously increased from 4 °C for $x = 25\%$ to 16 °C for $x = 40\%$ at 10 kHz. It can be interpreted that the substitution of Sr^{2+} for Mg^{2+} in the MA lattice is driven by the combination of size and electronegativity difference between Sr^{2+} and Ba^{2+}, resulting in the increase in Ba/Sr ratio of BST, therefore the Curie temperature increases.

An evident frequency dispersion feature is also observed in Fig. 4. It can be seen that the spectral features closely depend on the composition. For $x = 25\%$ and 30%, the dielectric peak appears relatively sharp at T_C with no frequency dispersion. The sharp dielectric peak gradually becomes a diffuse peak with increasing frequency for $x = 35\%$ and 40%. This behavior may be ascribed to the substitutions of Mg^{2+} and Al^{3+} for Ti^{4+} on the B site in the perovskite lattice leading to a disordered distribution of different ions on the equivalent crystallographic sites.

A modified Curie–Weiss law [13] has been proposed to describe the diffuseness of the phase transition in present ceramics:

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{(T-T_m)^{\gamma}}{C_1} \qquad (2)$$

where γ is the degree of relaxation ($1 < \gamma < 2$) and C_1 is assumed to be constant. The parameter $\gamma = 1$ describes a normal ferroelectric, whereas $\gamma = 2$ describes a complete diffuse phase transition, a classical relaxor behavior. The plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T - T_m)$ for four samples measured at 10 kHz are shown in Fig. 5. The dielectric data of all samples can be well fitted to a modified Curie–Weiss law. The monotonous increase of γ value from 1.52 to 1.76 with the increase of MA indicates the formation process of a relaxor ferroelectric. It can be attributed to the presence of polar clusters that are caused by the off-center Ti displacements in the present ceramics due to the Mg^{2+} and Al^{3+} ions substitution [14].

The dc electric field dependent dielectric constant was measured and presented in Fig. 6. From the results of Fig. 6, it is evident that the relative dielectric constant of the samples decreases with increasing the DC biasing field. It is well known that the change of dielectric constant under applied electric field is associated with the anharmonic interaction of Ti^{4+} ions for paraelectric $BaTiO_3$-based material system. This can be explained by Johnson's theory [15]. Their dielectric properties and calculated tunability are summarized in Table 2. It can be

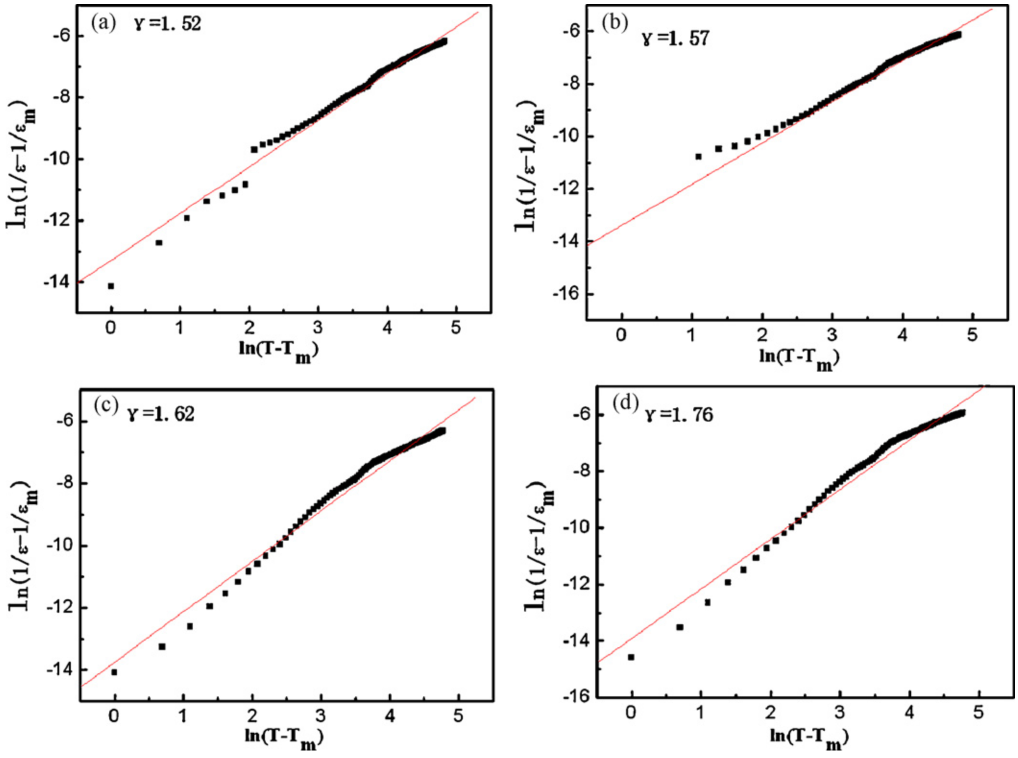


Fig. 5. The plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T - T_m)$ for $(1 - x)$BST–xMA composite ceramics at 10 kHz: (a) $x = 25\%$; (b) $x = 30\%$; (c) $x = 35\%$; (d) $x = 40\%$.

Table 2
Dielectric properties of $(1-x)$BST–xMA composite ceramics at 10 kHz.

MA content (wt%)	T_C (°C)	ε_{max} (T_C)	ε_r (25 °C)	tanδ (25 °C)	Tunability (1.0 kV/mm)
$x = 25$	4	2683	1428	0.002	18.0%
$x = 30$	9	2572	1503	0.003	23.6%
$x = 35$	13	2464	1313	0.168	20.4%
$x = 40$	16	1053	901	0.127	21.3%

seen that the tunability of BST–MA composite ceramics is above 18% and the maximum of that is 23.6% when doped with 20 wt% MA, which is higher than previously reported data [6,7]. According to Fig. 7, we can see the tunability of samples is reduced obviously when doped with 40 wt% MA, which because the connectivity between BST and BST grains weakens with the increase of $MgAl_2O_4$ resulting from the continuous decrease of the relative content of ferroelectric phase BST.

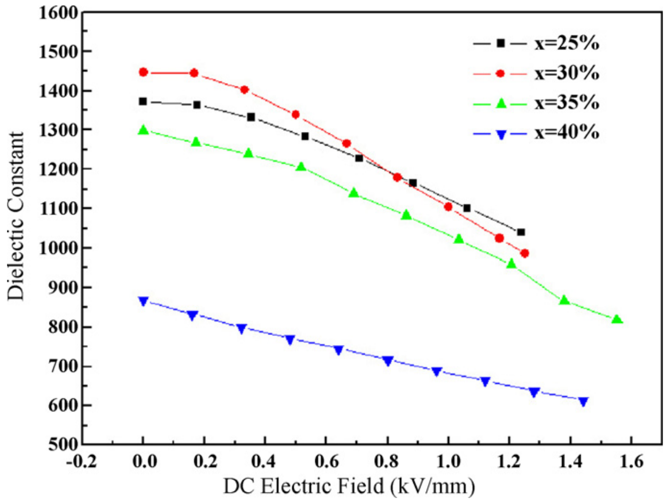


Fig. 6. Dc electric field dependence of the dielectric constant for $(1-x)$BST–xMA composite ceramics.

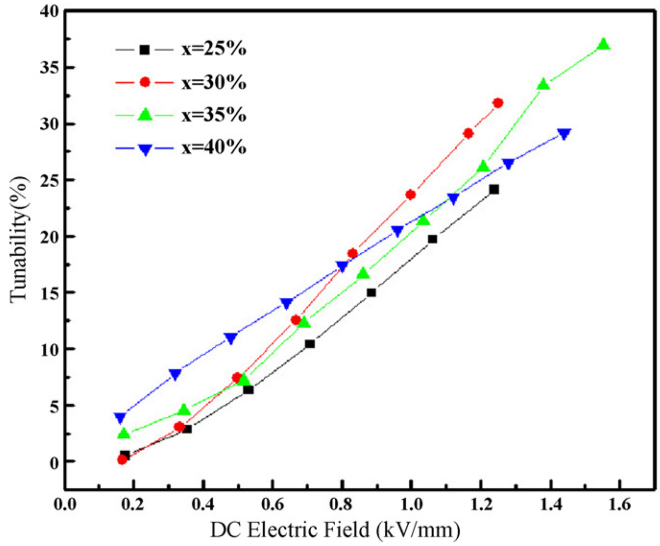


Fig. 7. Dc electric field dependence of the tunability for $(1-x)$BST–xMA composite ceramics.

4. Conclusions

Two crystalline phases, a cubic perovskite structured $Ba_{0.6}Sr_{0.4}TiO_3$ and a face-centered-cubic spinel-structured $MgAl_2O_4$ are observed in 1300 °C sintered BST-MA composite ceramics. The BST grains of ceramic samples exhibit significant agglomeration with increasing MA. A dielectric peak with very strong frequency dispersion is also observed at higher MA content and the Curie temperature initially moves toward higher temperatures. As the MA content increases, the dielectric constant decrease dramatically, nevertheless the tunability keeps a larger value (more than 20%). An optimum composite ceramic with dielectric constant 1503, dielectric loss 0.003 at 10 KHz and 25 °C, tunability 23.6% under a dc electric field of 1.0 kV/mm was attained. It is promising to be utilized in tunable device.

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