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Original article

Enhanced dielectric characteristics of $Ba_{0.94}Bi_{0.04}(Fe_{0.5}Nb_{0.5})O_3$ coated with SiO_2 and SiO_2/Al_2O_3 over a broad frequency and temperature range

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ABSTRACT

Pure phase of $Ba_{0.94}Bi_{0.04}(Fe_{0.5}Nb_{0.5})O_3$ (BBFN) nano-particles were obtained by chemical co-precipitation method. The core-shell structure of BBFN@SiO_2 and BBFN@SiO_2/Al_2O_3 particles and the target ceramics were successfully prepared by aqueous chemical coating approach. The microstructures and dielectric properties of BBFN@SiO_2 and BBFN@SiO_2/Al_2O_3 were studied. Both the BBFN@SiO_2 and BBFN@SiO_2/Al_2O_3 samples show significantly decreased dielectric loss and good frequency and temperature stability on relative permittivity. Compared to the rapid decline of relative permittivity of BBFN@SiO_2, the synergistic effect of SiO_2 and Al_2O_3 in BBFN@SiO_2/Al_2O_3 ceramics made the relative permittivity of which remains a relatively high level with very low dielectric loss, making it more suitable in colossal permittivity applications. Based on the impedance analysis, the grain boundary effect and IBLC models play the important role for the improvement of dielectric properties of BBFN@SiO_2/Al_2O_3 samples.

1. Introduction

The rapid development of microelectronics industry brings about the requirements for dielectric materials with giant permittivity and low loss over a wide frequency and temperature [1,2]. In recent years, Fe-containing complex perovskite-type $Ba(Fe_{1/2}Nb_{1/2})O_3$ ceramics has drawn much attention in the fields of material science and condensed matter physics for its attractive dielectric relaxation and colossal permittivity behavior [3–6]. Despite of various interesting features, a few of the serious drawbacks of BFN ceramics, especially such as high sintering temperature, the large room temperature dielectric loss, and relatively narrow relative permittivity step, still limit its practical applications.

Many efforts have been done to modify ceramic capacitors to meet the requirements of low dielectric loss and excellent frequency and temperature stability [7–11], such as doping ions [12,13], changing the synthesize method [6] and modifying the surface of particles [7,14,15]. The core-shell structure prepared by chemical coating method is an effective way to enhance the dielectric properties of dielectric materials. The colossal permittivity materials core is used to increase the permittivity due to the interfacial polarization, and the insulator shell serves as a barrier layer to control the dielectric loss effectively through blocking the electron transfer between adjacent metal cores [7,16–19]. It has been reported that the dielectric properties (especially dielectric loss) can be improved effectively when the insulating shell has a low dielectric loss, i.e. Al_2O_3, SiO_2, La_2O_3 [15,20–22]. Therefore, it is expected that the dielectric properties of BBFN ceramics will be improved through this core-shell structure. Besides, Chai et.al reported that the permittivity of $Ba_{1-x}Bi_x(FeTa)_{0.5}O_3$ ceramic synthesized by a solid state reaction could be increased obviously over a relatively broad temperature ranges when $x < 0.06$ [23]. Combining the advantages of chemical method and report by Chai et.al, we synthesized the high-valence Bi^{3+} ion doped-$Ba(Fe_{0.5}Nb_{0.5})O_3$ ceramics (i.e. $Ba_{0.94}Bi_{0.04}(Fe_{0.5}Nb_{0.5})O_3$, abbreviated to BBFN) via solution precipitation method.

In this work, the SiO_2 coating and SiO_2/Al_2O_3 synergistic coating on BBFN (i.e. BBFN@SiO_2 and BBFN@SiO_2/Al_2O_3) are designed to reduce the dielectric loss, improve the frequency and temperature stability and still remains relatively higher permittivity in the meantime. We investigated the effect of SiO_2 coating and SiO_2/Al_2O_3 synergistic coating on the microstructure and dielectric properties. It will lay the foundation for the further improvement of dielectric characteristics of BFN ceramics, and the physics mechanism is further studies.

2. Experimental details

Pure BBFN powders were prepared by the co-precipitation method using $Fe(NO_3)_3{\cdot}9H_2O$ (purity: 98.5%), $Ba(NO_3)_2$ (purity: 99.5%), Bi

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$(NO_3)_3{\cdot}5H_2O$ (purity: 99%) and $NbCl_5$ (purity: 99%) as raw materials. All chemicals come from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). $Fe(NO_3)_3{\cdot}9H_2O$ and oxalate were dissolved in deionized water. The $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in dilute nitric acid and then drops into $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$ mixed solutions. $NbCl_5$ dissolved in ethanol was then dropped into the mixed solution, and aqueous ammonia was used to adjust the pH value of the solution to be 10 to realize the co-precipitation of Ba^{2+}, Fe^{3+}, $Bi^{3+}$and Nb^{5+} ions. After drying, the precipitates were calcined at 950 °C for 4 h to produce BBFN powders.

For BBFN@$x$$SiO_2$ ($x = 0$; $x = 1$ wt%; $x = 2$ wt%; $x = 3$ wt%) powders, the precursor liquor was prepared by suspending 3 g of BBFN in 300 ml ethyl alcohols, followed by the dropping of H_2O_2 and the addition of PVP. The suspension was agitated ultrasonically for 2 h and stirred under magnetic stirring for 2 h at room temperature to break up the BBFN agglomerates. The pH of the suspension was adjusted to 8–9 by adding aqueous ammonia and then the suspension was ultrasonically for 30 min at room temperature. After that, tetraethyl orthosilicate (TEOS) was added into the suspension and stirred at 40 °C for 24 h under the water-bath heating. The BBFN@SiO_2 powders were obtained by calcining at 500 °C for 2 h. The as-prepared BBFN and BBFN@SiO_2 powders were pressed into pellets through cold isostatic pressing respectively.

Preparation of BBFN@SiO_2/Al_2O_3 was similar to BFN@SiO_2, one more step was to add $Al(NO_3)_3$ (purity: 99%) into the suspension after the addition of TEOS, the other steps were almost the same. The BBFN@SiO_2 ceramics was sintered at 1130 °C for 3 h, the BBFN and BBFN@SiO_2/Al_2O_3 composite ceramics were sintered at 1170 °C for 3 h, respectively. The electrodes for electric measurements were deposited with Ag paste on both sides of the pellets and heat treated at 600 °C for 15 min.

The phase composition and crystal structure of the synthetic powders were identified by X-ray diffraction (XRD, D/max-2200PC, Rigaku, Japan). The microstructures of the ceramics and the coated powders were evaluated by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, Tecnai G2 F30, USA), respectively. The dielectric characteristics of these samples were measured in broad temperature (−175 to 100 °C) and frequency ranges (20–2 M Hz) with the precision LCR meter (Agilent-E4980A, USA).

3. Results and discussion

Fig. 1(a) shows the XRD results for pure BBFN powders calcined at 950 °C for 4 h and BBFN@$x$$SiO_2$ powders heat treated at 500 °C for 2 h. It is shown that the BBFN particles with a single perovskite phase in the space group $Pm\bar{3}m(221)$ are obtained without visible signal of secondary phases which is corresponded to that of BFN structure. Also, it can be seen that the amorphous SiO_2 did not show the crystallization peaks which are consistent with the non-crystalline SiO_2, which indicates that SiO_2 is amorphous. The amorphous SiO_2 layer will effectively accelerate the sintering behavior and reduce the sintering temperatures of ceramic samples. Fig. 1(b) shows the microstructures of BBFN powders synthesized by chemical co-precipitation method calcined at 950 °C for 4 h. It is obvious that BBFN powders mainly distribute at the nanoscale about 50–60 nm, and it even shows good dispersibility and homogeneity which is beneficial for the subsequent coating process.

The surface of pure BBFN powders exhibit smooth edge lines without any coating layers as shown in Fig. 2(a). Compared with Fig. 2(a), it is clearly observed from Fig. 2(b)–(d) that a compact thin translucent layer with a nanoscale thickness covered the surface of BBFN particle, which confirms the successful coating of the continuous SiO_2 shell. Even more, thicknesses of SiO_2 shell gradually increase with increasing the weight ratios of SiO_2 layers. The homogeneous coating is beneficial for the more uniform distribution of SiO_2 at the sintered ceramic grain boundaries. It is a fundamental improvement comparing with mechanical milling-mixing process. Fig. 2(e)–(f) illustrate the SEM images of BBFN@$x$$SiO_2$ (x = 0, 1 wt%, 2 wt%, 3 wt%) ceramics, from which it can be seen that all samples are well densified without any pores. All the samples are sintered at much a lower temperature comparing with BFN ceramics [23,24] The grain sizes of the samples decrease gradually and are distributed evenly after coating SiO_2 layer due to the inhibition effect of SiO_2 as sintering additives. The more uniform and smaller grains may lead to the increase of grain boundaries density and the following decrease of dielectric loss.

The frequency dependence of dielectric characteristics of BBFN and BBFN@$x$$SiO_2$ ceramics is shown in Fig. 3. The relative permittivity of the pure BBFN ceramics reached the highest value (about 3.6×10^4) at room temperature. As the content of SiO_2 increased, the relative permittivity decreased significantly, which is in accordance with the decreased of the grain sizes and the intrinsic extremely low relative permittivity. However, from Fig. 3(b), it is worth noting that the dielectric loss (tan δ) decreased from 0.647 to 0.035、0.041、0.046 orderly at 10 kHz when the contents of SiO_2 increase in turn, this is due to the presence of low dielectric loss SiO_2 layers and the hindrance of SiO_2 barrier layers for the movement of change carriers. It can also be found when increasing the frequency to a certain value, the relative permittivity of pure BBFN ceramics shows sharp decrease, and at the same time the dielectric loss (tan δ) shows a peak, meanwhile, those of BBFN@SiO_2 composite ceramics is nearly frequency independent, which indicates that the synergistic effect of the core and shell material can improve the frequency stability of BBFN ceramics. Fig. 3(c) and (d) show the dielectric properties measured at 10 kHz as a function of temperature (−175 to 100 °C) for the BBFN and BBFN@xSiO2 ceramics. It is found that the relative permittivity shows significant temperature dependence for pure BBFN ceramic, and two dielectric

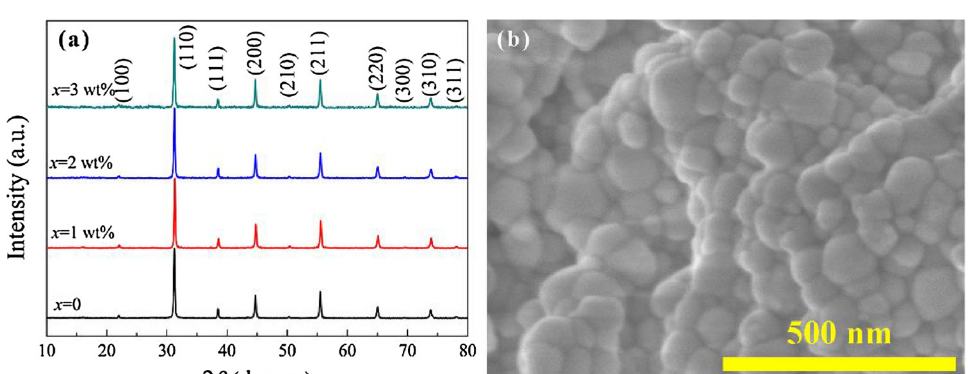

Fig. 1. (a) XRD patterns of BBFN powders calcined at 950 °C for 4 h and BBFN@$x$$SiO_2$ (1 wt% < x ≤ 3 wt%) powders heat treated at 500 °C for 2 h; (b) SEM image of pure BBFN nano-powders prepared by co-precipitation method.