

Dielectric tunability and microwave properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3\text{-BaMg}_6\text{Ti}_6\text{O}_{19}$ composite ceramics for tunable microwave device applications

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Abstract $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3\text{-BaMg}_6\text{Ti}_6\text{O}_{19}$ microwave composite ceramics with low dielectric constant and relatively high tunability were fabricated via the solid-state reaction method. The microstructures and microwave dielectric properties of the composite ceramics have been investigated. $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ can be friendly coexistent in the composite material system without obvious chemical reactions. With increasing content of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ from 10 wt.% to 60 wt.%, the dielectric anomalous peaks of ferroelectric-paraelectric phase transition for the composite ceramics are suppressed and broadened. The dielectric constant can be effectively tailored from 2035 to 129. For composite ceramics with 60 wt.% content of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$, the dielectric loss still keeps around 0.002 and the tunability is 13.4% measured at a dc-applied electric field of 30 kV/cm. The Q value of composite ceramics with 20 wt.% content $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ is 367 and the dielectric constant is cut down to 665 at the microwave band of 1.579 GHz.

Keywords Composites · Dielectric properties · Ferroelectricity · Microstructure · $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ · $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ · Tunability

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1 Introduction

In recent years, tunable microwave devices with high dielectric performance are urgently required with the dramatic development of wireless communication systems [1–3]. BaTiO_3 -based ferroelectrics exhibiting high dielectric nonlinearity has become one of the most promising materials to realize the potential applications for tunable ceramic capacitors and tunable microwave devices [4, 5]. In such applications, 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. Barium strontium titanate (BST), as an important member of the BaTiO_3 -based ferroelectric materials family, has attracted considerable attentions due to its eminent dielectric performance. However, pure barium strontium titanate ferroelectric ceramics with relatively high dielectric constant at room temperature is difficult to satisfy the requirements of impedance matching and high power [6]. Therefore, significant decrease in dielectric constant and loss without eliminating tunability for Barium strontium titanate ferroelectric material system is needed in tunable microwave applications.

Many researchers [7–9] have reported that better dielectric properties of BaTiO_3 -based ferroelectric ceramics have been obtained by adding non-ferroelectric materials. In this paper, various amounts of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ (10 wt%~60 wt%), which has a hexagonal structure with low dielectric constant ($\epsilon_r=39$) and excellent microwave properties ($Q\geq 10000$) are induced to synthesize barium strontium titanate (BST)-based composite ceramics. The phase purity, dielectric non-linear characteristics, and microwave properties of BST composite ceramics have been investigated. The

main purpose of this research is to decrease the sintering temperature of barium strontium titanate (BST) ceramics with moderate dielectric permittivity, low dissipation factor and moderate tunability.

2 Experimental procedure

The $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder was prepared by the conventional solid-state reaction method. The starting raw materials BaTiO_3 (99.9%) and SrTiO_3 (99.9%) powders were weighed according to the stoichiometry using alcohol and zirconia milling media for 24 h. After drying, the wet mixtures were calcined in alumina crucible at 1100°C for 4 h in air. Meanwhile, the $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ powder were prepared in the same method with raw materials BaTiO_3 (99.9%), TiO_2 (99.7%), and MgO (99.0%) at a calcining temperature of 1250°C . Then various amounts of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ (10 wt%, 20 wt%, 40 wt%, 50 wt%, and 60 wt%) were added into the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder, remilled for 24 h and redried. The obtained powders were pulverized with 8 wt% polyvinyl alcohol binder and pressed into disk-shaped pellets at the pressure of 100 MPa. The green pellets of pure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics (termed as samples A) and the composite ceramics with 10, 20, 40, 50, and 60 wt% $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ (termed as samples B, C, D, E, and F) were sintered at the temperature of 1400°C for 4 h in air.

X-ray diffraction (XRD, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation was utilized to characterize the phase identification. Microstructures and chemical component elements of the specimens were examined by scanning electron microscope (SEM), (JSM EMP-800) with energy dispersive spectroscopy (EDS). The temperature dependence of dielectric constant and loss were measured from -120 to 100°C at frequency of 10 kHz using a high-precision LCR meter (HP 4284A) connected with a temperature controlled chamber. The tunability was measured at 10 kHz and room temperature up to the maximum bias voltage of 30 kV/cm by a Keithley model 2410 electrometer coupled with a TH2613A LCR meter. The dielectric constant and the Q values at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method [10] by the network analyzer Agilent 8753E coupled with a resonating cavity.

3 Results and discussion

The X-ray patterns of the sintered samples shown in Fig. 1 reveals that the composite ceramics have a two-phased structure, a cubic perovskite structure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and a hexagonal structure $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$. It indicates that no obvious chemical reactions between $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ and

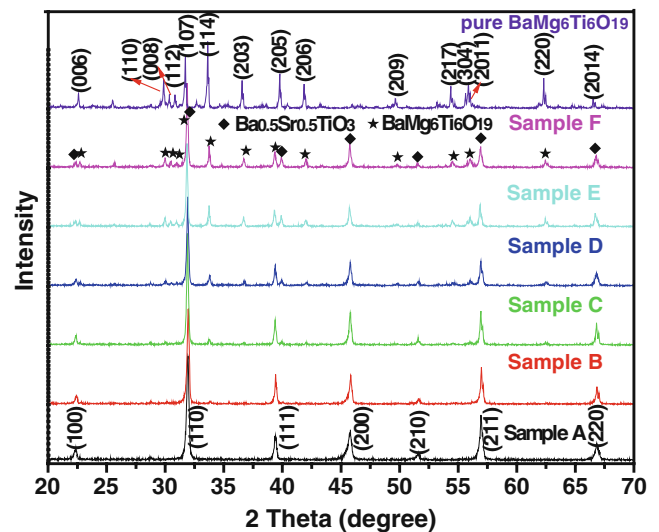


Fig. 1 X-ray diffraction (XRD) patterns of pure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ and $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ -doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ composite ceramic samples

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ were detected during the composite ceramics preparation process. However, this does not exclude low amount of Mg^{2+} entering the lattice structures. The substitution of Mg^{2+} (0.117 nm) for A sites (Ba^{2+} (0.161 nm) and/or Sr^{2+} (0.158 nm)) would lead to the decrease of lattice constant, while the Mg^{2+} incorporation in the Ti^{4+} (0.061 nm) sites would cause an increase of lattice constant. This two-folded effect would lead to the diffraction peaks hardly shift [11]. It was observed that Mg^{2+} ions initially entered into the A sites of perovskite structure, then into the B sites when the Mg^{2+} concentration exceeds 5 at% in the barium strontium titanate and up to the solubility limit (~ 15 at%) [12]. The concentration of Mg^{2+} in our samples preponderates over the solubility limit of Mg^{2+} in BaTiO_3 , so the diffraction peak position does not change when the content of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ increases from 10 to 60 wt%.

Figure 2 shows the back-scattered electron images (BSI) of some samples. All samples were sintered at 1400°C for 4 h. Combined with energy-dispersive spectroscopy (EDS) (shown in Fig. 3) and XRD analysis results, the light-colored cubic-like grains marked as 'A' are $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ while the dark-colored tiny grains marked as 'B' are $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$. Obviously, the grains growth of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ is inhibited by $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$, which has a lower sintering temperature. The grain size of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ decreases from more than $10\ \mu\text{m}$ to less than $1\ \mu\text{m}$ when the content of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ increases from 10 wt% to 60 wt%.

The temperature dependence of dielectric constant and loss tangent for pure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and composite ceramics samples are given in Fig. 4. The dielectric anomalous peaks of ferroelectric-paraelectric phase transition

Fig. 2 Back-scattered electron images (BSI) SEM micrographs of pure $Ba_{0.5}Sr_{0.5}TiO_3$ and $BaMg_6Ti_6O_{19}$ -doped $Ba_{0.5}Sr_{0.5}TiO_3$ composite ceramic samples

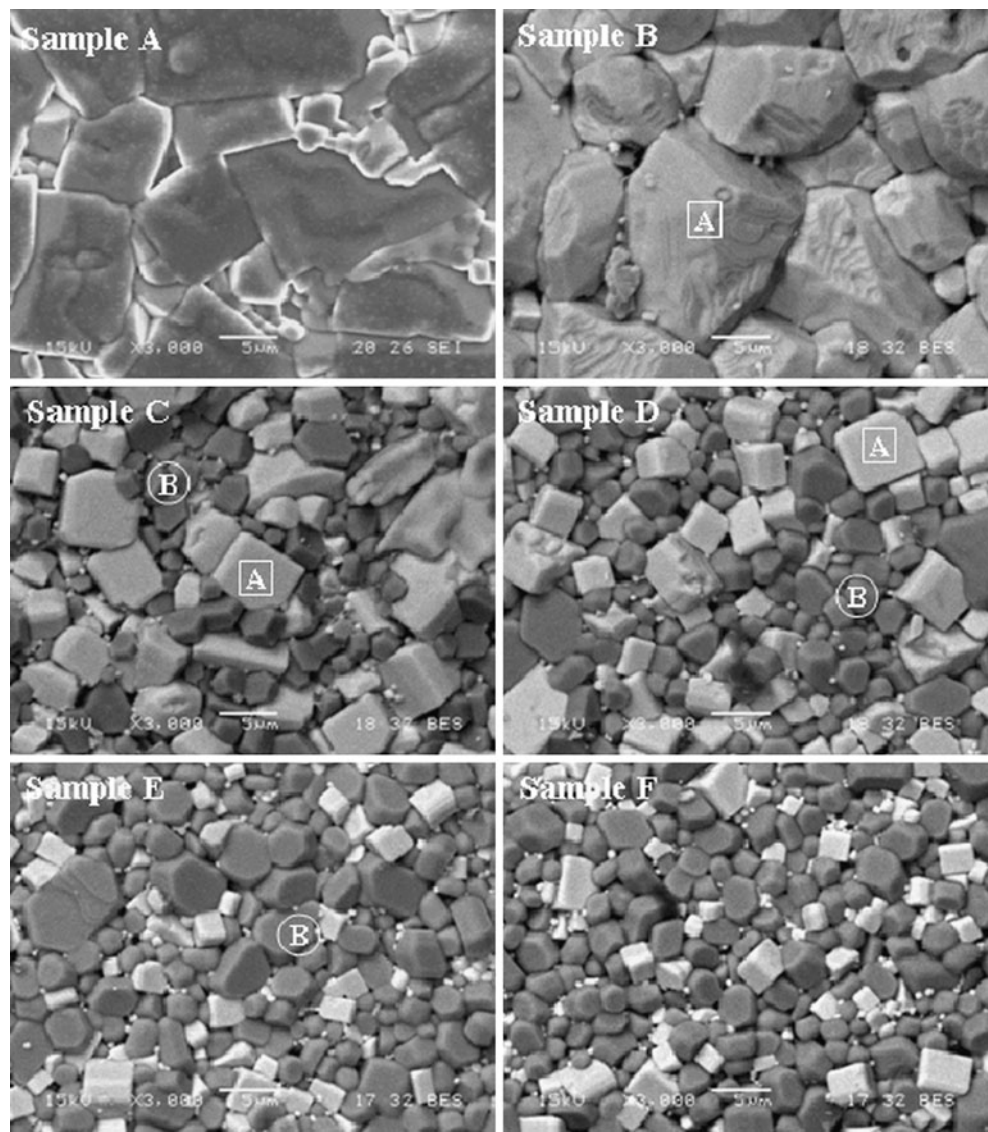
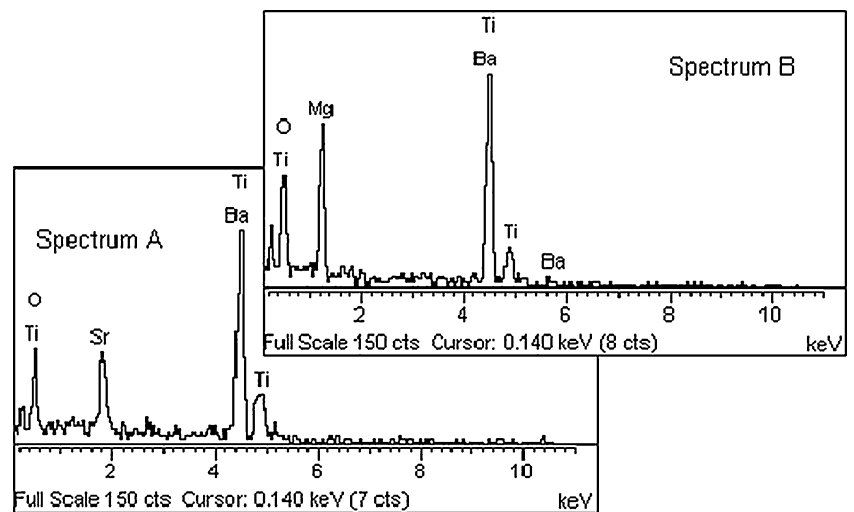


Fig. 3 Energy dispersive spectroscopy (EDS) micrographs of $BaMg_6Ti_6O_{19}$ -doped $Ba_{0.5}Sr_{0.5}TiO_3$ composite ceramic samples



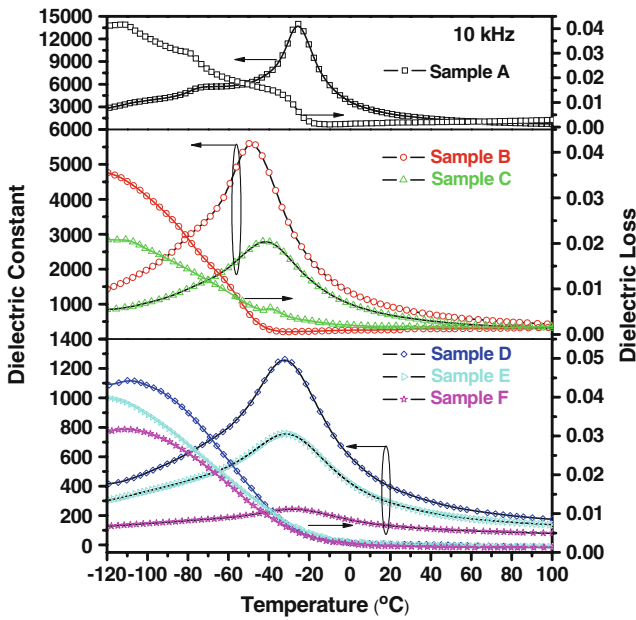


Fig. 4 The temperature dependence of dielectric constant and loss of pure Ba_{0.5}Sr_{0.5}TiO₃ and BaMg₆Ti₆O₁₉-doped Ba_{0.5}Sr_{0.5}TiO₃ composite ceramic samples

for the composite ceramics are suppressed and broadened by increasing the BaMg₆Ti₆O₁₉ content from 10 wt% to 60 wt%. The dielectric constant is effectively reduced from 930 to 129 at 10 kHz and room temperature. It indicates that BaMg₆Ti₆O₁₉ dielectrics can effectively dilute the ferroelectricity of Ba_{0.5}Sr_{0.5}TiO₃ and originate the diffuse transition. It can be explained that the main cause of the suppression of the dielectric constant peak is the introduction of BaMg₆Ti₆O₁₉ and the increase of grain boundary which is caused by the decrease of Ba_{0.5}Sr_{0.5}TiO₃ grain size. Meanwhile, the dielectric loss has no obvious deterioration and keeps around 0.002.

The changes of the curie temperature are more complex. First the *T_c* shifts to lower temperature with certain addition of BaMg₆Ti₆O₁₉, and then to higher temperature with the increasing content of BaMg₆Ti₆O₁₉. The frequency of the low transverse-optic model of vibration can be expressed as

$$\omega^2 = (BT - K_L + K_S)/m = \frac{B}{m} \left(T - \frac{K_L - K_S}{B} \right) \quad (1)$$

Where B is the anharmonic coefficient, *T* is temperature, *K_L* is long-range electrostatic force constant, and *K_S* is the short-range harmonic restoring force constant, *m* is the mass of the ion, and $(K_L - K_S)/B$ here is just the curie temperature *T_c* [13]. The grain size of the samples decreases and the internal stress (both long-range force and short-range force) increases when BaMg₆Ti₆O₁₉ was introduced to BST. It is known that the increase of short-range repulsive *F_S* is quite larger than the increase of long-range

electrostatic force *F_L* when adjacent ion-distance *r* decreases. Therefore, from the equation $T_C = (K_L - K_S)/B$, it is clear that the *T_C* of Ba_{0.5}Sr_{0.5}TiO₃-BaMg₆Ti₆O₁₉ ceramic samples is shifted to lower temperature with the increase of BaMg₆Ti₆O₁₉ content. In addition, the substitution of Mg²⁺ together with the decrease of grain size, bring on the downward shift of *T_C* points of the samples [11]. However, *T_C* is observed to shift slightly to higher temperature (still below the *T_C* of pure Ba_{0.5}Sr_{0.5}TiO₃) with increasing BaMg₆Ti₆O₁₉ content from 40 wt% to 60 wt%. The amount of BaMg₆Ti₆O₁₉ exceeds over the solubility limit of Mg²⁺ ions in pure barium strontium titanate, the extra addition of BaMg₆Ti₆O₁₉ does not further affect the *T_C*. So the increment of *T_C* results from the existence of poor grain sizes and the decreases of internal stress [14].

The dc electric field dependence of the dielectric constant at 10 kHz and room temperature of the samples are shown in Fig. 5. Table 1 presents their dielectric properties and calculates tunability which is defined as

$$Tunability(\%) = \frac{\epsilon_{r(0)} - \epsilon_{r(E)}}{\epsilon_{r(0)}} \times 100 \quad (2)$$

Where $\epsilon_{r(0)}$ is the zero-field dielectric constant and $\epsilon_{r(E)}$ is the dielectric constant that results from an applied electric field of *E*. The dielectric constant of pure Ba_{0.5}Sr_{0.5}TiO₃ is 2035 at the temperature of about 20°C. It can be seen that the tunability decreases from 21.2% to

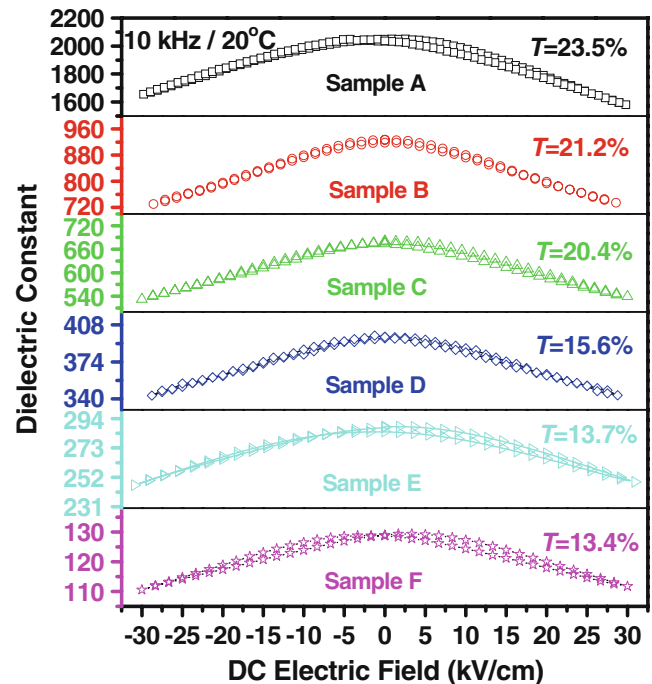


Fig. 5 ϵ_r -*E* characteristics of pure Ba_{0.5}Sr_{0.5}TiO₃ and BaMg₆Ti₆O₁₉-doped Ba_{0.5}Sr_{0.5}TiO₃ composite ceramic samples

Table 1 Dielectric and microwave properties of pure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and the composite ceramic samples

Ceramic samples	Dielectric properties (at 10 kHz)			Microwave properties			
	T_C (°C)	At about 20°C		Tunability 30 kV/cm	Resonant frequency (MHz)	ϵ_r (at resonant frequency)	Q value ($1/\tan\delta$)
		ϵ_r	$\tan\delta$				
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST50)	-25.5	2035	0.0010	23.5%	1130	1611	424 (0.0024)
BST50-10 wt% $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$	-49.8	930	0.0017	21.2%	1398	907	330 (0.0030)
BST50-20 wt% $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$	-43.0	680	0.0020	20.4%	1579	665	367 (0.0027)
BST50-40 wt% $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$	-32.1	396	0.0021	15.6%	1810	351	116 (0.0086)
BST50-50 wt% $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$	-30.5	288	0.0022	13.7%	2575	245	91 (0.0109)
BST50-60 wt% $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$	-28.5	129	0.0022	13.4%	4206	84	78 (0.0126)

13.4% with the content of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ increasing from 10 wt% to 60 wt%, the tunability of pure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, which is ferroelectric phase at room temperature, is about 23.5% at an applied electric field of 30 kV/cm. It is well known that the change of dielectric constant under applied electric field is associated with the anharmonic interactions of Ti^{4+} ions for paraelectric BaTiO_3 -based material system. In our present work, the dielectric constant of composite ceramics is available reduced due to the $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ which was introduced to BST material system. However, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ - $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composite ceramics still keep relatively high tunability than previously reported data [15]. The experiments of BST-based composites with Mg_2SiO_4 and MgO have been reported to obtain low dielectric constant downward to 126.82 and 116.86, respectively [13, 16, 17]. Nevertheless, the tunability was reduced to less than 10%. The main reason of the high tunability under dc electric field of the composites is due to the non-linearity of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ [15, 18]. Meanwhile, the existence of fine-grained microstructures of the composites together with the continuously connected chains of Ti-O-Ti bonds and the interactions of Ti^{4+} ions of $\text{BaSr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ - $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composites are not weakened, all of which can also contribute to the high tunability.

The microwave properties are very crucial to realize the microwave tunable device applications for this composite ceramics. Table 1 presents the microwave properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ - $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composite ceramics which were measured using the Hakki–Coleman dielectric resonator method. It is obviously that the dielectric constant of the composite ceramics is slightly decreased at microwave frequencies compared with those at low frequencies (10 kHz). Compared with pure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (the Q value is 424, terms as sample A), the Q values of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ - $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composites are slightly decreased at microwave frequencies. For the 10 wt% and 20 wt% $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ - $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composites (samples B and C), the Q values

are 330 and 367 respectively. These appropriate microwave properties implies $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ - $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composites are useful for wireless communication system components [19]. However, the Q value decreases obviously under microwave frequencies with increasing content of $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ from 40 wt% to 60 wt% (samples D, E, and F). This is because the extrinsic loss dominates the loss mechanism. With the results above we conclude that it is an effective way to optimize the Q value by proper addition of microwave dielectric materials into barium strontium titanate ceramics.

4 Conclusions

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composite ceramics are fabricated to form a two-phase structure, No obvious chemical reactions were detected between $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ during the composite ceramics preparation process. Compared with pure $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ - $\text{BaMg}_6\text{Ti}_6\text{O}_{19}$ composite ceramics exhibit properties of low dielectric constant and high tunability. The dielectric constant of the composites can be effectively tailored from 2035 to 129, the dielectric loss still keeps around 0.002 and the tunability is 21.2% under dc electric field of 30 kV/cm. These composites with good impedance characteristic and high tunability and Q value (up to 330), could be attractive materials for potential microwave tunable applications.

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