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Preparation and microwave properties of Mg doped barium strontium titanate (BSTO) ceramics sintered from Sol–Gel-derived powders

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Abstract Studies on the Preparation and microwave properties of Mg doped barium strontium titanate (BSTO) ceramics sintered from Sol–Gel-derived powders. The crystal structure and microstructure of $Ba_{0.60}Sr_{0.40}TiO_3$ ceramics doped with Mg has been investigated. The microwave complex permittivity of BST ceramics doped with Mg powders is investigated in 100 MHz–6 GHz ranges by coaxial-transmission technique and the calculation of the equivalent medium theory. Experimental results showed that the typical cubic phase structure and the diffraction peaks of secondary phase that MgO phase become stronger with increasing Mg^{2+} content in the XRD pattern of the Mg doped BST ceramic sintered at 1250 °C. The real part of the microwave complex permittivity of BSTM30 ceramic powders is excellent described by results of calculation of Bruggeman theory in wide powder content.

Keyword $Ba_{0.60}Sr_{0.40}TiO_3$ · Microwave properties · Mg doped · Sol–Gel method

1 Introduction

Ferroelectric barium strontium titanate (BSTO) ceramics have shown tunable dielectric properties and low dielectric losses at room temperature and microwave frequencies, which makes them attractive for applications in frequency agile microwave devices [1, 2]. The higher insertion loss and high permittivity of barium strontium titanate (BSTO) has restricted its application in phased array antennas [3, 4]. It has been reported that Mg doping or MgO addition could be used in BSTO ceramics and thin films to suppress the permittivity and losses [5, 6]. L.C.Sengupta and S.Sengupta [7] reported the effects of Mg contents on the permittivity, tunability (at a dc field of 20 kv/cm) and loss tangent (at 10 GHz) of the BSTO ceramics with various compositions. But no detailed results on the microwave complex permittivity of BST ceramics doped with Mg are investigated in 1 MHz–10 GHz ranges. Methods for complex permittivity determination at microwave frequencies can be divided into two main categories: resonant techniques using resonant structures of different kind and non-resonant techniques that typically utilize transmission/reflection measurements. Resonant techniques provide higher precision and better resolution for loss measurements, but they are usually limited to a single frequency. Transmission/reflection methods allow broadband measurements over a certain frequency range, but with limited resolution for losses.

In this article, we report our experimental results that the real part of the relative microwave permittivity of BSTM30 ceramics powders from sol–gel-derived gel powders is investigated in 100 MHz–6 GHz ranges by coaxial-transmission/reflection technique and the calculation of the Bruggeman equivalent medium theory [8, 9].

2 Experimental procedure

The precursors used for preparing Ba–Sr–Ti–Mg–O gels were barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$),

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Table 1 The composition, sintering temperature, and relative density of BSTM samples.

Sample	Sintering temperature(°C)	Mg^{2+} content	relative density (%)
	Sintering time (2 H)	X(mol)	
BSTM03	1300 °C	0.03	96.6
BSTM05	1300 °C	0.05	96.7
BSTM10	1300 °C	0.10	97.8
BSTM20	1300 °C	0.20	94.1
BSTM30	1200 °C	0.30	98.3
BSTM40	1200 °C	0.40	98.3

tetra-n-butyl titanate ($C_{16}H_{36}O_4$ Ti) ,magnesium nitrate ($Mg(NO_3)_2$) and citric acid. The atomic ratio of Ba:Sr:Ti=0.60:0.40:1.0 is used. For composition with Mg additive, Their atomic ratios were (Ba,Sr,Ti):(Mg)=97:3(BSTM3), 95:5(BSTM5), 90:10(BSTM10), 80:20(BSTM20), 70:30 (BSTM30)and 60:40(BSTM40). The barium nitrate, strontium nitrate and magnesium nitrate ($Mg(NO_3)_2$) powders were at first dissolved in appropriate amounts of H_2O, citrate acid stirred at 90 °C until the solution become transparent and cooled it down to room temperature. The tetra-*n*-butyl titanate solution was added in an appropriate amount of citric acid solution by stirring at 50 to 80 °C. After the above solution turned clear, the (Ba,Sr,Ti,Mg) solution was prepared by mixing titanium solution and barium and strontium solution and magnesium solution stoichiometrically. The resulting (Ba,Sr,Ti,Mg) solution formed transparent sols at 50 to 60 °C. The gels were formed at 80 to 90 °C. Thermal decomposition of the gels was conducted at a heating rate of 1 K/min in static air, at 600 to 800 °C, in an Al_2O_3 boat, and cooled it to room temperature. Small BST crystallites were formed in these firing processes. The fired gels (800 °C) were then crushed and ground by ball mill with ethanol for 24 h to obtain fine Mg doped BST ceramic powders. The fine Mg doped BST ceramic powders were pressed into disc-shaped pellets with a diameter of 10 mm. The pellets were subsequently sintered in air for 2 h at various temperatures. The surfaces of these Mg doped BST ceramics samples were polished before the Ag paste electrodes were formed at 600 °C.

The bulk density of the Mg doped BST ceramics pellet was measured with Archimedes method, using distilled water as liquid medium. Powder X-ray diffraction (XRD; CuK_α) measurements were carried out to examine the crystallization and the structural development of Mg doped BST ceramics samples. An X-ray powder diffractometer (Model BRUKER Advanced, Bruker axs co.,Germany) was used with CuK_α radiation at 40 KV and 40 mA and scan rates of 4^0/min from 10 to 7 ° (2θ). Scanning electron microscopy (SEM, Model JSM-5510LV, Japan) was used to examine the microstructure of Mg doped BST ceramics samples. The BSTM30 ceramics pellets at sintering temperature 1200 °C were crushed, milled and sieved through 400-mesh screen and the BSTM30 ceramics powders were obtained. The BSTM30 ceramics powders–paraffin wax composites with various percent of BSTM30 ceramics powders by volume were prepared. The microwave complex permittivity of BSTM30 ceramics powders is investigated in 100 MHz–6 GHz ranges by coaxial-transmission technique using the Agilent8753 network analyzer at room temperature (22 °C). For this, toroidal-shaped samples of 3.0 mm inner diameter and 7.0 mm outer diameter were tightly inserted into a standard coaxial line having air length, diameter of central conductor, and inner diameter of the outer conductor 20 cm, 3.0 and 7.0 mm, respectively. Samples of lengths approximately equal to one quarter of the guide wavelength were chosen for accurate measurements. The sample length varied from 2 to 4 mm in the whole measuring frequency range. A mixture equation is used to calculate the real part of the relative microwave permittivity of the BST ceramics doped with Mg powders. The validity of five known mixture equations is examined. All the electrical measurements were performed at a relative humidity of about 60%.

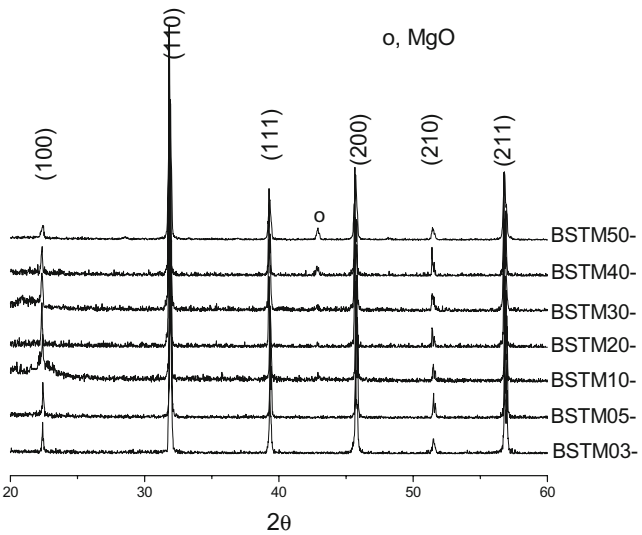

Fig. 1 XRD patterns of BSTM ceramics with different stoichiometry sintered at 1250 °C

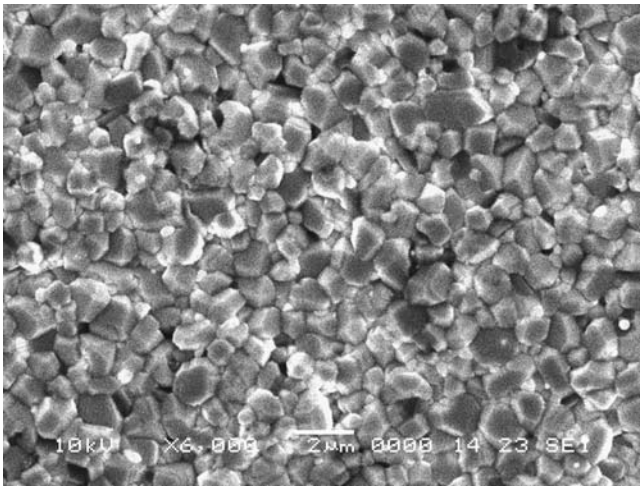

Fig. 2 SEM image of the BSTM30 ceramic samples sintering at 1200 °C in air for 2 h

3 Results and discussion

Table 1 shows the composition, sintered temperature, and relative density of all samples. When the Mg^{2+} content is <10 mol% and >20 mol%. The density of the samples is above 95% of the theoretical value.

The XRD pattern of BSTM sintered at 1250 °C shows that the typical cubic phase structure in the Fig. 1. When the Mg^{2+} content is ≥10 mol%, the diffraction peaks of secondary phase MgO appear and become stronger with increasing Mg^{2+} content.

Figure 2 gives the SEM pictures of the BSTM30 ceramics samples sintered in air for 2 h at 1200 °C. The BSTM30 sample can be well sintered at 1200 °C. As the Mg^{2+} content increase, some of them may precipitate out as MgO discrete particles as indicated in the XRD result, which hinder the abnormal grain growth and much smaller sized BST microstructures are obtained in the Mg doped BST ceramics samples in the SEM results. Because the MgO phases and the BST phase are homogeneously mixed, the Mg doped BST ceramic samples when the Mg content > 20 mol% can be sintered well at much lower temperature than pure BST ceramic [4].

The BSTM30 ceramic powders–paraffin wax composites with various percent of BSTM30 ceramic powders by volume were prepared. Figure 3 show the frequency dependence of the real part of the complex permittivity for the BSTM30 ceramic powders–paraffin wax composites. It can be observed that the real part of the microwave complex permittivity of composites decreases monotonously with frequency for all the samples. However, this decrease is more rapid at low frequency than at high frequency.

Five mixture equations are used to calculate the permittivity of the BSTM30 ceramic powders from the permittivity of the samples. Five mixture equations are the following:

Logarithm mixture equation :

$$ln\,\varepsilon_{eff} = f\,ln\,\varepsilon_t + (1-f)\,ln\,\varepsilon_m, \tag{1}$$

Lichtenecker mixture equation :

$$(\varepsilon_{eff}) = f(\varepsilon_t) + (1-f)(\varepsilon_m), \tag{2}$$

Looyenga mixture equation :

$$(\varepsilon_{eff})^{\frac{1}{3}} = f(\varepsilon_t)^{\frac{1}{3}} + (1-f)(\varepsilon_m)^{\frac{1}{3}} \tag{3}$$

Maxwell – Garnett mixture equation :

$$\frac{\varepsilon_{eff}-\varepsilon_m}{\varepsilon_{eff}+2\varepsilon_m} = f\,\frac{\varepsilon_t-\varepsilon_m}{\varepsilon_t+2\varepsilon_m}, \tag{4}$$

Bruggeman mixture equation :

$$f\,\frac{\varepsilon_t-\varepsilon_{eff}}{\varepsilon_t+2\varepsilon_{eff}} + (1-f)\,\frac{\varepsilon_m-\varepsilon_{eff}}{\varepsilon_m+2\varepsilon_{eff}} = 0 \tag{5}$$

Where f is fractional volume, ε_{eff} is the complex permittivity of the BSTM30 powders–paraffin wax composites, ε_t is the complex permittivity of BSTM30 powders, and ε_m is the complex permittivity of wax. The real part of

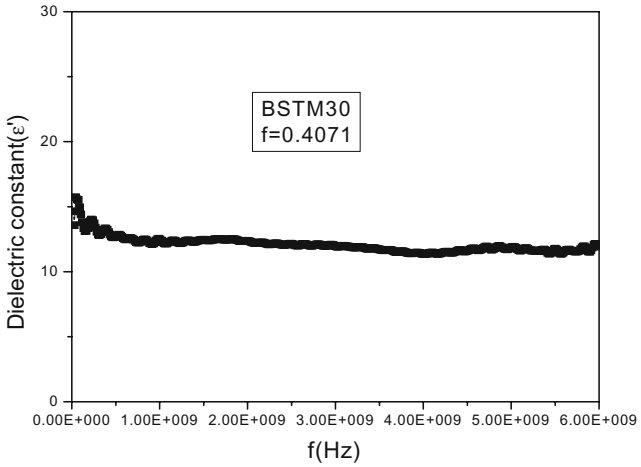

Fig. 3 Frequency dependence of the real part of the complex permittivity for BSTM30 ceramic powders–paraffin wax composites

complex permittivity of the BSTM30 ceramic powders by results of calculation of Maxwell-Garnett mixture equation is negative and the Maxwell-Garnett mixture equation is not suitable. Figure 4 shows that the Bruggeman mixture equations can describe the real part of microwave permittivity of the BSTM30 ceramic powders over the wide

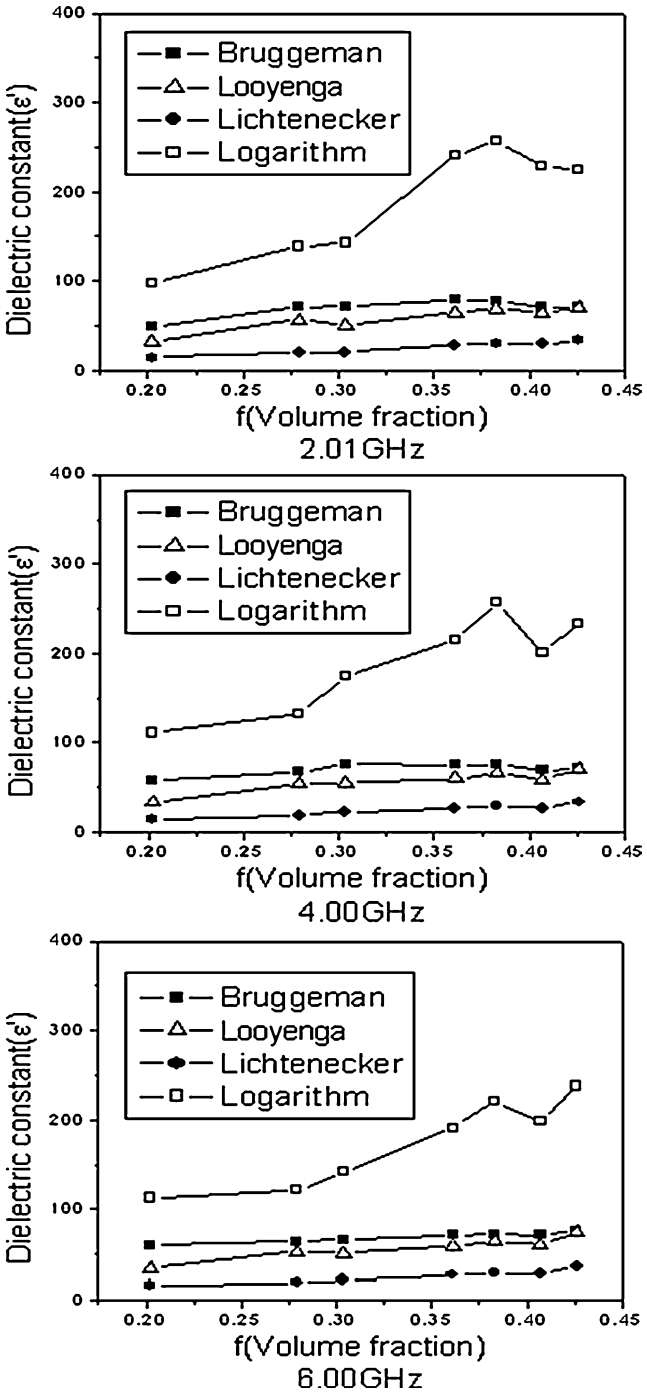

Fig. 4 The real part of the complex permittivity ($|\varepsilon_t|$) for BSTM30 ceramic powders with different fractional volume at different frequencies are calculated by four mixture equations

Table 2 Frequency dependence of the real part of the complex permittivity ($|\varepsilon_t|$) for BSTM30 ceramic powders sintering at 1200 °C, for 2 h (Bruggeman mixture equation).

f (GHz)	$\lvert\varepsilon_t\rvert(\pm\Delta)\lvert\varepsilon_t\rvert/\lvert\varepsilon_t$
0.72	77.98, ±6%
1.01	80.03, ±8%
1.26	81.27, ±10%
2.01	77.97, ±6%
2.46	76.31, ±5%
3.00	73.27, ±4%
3.45	73.04, ±4%
4.00	73.59, ±3%
4.50	75.58, ±3%
5.00	75.09, ±5%
5.50	73.69, ±3%
6.00	72.93, ±3%

$|\varepsilon_t|$: The real part of the complex permittivity of BSTM30 ceramic powders; f: Frequency

particle concentration range, and that the Lichtenecker, Logarithm, and Looyenga mixture equations are not suitable for characterizing the BSTM30 ceramic powders over a wide particle concentration range at microwave frequencies. The real part of the microwave complex permittivity of BSTM30 ceramic powders in the 0.72–6 GHz at room temperature (22 °C) is shown in Table 2. The real part of the microwave complex permittivity of BSTM30 ceramic powders deceases with frequency increasing, and is excellent described by results of calculation of Bruggeman mixture equations in wide powder content in the Table 2 at high microwave frequencies (f :2–6 GHz, $\Delta|\varepsilon_t|/|\varepsilon_t| \leq 5\%$).

4 Conclusions

The effect of Mg^{2+} content on the sintered BSTM ceramics is correlated with their densification, grain growth behavior and microwave properties. The Mg doped BST ceramics samples showed the typical cubic phase structure of BST and secondary phase MgO. The microwave complex permittivity of BSTM30 ceramics powders deceases with frequency increasing. The real part of the microwave complex permittivity of composites decreases monotonously with frequency for all the samples. However, this decrease is more rapid at low frequency than at high frequency. The real part of the microwave complex permittivity of BSTM30 ceramic powders is excellent described by results of calculation of Bruggeman theory in wide powder content.

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