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Influence of low concentration $MgCo_2(VO_4)_2$ addition on microwave dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics

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Abstract

$Ba_{0.6}Sr_{0.4}TiO_{3-x}$ $MgCo_2(VO_4)_2$ ceramics with $x = 0$, 0.5, 1.0, 2.0, and 5.0 wt% was fabricated via conventional solid-state reaction process. The effects of such additives on the structure, dielectric and tunability properties were systemically investigated. A small number of secondary phase identified as $Ba_3(VO_4)_2$ appeared in $Ba_{0.6}Sr_{0.4}TiO_{3-x}$ $MgCo_2(VO_4)_2$ ceramics when x is more than 5.0 wt%. With increasing of $MgCo_2(VO_4)_2$ content, the peak values of permittivity gradually decreased and shifted to low temperature. The $Ba_{0.60}Sr_{0.40}TiO_3$ added with 0.5 wt% $MgCo_2(VO_4)_2$ possesses a dielectric constant of 2763, Q value of 267 at ~1 GHz and tunability of 35.9% under dc electric field of 30 kV/cm at 10 kHz.

Keywords: D. $BaTiO_3$ and titanates; Structure; Microwave dielectric properties

1. Introduction

In recent years, there is a rapidly growing demand for electrically tunable microwave devices, such as voltage tunable phase shifters, oscillators, and filters, for advanced radar and communication devices [1–5]. Many efforts have been focused on the ferroelectric $Ba_xSr_{1-x}TiO_3$ (BST) systems. BST ceramics are considered to be one of the most promising candidates for microwave elements because of their high dielectric nonlinearity and adjustable dielectric properties by tuning ratio of Sr and Ba. However, the relatively large dielectric insertion loss at high frequency region restricts its practical applications. Both low loss and large tunability techniques have been adopted to modify the microwave dielectric properties of this ferroelectric ceramics by introducing small content of dopants. This approach is found to dramatically alter the properties of ferroelectric materials.

A recent study [6] showed that $Mg_{3-x}Co_x(VO_4)_2$ ceramics with $x = 2$, prepared by a conventional solid-state reaction process, had a high $Q \times f$ value at low sintering temperature (below 950 °C) with optimum microwave dielectric properties. These properties offer us a good opportunity to use $MgCo_2(VO_4)_2$ (MCV) as a dopant into the BST ceramics. This dopant is supposed to cause a relatively low dielectric constant to improve the microwave dielectric properties of BST ceramics. It is logical to explore MCV doped composite ceramics to modify the electrical properties of BST ceramics. In present study, we prepared BST–MCV composite ceramics and evaluated its electric properties. Moderate dielectric constant, high dielectric tunability and low dielectric loss were obtained. These optimum properties show that the composite ceramics are promising materials for application in tunable microwave devices.

2. Experimental

The nominal $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) powder was prepared by a solid-state reaction method. Appropriate amounts of $BaTiO_3$(99.9%) and $SrTiO_3$(99.9%) powders were dried at 500–700 °C before mixing together and then ball-milled in a nylon jar with zirconia balls. The mixture was fired at 1100 °C for 4 h. X-ray diffraction (XRD) patterns showed that all the peaks belong to BST which indicated the accomplishment of the reaction. The $MgCo_2(VO_4)_2$ powder was also prepared by the solid-state reaction method. The powders of MgO (99.9%), Co_2O_3 (99%) and V_2O_5 (98.0%) were used as starting materials. These materials were weighed and mixed by ball

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milling for 8 h. After drying, the mixture was calcined at 700 °C for 20 h. The phase of the calcined powders was determined by X-ray diffraction and identified as a single phase of $MgCo_2(VO_4)_2$. The calcined BST powders with 0.5, 1.0, 2.0 and 5.0 wt% MCV, named as BST–MCV–0.5 wt%, BST–MCV–1.0 wt%, BST–MCV–2.0 wt% and BST–MCV–5.0 wt%, were mixed again. The mixture was granulated and pressed into disk shaped pellets. The pellets were sintered at 1275 °C for 4 h with a heating rate of 3 °C/min.

Phase structures of sintered samples were analyzed by X-ray diffraction (XRD) (Model, D8 ADVANCE, Bruker, Germany). The patterns were recorded between 20° and 80° with 2θ increments of 0.02°. The microstructure was observed on the free surfaces of the specimens using scanning electronic microscopy (SEM) (Model, JSM EMP-800, JEOL, Tokyo, Japan). The densities of the sintered ceramics were measured using the Archimedes method.

Ag electrodes were painted on the major faces of thinned ceramic disks and sintered at 600 °C for electrical characterization. The dependence of the dielectric constant and loss on temperature from −165 °C to 130 °C at 10 kHz was measured using a high-precision LCR meter (HP 4284A, Agilent, Palo Alto, CA). Tunability was tested at 10 kHz and 20 °C up to maximum bias voltage of 30 kV/cm using a Keithley 2410 (Cleveland, OH) high voltage source coupled with a TH2816 LCR (Changzhou, China) analyzer. The dielectric constant and Q values at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method with a network analyzer (HP 8753E, Agilent, Palo Alto, CA) combining a resonating cavity. The values of ε and $\tan\delta$ were calculated from the resonant frequency and the geometric dimensions of the samples using Hakki–Coleman program.

3. Results and discussion

Fig. 1 shows the XRD patterns of all the samples. It is found that new phases $Ba_3(VO_4)_2$ is detected as the value of x increased to 5.0 wt% and the intensities of diffraction peaks increase with increasing of MCV content.

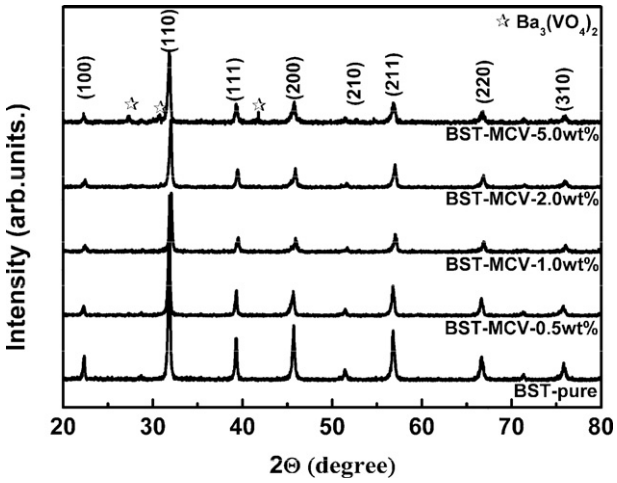

Fig. 1. XRD patterns of the BST ceramics with different contents of MCV.

In order to clarify the effect of MCV addition on the microstructure of BST ceramics, the morphological changes of the BST ceramics were investigated. Fig. 2 shows the free surface micrographs of samples with different amounts of MCV doping. Compared with pure BST ceramic, the addition of MCV obviously increased the density and enhanced the grain growth of BST. For BST with addition of 0.5 wt% MCV, some abnormal large cubic grains appeared. This may be due to the effect of the low melting point of $MgO–V_2O_5$ system on the grain growth behavior of the ceramics. In the binary phase diagrams of $MgO–V_2O_5$ systems, it was reported that the $Mg_3(VO_4)_2$ compounds decomposed into the liquid phase at the temperature of 1074 °C [7]. This low-melting-point additive diffuses into the grain boundary consequently allows BST grains grow rapidly with cubic shape corresponding to their crystal structure. When the content of MCV exceeded 1.0 wt%, the number of abnormal grain increased and more pores appeared, as a result the density of the sample decreased. The relative density of the BST ceramics with various contents of MCV is approximately 91.2% for BST-pure, 95.5% for BST–MCV–0.5 wt%, 93.2% for BST–MCV–1.0 wt%, 92.3% for

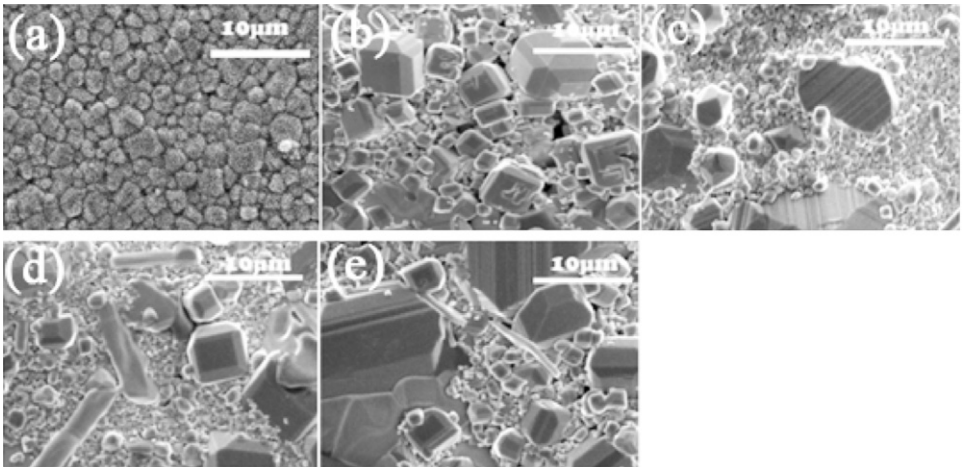

Fig. 2. Scanning electron microscopy micrograph of the BST ceramics with various contents of MCV (a) BST-pure, (b) BST–MCV–0.5 wt%, (c) BST–MCV–1.0 wt%, (d) BST–MCV–2.0 wt% and (e) BST–MCV–5.0 wt%.

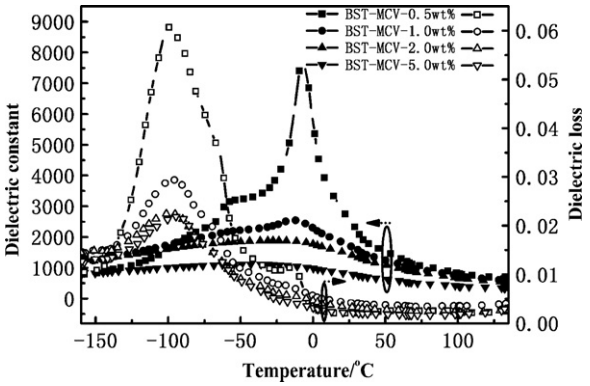

Fig. 3. Temperature dependence of dielectric constant and dielectric loss for BST ceramic with various amounts of MCV.

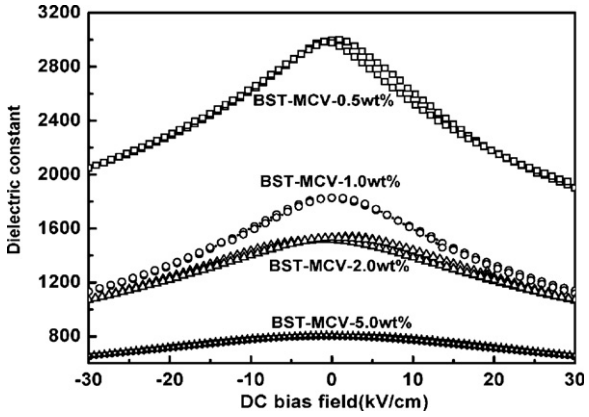

Fig. 4. Dielectric constant as a function of dc applied electric field for BST ceramic with various amounts of MCV.

BST–MCV–2.0 wt% and 90.7% for BST–MCV–5.0 wt%, respectively. This is in good agreement with the observations reported in the literature [8].

Fig. 3 shows the dielectric constant and dielectric loss of sintered BST with different amount of MCV as a function of temperature. The dielectric constant of BST was decreased with increasing of MCV content. The Curie temperature shifted to low temperature slightly. The shift of the Curie temperature may be due to the substitution of V and Co [9]. The ionic radii of Ba, Sr, Ti and O are summarized as follows: A-site (12 coordinates): Ba^{2+} = 1.61 Å, Sr^{2+} = 1.58 Å. B-site (6 coordinate): Ti^{4+} = 0.605 Å. Co^{3+} = 0.55 Å and V^{5+} = 0.58 Å [10]. V^{5+} is too small for the A-site and would occupy the B-site with Ti^{4+}[11]. Accept Co^{3+} replaces Ti^{4+} in the BST lattice and a doubly ionized oxygen vacancy is formed, which lead to a ''break'' of the cooperative vibration of Ti–O chains. This ''break'' is responsible for the low T_c of the doped BST [12]. The dielectric loss of BST with a small amount of MCV was higher than that of pure BST, and all samples have loss tangent values less than 0.005 at 10 kHz and room temperature.

Fig. 4 shows the dielectric constant versus electric field characteristics at 10 kHz and 20 °C. All samples added MCV have loss tangent values less than 0.005 at 10 kHz and room temperature (not shown in Fig. 4). The dielectric properties and calculated tunability are summarized in Table 1. The tunability for all samples with MCV additions kept between 38.3% and 47.2%.

Dielectric materials should have not only high tunability but also high Q (=1/tan δ) value or low loss tangent for practical applications of tunable devices. The microwave dielectric data are presented in Table 1. It can be seen that the dielectric constants of all samples were decreased at microwave frequencies compared with those at low frequencies (below 1 MHz). It was reported that the Q value of pure BST sintered at 1400 °C for 4 h was about 133 under 0.632 GHz [13]. The Q values of all samples were varied with different amount of additives. There are two kinds of microwave dielectric loss, including intrinsic loss and extrinsic loss [14]. The lattice vibration modes cause the intrinsic losses while the extrinsic losses were dominated by grain sizes, oxygen vacancies, second phases, densification/porosity, etc. Compared with pure BST, the Q value of BST–MCV–0.5 wt% sample was increased to 267 near 1 GHz. The increase of Q value of BST ceramics with MCV should attribute to the higher densification and the decrease of oxygen vacancies which increased the anharmonic interaction. Since V^{5+} act as a donor, the reaction can be represented by the following formula [14].

$$V_2O_5 + V_o'' \rightarrow 2V_{Ti}' + 5O_o \quad (1)$$

Further increasing the amount of MCV in BST ceramics would result in the decrease of Q value. The lower Q value of BST ceramics for the further addition of MCV is attributed to the increase of abnormal grain growth (as observed in Fig. 2) and excessive compensation.

Table 1
Microwave and dielectric properties of all the samples with MCV addition sintered at 1275 °C for 4 h.

Samples	Dielectric properties (at 10 kHz)				Microwave properties		
	ε		tan δ	Tunability (%) at 30 kV/cm bias	Resonant frequency (GHz)	ε (at resonant frequency)	Q (1/tan δ)
	Zero bias	30 kV/cm bias	Zero bias				
BST [13]	11,377	4176	0.0013	63.3	0.632	4423	133
BST–MCV–0.5 wt%	2976	1908	0.0020	35.9	0.925	2763	267
BST–MCV–1.0 wt%	1825	1139	0.0043	37.6	1.109	1790	182
BST–MCV–2.0 wt%	1516	1067	0.0035	29.6	1.187	1487	151
BST–MCV–5.0 wt%	807	658	0.0022	18.5	1.552	784	84

4. Conclusions

It is found that a small addition of $MgCo_2(VO_4)_2$ to $Ba_{0.6}Sr_{0.4}TiO_3$ can increase the density of BST. This attributed to the formation of $MgO–V_2O_5$ liquid phase. The addition of a small amount of MCV can effectively promote the microwave dielectric properties of BST. For BST ceramics with 0.5 wt% MCV addition, the dielectric loss keeps around 0.0020 and the tunability is above 35%. The Q value is 267 at the frequency of 0.925 GHz.

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