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Property optimization of $Ba_{0.4}Sr_{0.6}TiO_3$–$BaMoO_4$ composite ceramics for tunable microwave applications

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Abstract

$(1-x)Ba_{0.4}Sr_{0.6}TiO_3$–$xBaMoO_4$ ceramics with x = 5, 10, 20, 30, 40 and 60 wt% were prepared by traditional solid-state reaction method. Two crystalline phases, a cubic perovskite structure $Ba_{0.4}Sr_{0.6}TiO_3$ (BST) and a tetragonal scheelite structure $BaMoO_4$ (BM) were obtained by XRD analysis. The microwave dielectric properties of $Ba_{0.4}Sr_{0.6}TiO_3$–$BaMoO_4$ composite ceramics were investigated systematically. The results show that the composite ceramics exhibited promising microwave properties. The dielectric constant can be adjusted in the range from 900 to 78, while maintaining relatively high tunability from 27.3% to 12.8% under a direct current electric field of 60 kV/cm and Q values from 619 to 67 in the gigahertz frequency region.

Keywords: B. Composites; Tunability; Microwave property

1. Introduction

Dielectric tunable materials have been widely investigated for applications in microwave tunable devices, such as tunable oscillators, phase shifters and embedded passive capacitors. For practical applications, materials should have moderate dielectric constant ($30 < \varepsilon' < 1500$), high dielectric tunability ($T \geq 10\%$), low loss tangent ($\tan\delta < 0.01$) in the frequency range of practical application [1,2]. $Ba_xSr_{1-x}TiO_3$(BST) is a promising candidate for the applications in microwave tunable devices, owing to its high dielectric tunability and relatively low loss [3]. However, its application has been hindered by its high dielectric constant [4]. The composite materials exhibiting relatively high tunability in combination with reduced dielectric constant, reasonable loss level and good temperature stability have been experimentally obtained. Recent studies have indicated that dielectric constant values of ferroelectric materials can be readily reduced by introducing various non-ferroelectric phase (such as MgO [5], $MgAl_2O_4$ [6], $Mg_2B_2O_3$ [7], and Mg_2TiO_4 [8]) into ferroelectric materials meanwhile maintain acceptable dielectric tunability. The main goal of this work was to search a new kind of composites with high tunability, low dielectric constant and high Q value.

In this paper, the $BaMoO_4$ (BM) microwave dielectric material [9] with low dielectric constant ($\varepsilon' = 9.3$) and high quality factor values ($Q \times f = 37\,200$ GHz) introduced to form composites with $Ba_{0.4}Sr_{0.6}TiO_3$ (BST40) ferroelectric ceramics was investigated. It is possible that $Ba_{0.4}Sr_{0.6}TiO_3$–$BaMoO_4$ composite ceramics will have good dielectric behavior to satisfy the requirements of tunable devices. As we expected, the dielectric properties of $Ba_{0.4}Sr_{0.6}TiO_3$ were greatly improved by adding $BaMoO_4$.

2. Experimental procedure

The ceramics based on $Ba_{0.4}Sr_{0.6}TiO_3$–$BaMoO_4$ specimens were prepared through the conventional solid-state reaction. High-purity $BaTiO_3$ (99.9%), $SrTiO_3$ (99.9%), $BaCO_3$ (99.9%) and MoO_3 (99.99%) were used as starting materials for the synthesis of $Ba_{0.4}Sr_{0.6}TiO_3$ powders at 1100 °C and $BaMoO_4$ powders at 700 °C, respectively. Then, the obtained powders were mixed according to the stoichiometric ratio $(1-x)Ba_{0.4}Sr_{0.6}TiO_3$ (BST40)–$xBaMoO_4$(BM) (x = 5%, 10%, 20%, 30%, 40%, and 60 wt%) and milled in polypropylene bottles with zirconia grinding media for 24 h. The dried powders, mixed with 8 wt% polyvinyl alcohol (PVA),

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were pressed into pellets. Samples for low frequency dielectric measurement are 10 mm in diameter and 1.2 mm in thickness, while those for microwave frequency measurements have dimensions of 10/5 mm, 12/6 mm, 15/7 mm and 17/8 mm in diameter/thickness, respectively. The green pellets were burned out at 550 °C for 6 h in air to remove the solvent as well as the binder, and then sintered at 1350 °C for 4 h in air.

X-ray diffraction (XRD) (D8 Advanced, Bruker, Germany) was used to identify the phase structure. Scanning electron microscopy (JSM EMP-800, JEOL, Tokyo, Japan) was used to characterize the microstructure. The samples were polished to 1 and 0.15 thicknesses and gold electrodes were sputtered on both sides of the samples for dielectric property measurements. Temperature dependences of dielectric constant and loss at 10 kHz were measured in the temperature range from −140 °C to 140 °C using an E4980A LCR meter (Agilent, Palo Alto, CA). The dielectric constant as a function of electric field was tested using a Keithley 2410 (Cleveland, OH) high-voltage source and a TH2816A LCR (Tonghui Electronics, Changzhou, China) analyzer. Dielectric properties at microwave frequencies were obtained using the Hakki–Coleman dielectric resonator method with a network analyzer (HP8753E, Agilent) combining a resonating cavity. The values of ε' and Q were calculated from the resonant frequency and the geometric dimensions of the samples.

3. Results and discussion

XRD patterns of the BST40–xBM (x = 0, 5, 10, 20, 30, 40, 60, and 100 wt%) composite ceramics are shown in Fig. 1. Only cubic perovskite structure BST and a scheelite structure BM were detected. Partial reaction between BaMoO4 and BST occurred in the sintering process according to the Curie temperature (T_c) upwards as presented in Fig. 3. BST and BM corresponding to formation of complex solid solutions by incorporation of foreign ions in each phases. The formation of the BST and $BaMoO_4$ can be described by the following reaction of Eq. (1):

$$Ba_{0.4}Sr_{0.6}TiO_3 + BaMoO_4 = Ba_{0.4+z}Sr_{0.6-z}TiO_3 + Ba_{1-z}Sr_zMoO_4 \quad (1)$$

Both $BaMoO_4$ and $SrMoO_4$ are belong to the space group I41/a(88), as a result, only tetragonal scheelite structure $BaMoO_4$ ($SrMoO_4$ or $Ba_{1-z}Sr_zMoO_4$) can be detected in the XRD patterns as shown in Fig. 1.

$BaMoO_4$ ($SrMoO_4$ or $Ba_{1-z}Sr_zMoO_4$) phase is gradually observed at grain boundaries of the BST matrix above the solubility limit, which is clearly shown in the back scattered electron images of the ceramic samples (Fig. 2). The gray grains are BST ($Ba_{0.4+z}Sr_{0.6-z}TiO_3$) phase, and the homologous white grains are $BaMoO_4$ ($SrMoO_4$ or $Ba_{1-z}Sr_zMoO_4$) phase. All samples have dense and homogeneous microstructures, suggesting the composite ceramics have been well sintered. Obviously, the connectivity levels of the BST phase decreased gradually with increasing of $BaMoO_4$ content, which is the major factor for the decrease of its tenability at higher $BaMoO_4$ concentration.

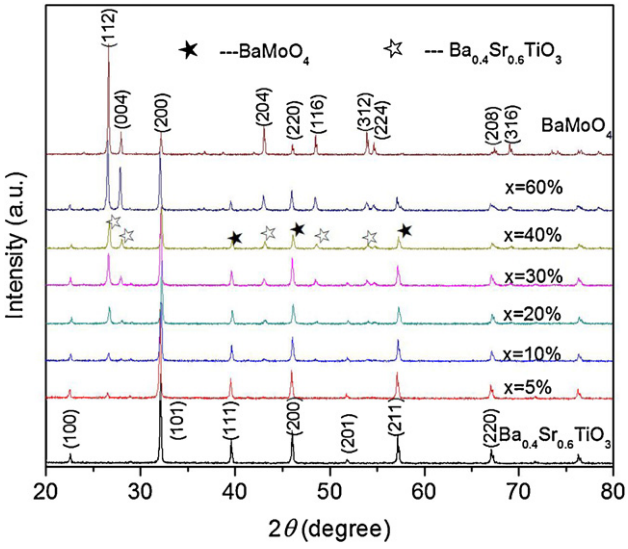

Fig. 1. X-ray diffraction patterns of $(1-x)$ $Ba_{0.4}Sr_{0.6}TiO_3$–$x$$BaMoO_4$ composite ceramics.

Fig. 3 shows the dielectric constant and loss versus temperature (T) measured at 10 kHz. The results show that ferroelectric–paraelectric phase transition of samples is strongly suppressed and broadened. Compared with pure $Ba_{0.4}Sr_{0.6}TiO_3$, the Curie temperature (T_c) is increased due to the Sr^{2+} substitution by Ba^{2+} in the BST lattice. With increasing of $BaMoO_4$ content from 5 to 60 wt% (5.53–62.5 vol%), the T_c shifts from −61.9 °C to −35.6 °C. The change of T_c can be explained by Ba/Sr ratio raise which is originate from the inter-diffusion as discussed above.

The dielectric constant of BST40–xBM is gradually decreased with increasing of the x value (Fig. 3 and Fig. 4). The model of BST40–BM binary composite structure, consists of a ferroelectric phase (BST) and a dielectric phase (BM) with a low dielectric constant and low loss. Based on the Bruggeman Effective Medium theory and nonlinearity model [10,11], dielectric constant as a function of volume fraction of dielectric inclusion is approximately calculated in the case of weak DC electric fields and small volume fractions of dielectrics, as follows:

$$\varepsilon_{eff}(q) = \varepsilon_f(1 - 1.5q) \quad (2)$$

where ε_{eff} and ε_f are the dielectric constant of composites and ferroelectrics, respectively, and q is the volume fraction of dielectric [12,13]. The experimental data of dielectric constant as a function of volume fraction of $BaMoO_4$ measured at 10 kHz and 20 °C are fitted using Eq. (2), as shown in Fig. 4. The q value is up to 0.625 (62.5 vol% or 60 wt%). The Sr^{2+} substitution by Ba^{2+} in the BST may be the reason for the slightly variance between theoretical data and the experimental data.

Fig. 5 shows dielectric constant of BST–BM ceramics under the DC electric field of 60 kV/cm (at 10 kHz and 20 °C). The tunability even slightly increases from 26.5% to 27.3% with

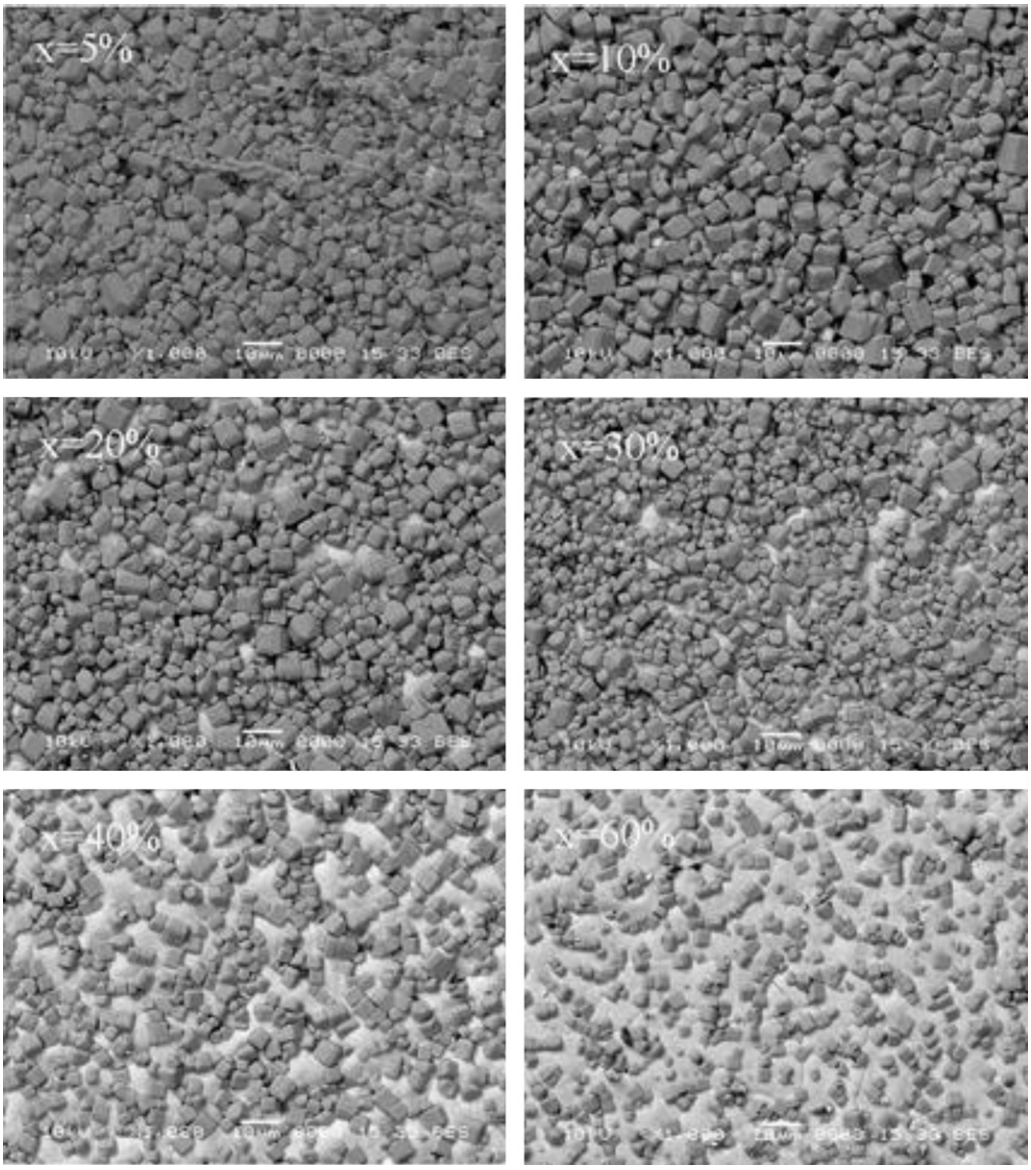

Fig. 2. Backscattered images of $(1-x)$ $Ba_{0.4}Sr_{0.6}TiO_3$–$x$$BaMoO_4$ composite ceramics samples.

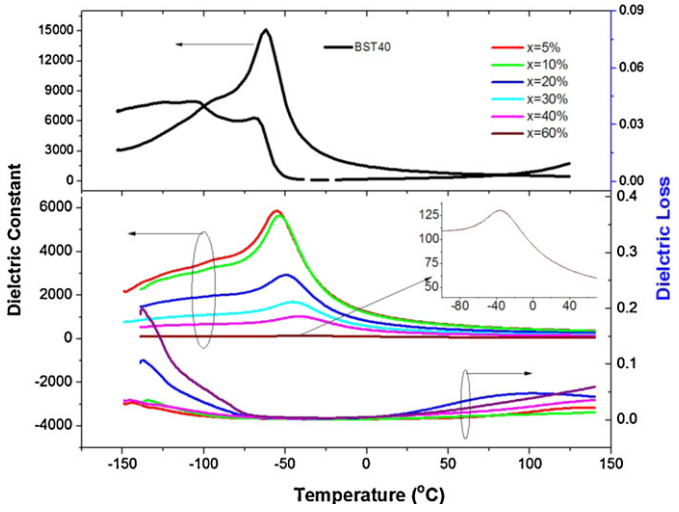

Fig. 3. Temperature dependences of dielectric constant and dielectric loss of the $(1-x)Ba_{0.4}Sr_{0.6}TiO_3$–$x$$BaMoO_4$ composite ceramics.

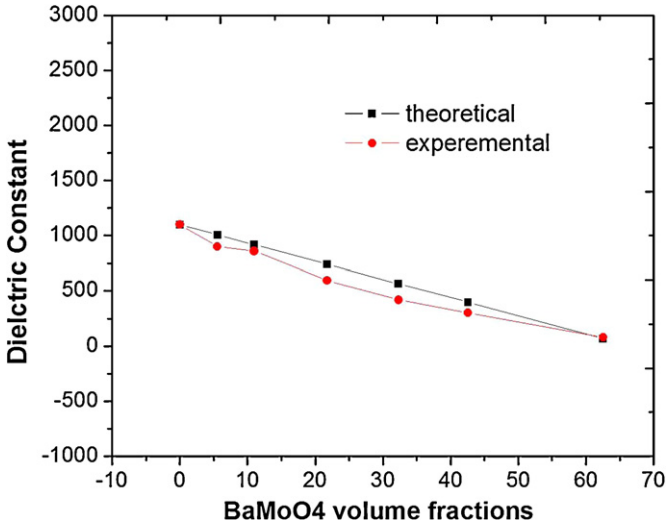

Fig. 4. Experimental dielectric constant of $BaMoO_4$ volume fraction and the fitted line by Eq. (1).

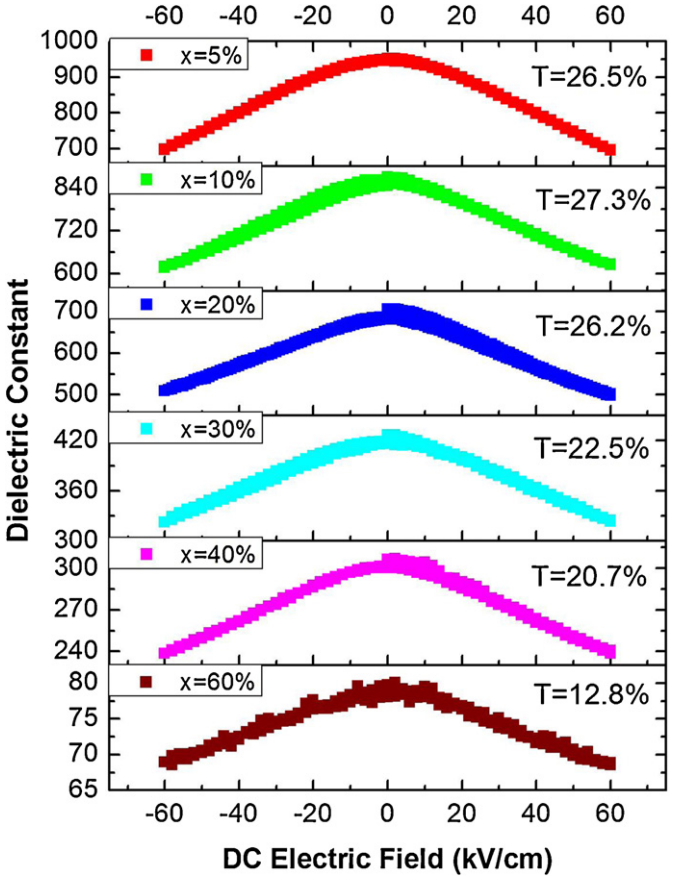

Fig. 5. DC electric-field-dependent dielectric constant for $(1-x)Ba_{0.4}Sr_{0.6}TiO_3$–$x$BaMoO4 composite ceramics at 10 kHz.

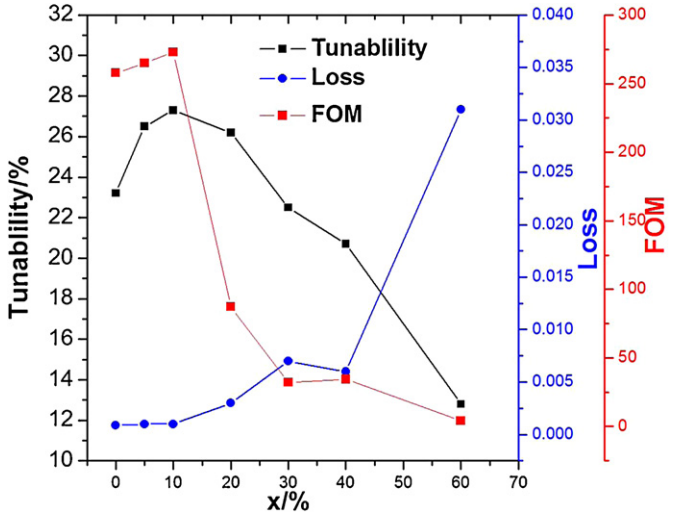

Fig. 6. Tunability, dielectric loss, and the figure of merit (FOM) of BST as a function of $BaMoO_4$ content at 10 kHz.

increasing of $BaMoO_4$ content from 5 to 10 wt%. As mentioned above, $BaMoO_4$ addition can influence the composition and microstructure of the composites, which in turn affect the dielectric parameters of this material. The increase of T_c in the composite ceramics result in the slightly increase of tunability. However, with increasing volume fraction of $BaMoO_4$, the ferroelectric phase was diluted and the connectivity levels of the BST phase was decreased obviously [12,14]. The tunability decreases from 27.3% to 12.8% with the increase of $BaMoO_4$ content from 10 to 60%.

The figure of merit (FOM) defined as FOM = tunability/tanδ is frequently used to characterize the quality of tunable materials, which is a balanced combination of tunability and dielectric loss [15]. Fig. 6 shows tunability, dielectric loss tangent and the figure of merit of $Ba_{0.4}Sr_{0.6}TiO_3$ as a function of $BaMoO_4$ content at 10 kHz and 60 kV/cm. The tunability and dielectric loss for the composite ceramics are 27.3% and 0.001 at the $BaMoO_4$ content of 10%, respectively, and the FOM value reaches a maximum value of 273. Such good properties are attractive for applications in tunable microwave electronics.

Microwave dielectric properties of the composite ceramics measured at room temperature are listed in Table 1. It can be found that the Q values (from 935 to 67) gradually decreased with the increasing $BaMoO_4$ content from 0 to 60 wt%. The Q value of composite ceramics is much lower than that of pure $Ba_{0.4}Sr_{0.6}TiO_3$, and decreases with the increase of $BaMoO_4$, which is ascribed to the deterioration on A-site or B-site ordering of ABO_3 perovskite structure by adding $BaMoO_4$ .The other reason is related to polar nano-regions (PNRs) and the dielectric relaxation in gigahertz frequencies, as in $BaTiO_3$-based ceramics reported by Nakayama and Teranishi [16,17]. At microwave frequencies, lower loss tangent is needed to provide a lower insertion loss in the devices for its applications. The composite ceramic can maintain a relatively high Q from 925 to 337 in the gigahertz frequency region when the $BaMoO_4$ content from 0 to 30 wt%. So $Ba_{0.4}Sr_{0.6}TiO_3$–$BaMoO_4$ composite ceramic is a promising candidate for electrically tunable microwave device applications.

Table 1
Dielectric properties of $(1-x)Ba_{0.4}Sr_{0.6}TiO_3$–$x$BaMoO$_4$ composite ceramics.

Ceramic samples	Dielectric properties (at 10 kHz)				Microwave properties		
	T_c (°C)	ε' (20 °C)	tanδ (20 °C)	Tunability (20 °C) 60 kV/cm	Frequency (MHz)	ε'	Q
$Ba_{0.4}Sr_{0.6}TiO_3$	−61.9	1098	0.0009	23.2%	1409	1021	935
BST40–5%BM	−55.4	900	0.001	26.5%	998	809	619
BST40–10%BM	−53.5	858	0.001	27.3%	1020	720	440
BST40–20%BM	−49.1	593	0.003	26.2%	1180	529	346
BST40–30%BM	−45.3	420	0.007	22.5%	1380	391	337
BST40–40%BM	−40.7	302	0.006	20.7%	1760	229	154
BST40–60%BM	−35.6	78	0.031	12.8%	2750	76	67

4. Conclusions

The $Ba_{0.4}Sr_{0.6}TiO_3$–$BaMoO_4$ composite ceramics were prepared by conventional solid-state reactions. Only cubic perovskite structure BST and a scheelite structure BM were detected. The T_c peaks of the composite ceramics were suppressed, broadened and shifted to higher temperatures with the increasing $BaMoO_4$ content. The tunability and dielectric loss for the composite ceramics are 27.3% and 0.001 when $BaMoO_4$ content was 10%, respectively, and the FOM value reaches a maximum value of 273. At $x \leq 30\%$, the $(1-x)Ba_{0.4}Sr_{0.6}TiO_3$–$xBaMoO_4$ composite ceramics has an acceptable level of Q value ($\geq$337), a high tunability ($\geq$22.5%, 60 kV/cm) and a moderate value of dielectric constant ($\geq$420). So it is a promising way to prepare $Ba_{0.4}Sr_{0.6}TiO_3$-based dielectric tunable materials with excellent microwave dielectric performance by adding $BaMoO_4$.

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