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Microstructures and dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$–MgO ceramics prepared by non-aqueous gelcasting and dry pressing

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ABSTRACT

Non-aqueous gelcasting and dry pressing were used to prepare 45 wt% $Ba_{0.6}Sr_{0.4}TiO_3$–55 wt% MgO (BSTM) ceramics. The effects of different forming methods on the microstructures and dielectric properties of the BSTM ceramics were investigated. The densities of the BSTM ceramics prepared by non-aqueous gelcasting are lower but more uniform than that of the BSTM ceramics prepared by dry pressing. The XRD analysis illustrates that phase compositions are completely the same no matter what forming method is adopted. The SEM results show that the BSTM green samples and sintered ceramics prepared by non-aqueous gelcasting are more uniform than that prepared by dry pressing. Furthermore, it is found that the BSTM ceramics prepared by non-aqueous gelcasting have higher and more uniform dielectric constant, tunability and loss tangent (measured at 10 kHz and 20 °C). Meanwhile, the BSTM ceramics prepared by non-aqueous gelcasting have higher dielectric constant and lower $Q \times f$ value (namely more loss) when they are measured at microwave frequencies.

1. Introduction

Barium–strontium titanate ($Ba_{1-x}Sr_xTiO_3$, $0 \le x \le 1$, BST) has been investigated with considerable interest and has become one of the most promising materials for tunable devices [1–4]. For these devices, it is required to have a low dielectric constant for good impedance matching, a low dielectric loss to minimize the insertion losses of devices, and a high dielectric tunability for lower power driving and high speed of phase shift. Much work has been done to reduce the dielectric constant, loss tangent and improve the dielectric tunability. Some non-ferroelectric materials such as Al_2O_3 [5], Bi_2O_3 [6], Fe_2O_3 [7] and $BaWO_4$ [8] were added to adjust the dielectric properties of the BST system. The dielectric constant of pure BST is considerably high ($\varepsilon_r > 1000$), the addition of non-ferroelectric oxide will cause a dramatic decrease in the relative permittivity of BST. It has been reported that the MgO–mixed BST (BSTM) bulk ceramics possess low dielectric constant, low loss tangent and suitable tunability [9]. However, there are few researches about the effects of different forming methods on the dielectric properties of the BSTM ceramics. At present, the most comprehensive forming method for the BSTM ferroelectric materials is dry pressing. Nevertheless, dry pressing cannot guarantee the uniformity of the prepared samples. The non-uniform structures existing in the BSTM ceramics prepared by dry pressing are mainly attributed to the considerable differences of densities between $Ba_{1-x}Sr_xTiO_3$ and MgO. In order to overcome the disadvantages existing in the dry pressing method, a novel forming method, gelcasting, has attracted more attention. Gelcasting, which was invented by researchers at Oak Ridge National Laboratory [10], has been successfully used to form many kinds of materials with uniform structures such as ferroelectric materials [11], piezoelectric materials [12–14] and microwave dielectric materials [15–17]. In this process, the high solids loading slurry is solidified by the polymerization of monomers to form green bodies. This forming method has many outstanding advantages, such as high strength of the dried green body, facile fabrication of devices with complicated shape and comprehensive application in a wide range of materials, etc. Generally, non-aqueous solvents and aqueous solvents are used in gelcasting. However, the MgO existing in the BSTM powders could readily react with water to form $Mg(OH)_2$, which could result in the difficult preparation of slurry with high solids loading and low viscosity, so the aqueous gelcasting is not suitable for the preparation of the BSTM samples. In this paper, non-aqueous gelcasting was used to prepare the BSTM samples. For comparison purpose, dry pressing was also used to prepare the BSTM samples. The microstructures, phase compositions and dielectric properties of the BSTM samples prepared by the two forming methods were investigated.

2. Experimental procedure

The solvent used in the non-aqueous gelcasting was glycol. The monomer used in non-aqueous gelcasting was acrylamide (AM)

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and cross-linker was *N*,*N*′ -methylenebisacrylamide (MBAM). 3 wt.% ammonium persulfate (APS) aqueous solution and *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine (TEMED) were used as initiator and catalyst, respectively. The dispersant used in non-aqueous gelcasting was 18 wt.% ammonium polyacrylate (PAA-NH_4) aqueous solution. The BSTM powder was prepared by the conventional solid state reaction method. Reagent grade ceramic powders $BaCO_3$ (99.8%), $SrCO_3$ (99.5%), TiO_2 (rutile, 99.6%) were milled according to the composition $Ba_{0.6}Sr_{0.4}TiO_3$ with zirconia balls and alcohol for 5 h at a speed of 365 rpm. After the slurry was dried, the mixture was calcined at 1150 °C for 3 h to synthesize $Ba_{0.6}Sr_{0.4}TiO_3$. Then 55 wt.% MgO (98.5%) and a few other dopants (1.2 wt.% CeO_2, 0.8 wt.% SiO_2, 0.4 wt.% $MnCO_3$ (based on the weight of 45 wt% $Ba_{0.6}Sr_{0.4}TiO_3$–55 wt% MgO)) were added to 45 wt.% $Ba_{0.6}Sr_{0.4}TiO_3$ calcined powder. After mixing (with zirconia balls and alcohol for 5 h at a speed of 365 rpm) and drying, the powders were calcined at 1150 °C for 3 h, then re-milled (with zirconia balls and alcohol for 5 h at a speed of 365 rpm) and dried. Some dried BSTM powders were uniaxially pressed to form samples with dimensions of 15 mm diameter and 7–10 mm height under a pressure of 150 MPa, the other powders were used to prepare the same samples by non-aqueous gelcasting. The flow chart of non-aqueous gelcasting is shown in Fig. 1. The premix solution was prepared by mixing the monomer, cross-linker and glycol. The concentration of the premix solution was about 13 wt.% and the ratio of AM and MBAM was 20:1. The BSTM powder and dispersant (PAA-NH_4, 6 ml/100 g BSTM powder) were added into the premix solution to make slurry with solids loading of about 43 vol.%. Strong aqua ammonia was used to adjust the pH value of the slurry at about 8–10 [18]. After ball milling for 0.5 h, the high solids loading slurry was obtained, then degassing was subsequently carried out for 10 min under vacuum gauge pressure of −0.1 MPa. Afterwards, the catalyst (TEMED, 0.125 ml/1 g AM) and initiator (APS, 0.25 ml/1 g AM) were added into the slurry to initiate the gelation. After casting, demolding and drying, the binder was burned out of the green samples at 600 °C for 1 h and then all the samples prepared by the two forming methods were sintered at 1450 °C for 6 h to form ceramics. Finally, the sintered BSTM samples were cut into 1 mm thick slices, which were numbered 1–5 from the top to the bottom of the samples.

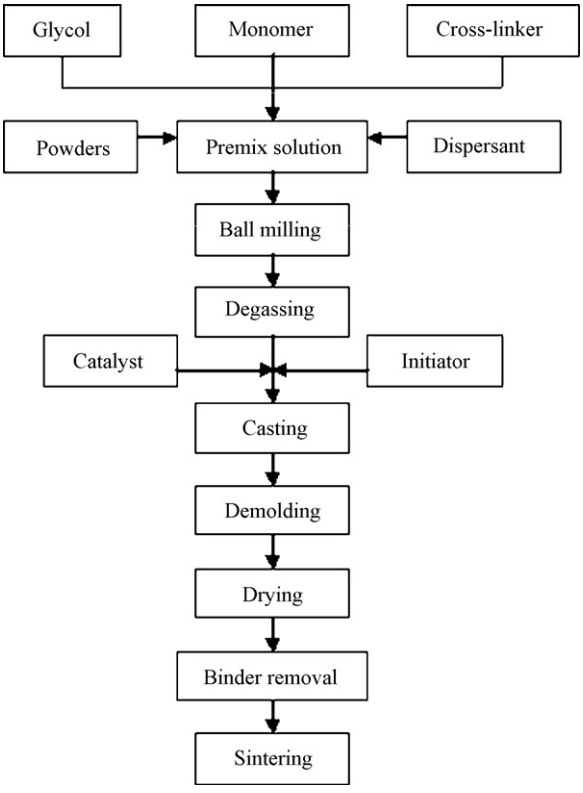

Fig. 1. The flow chart of non-aqueous gelcasting.

The density was measured with Archimedes method. The phases were analyzed by X-ray diffraction (XRD) method using Cu Kα radiation (X'Pert PRO, PANalytical B.V., Holand). The microstructure observation and quantitative analysis of the sintered samples were performed using environment scanning electron microscope (ESEM) (Quanta 200, FEI, Holand) and energy-dispersive X-ray spectroscopy (EDX) (Genesis 7000, EDAX Inc., USA), respectively. The low frequency dielectric properties (measured at 10 kHz) were measured using a TH2613A capacitance meter coupled with a 10 kV DC power supply. The tunability was measured at 2 kV/mm. The ε_r and $Q \times f$ values were measured in the $TE_{0\,1\,1}$ mode with the Hakki and Coleman method [19] using a vector network analyzer (Advantest R3767C, Advantest Corporation, Japan) and parallel silver boards.

3. Results and discussion

3.1. Microstructures

The densities of the BSTM ceramics prepared by non-aqueous gelcasting and dry pressing are shown as a function of layer number in Fig. 2. It could be found that the densities of the BSTM ceramics prepared by non-aqueous gelcasting are lower than that of the BSTM ceramics prepared by dry pressing, which could be attributed to the relatively low solids loading (lower than 50 vol.%) of the prepared BSTM slurry. However, due to the more uniform microstructures existing in the BSTM samples prepared by non-aqueous gelcasting, which will be shown later, the BSTM ceramics prepared by non-aqueous gelcasting have more uniform densities than that prepared by dry pressing.

Fig. 3 shows the XRD patterns of the BSTM ceramics. The XRD results show that the main phases in the BSTM ceramics are BST and MgO, which are indexed in JCPDS card No. 75-2116 and No. 75-0447, respectively. Meanwhile, it is found that the phase compositions are the same no matter what forming method is adopted. The SEM micrographs of the BSTM green samples, ceramics and EDX of grains are shown in Fig. 4. As shown in Fig. 4(a) and (b), it is obvious that the starting materials in the BSTM green samples prepared by non-aqueous gelcasting are more

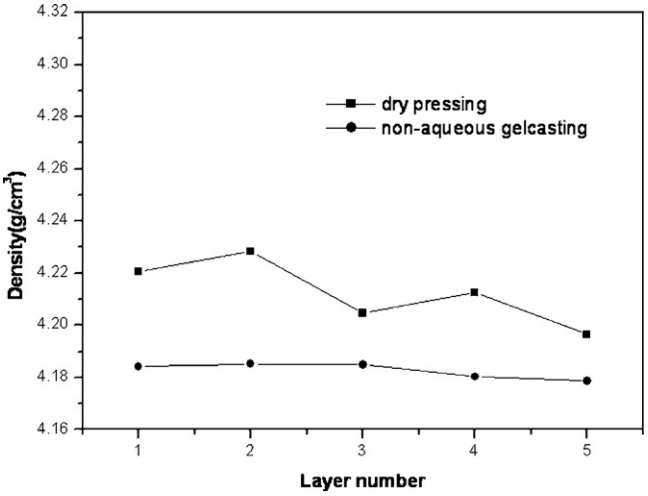

Fig. 2. Densities of the BSTM ceramics prepared by non-aqueous gelcasting and dry pressing as a function of layer number.