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$Ba(Fe_{0.5}Nb_{0.5})O_3@SiO_2$ core-shell structures with low dielectric loss over a broad frequency and temperature by aqueous chemical coating approach

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To decrease the dielectric loss over a broad temperature and frequency of $Ba(Fe_{0.5}Nb_{0.5})O_3$ (BFN) ceramics, the core-shell structure of $Ba(Fe_{0.5}Nb_{0.5})O_3@SiO_2$ (BFN@SiO_2) particles were successfully prepared by aqueous chemical coating approach, which still remains in the final ceramics. The mechanism of coating BFN with SiO_2 is also analyzed. The BFN@SiO_2 sample shows good frequency and temperature stability on dielectric constant and the dielectric loss is significantly decreased. The low tan δ is related to the homogeneous fine grains and the insulating grain boundaries of BFN@SiO_2 ceramics. The improved temperature stability in BFN@SiO_2 ceramics is a competing balance result of the low and high temperature dielectric relaxations. The enhancement resistance of grain boundaries plays a key role to reduce the dielectric loss of the BFN@SiO_2 ceramics. The XPS analysis confirms the blocking function of insulating SiO_2 shell on loss of the oxygen and matter transfer.

1. Introduction

With the development of microelectronics industry, dielectric materials with giant dielectric constant and low loss over a wide frequency and temperature are always of great interest due to the important application of such properties in many electronic devices, like high performance capacitor [1,2]. Recently, a number of Fe-containing complex perovskites $A(Fe_{1/2}B_{1/2})O_3$(A = Ba, Sr, and Ca; B=Nb, Ta, and Sb) [1,3,4]have attracted much scientific attention because of their giant dielectric response and the unique dielectric relaxation behavior. $Ba(Fe_{0.5}Nb_{0.5})O_3$(BFN), which generally exhibit a very high dielectric constant step (in the order of 10^3-10^5), is a relaxor-type material with partially disordered perovskite structure [5,6]. Despite of these various interesting features, a few of serious drawbacks of BFN ceramics, such as relatively narrow dielectric constant step, the large room-temperature dielectric loss, and high sintering temperature, still limit its practical applications. Therefore, keeping high and uniform dielectric constant, coupling to low dielectric loss over a wide operating frequency and temperature range are significantly important for BFN ceramics.

Many strategies have been proposed to tackle the issue during the past few years, for example, many efforts have been done to modify multilayer ceramic capacitors which requires lower dielectric loss and excellent temperature stability [7–11]. For these purpose, it requires the utilization of nano-sized or submicron-sized powders as the starting material, and the uniformity and the size of these particles must be effectively controlled to achieve this goal. Among these works, an effective approach to modify the properties is coating the target particles to prepare the “core-shell” structures [7,12–15]. It was found that the coating process could effectively reduce the grain sizes, decrease dielectric loss and increase the temperature stability effectively. It has been demonstrated that the dielectric characteristics (especially dielectric loss) of these materials can be improved by coating the grain with an insulating material which has low dielectric loss, i.e. Al_2O_3, SiO_2, La_2O_3 [16–19]. The insulating layer with low dielectric loss can act as sintering agents, which improves the sintering properties and reduce the aggregation of ceramics particles, thereby preventing the ceramics from breaking down in the boundaries. Thus the rational core-shell structure consisting of dielectric material core and insulating oxide shell is considered as an attracting and effective strategy to obtain low dielectric loss and the truth covered up by large conductivity simultaneously. Inspired by above works,

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the deliberate design of the microstructure called “core-shell” for individual grains must be essential with considerably thin dielectric layers since the microstructure has a decisive influence on the dielectric properties, and low sintering temperature can also reduce their production costs and become another hotspot.

Combining the giant dielectric constant of BFN ceramics and the advantages of coating insulating layer, we have coated $Ba(Fe_{0.5}Nb_{0.5})O_3$ with Al_2O_3 layers. However, all the complicated process of coating Al_2O_3 layer lead to the very inhomogeneous layers and low repeatability, which have not obtain the expectant low dielectric loss. Above all, the $Ba(Fe_{0.5}Nb_{0.5})O_3@SiO_2$ (BFN@SiO_2) core-shell structure is designed in this work to improve the temperature stability and still remains relative higher dielectric constant in the meantime. We investigated the effect of SiO_2 coating on the microstructure, dielectric properties, and the sintering temperature of the resulting core-shell particles and fine-grained BFN-based ceramics. It will lay the foundation for the further improvement of temperature stability and decrease of dielectric loss of BFN ceramics. The physics mechanism of the influence of SiO_2 coating on the BFN materials was also studied.

2. Experimental details

2.1. Synthesis of BFN@xSiO_2 composites

BFN@xSiO_2 (a: $x = 0$ wt%; b: $x = 1$ wt%; c: $x = 2$ wt%; d: $x = 3$ wt %) powders were synthesized by aqueous chemical coating approach. BFN powder was chosen for the core, SiO_2 powder for the shell to produce dense and fine-grained BFN-based ceramics. The tetraethyl orthosilicate (TEOS) were used to form SiO_2 layer. The polymer of polyvinyl pyrrolidone (PVP) was used as the surfactant and dispersant. The pH value was adjusted by adding aqueous ammonia. The following chemicals were all obtained from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Firstly, pure BFN powders were prepared by the conventional solid-state method. Stoichiometric mixtures of $BaCO_3$ (99%), Fe_2O_3 (99%) and Nb_2O_5 (99.5%) were homogenized by ball-milled in deionized water for 4 h and calcined at 1100 °C for 3 h. Secondly, the precursor liquor was prepared by suspending 3 g of BFN in 300 ml ethyl alcohol, followed by the dropping of H_2O_2 (5 ml) and the addition of PVP (1.2 g). The suspension was agitated ultrasonically for 2 h and stirred under magnetic stirring for 2 h at room temperature to break up the BFN agglomerates. The pH of the suspension was adjusted to 8–9 by adding aqueous ammonia and then the suspension was ultrasonicated 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 BFN@SiO_2 powders were obtained by calcining at 500 °C for 2 h with the heating rate of 2 °C/min. The as-prepared BFN and BFN@SiO_2 powders were mixed with polyvinyl alcohol (PVA), and then pressed into pellets. The BFN and BFN@SiO_2 composite ceramics were sintered at 1350 °C and 1150 °C for 3 h, respectively. The heating ramp is: from room temperature to 200 °C with the heating rate of 2 °C/min; from 200 °C to 500 °C with the heating rate of 3 °C/min; from 500 °C to the target temperature with the heating rate of 5 °C/min. The electrodes for measurements were fabricated with Ag paste on both sides of the pellets and heat treated at 600 °C for 15 min. In order to find or confirm the existence of SiO_2 in the coated particles, the pure SiO_2 powders were prepared by stöber method.

2.2. Characterization

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 and frequency ranges with the precision LCR meter (Agilent-E4980A, USA). X-ray photoemission spectroscopy (XPS) (K-Alpha) with Al Ka radiation (hm = 1486.68 eV) was used to analyze the mixed valence state. The experimental curve was fitted with a program (XPS-Thermo Avantage) that made use of a combination of Gaussian-Lorentzian lines.

3. Results and discussion

A concise schematic illustration showing the procedures of preparing core-shell structured BFN@SiO_2 particles and ceramic is presented in Fig. 1. As it is known, the hydroxyl groups can arbitrarily locate on the surface of particles suspended in ethyl alcohol by dropping H_2O_2. The hydroxyl groups surrounding the particles generate the repulsive forces to balance the Van der Waals attractive forces. Thus, BFN particles are stabilized in suspension. The hydroxyl groups are capable of forming hydrogen bonds with PVP. In the meantime, this process leads the more stability of the particles and less tendency to aggregate. The PVP existing on the surface of BFN particles can also form hydrogen bonding with TEOS. This mechanism of coating is shown schematically in Fig. 1 marked by step 1 and step 2. In the final ceramics, the SiO_2 mainly exists in the grain boundaries to form the barriers to reduce the dielectric loss of ceramics and enhance the frequency and temperature stabilities.

Fig. 2a and Fig. 2b show the XRD results for amorphous SiO_2 got from the hydrolyzed TEOS by stöber method, pure BFN powders calcined at 1100 °C for 3 h and BFN@xSiO_2 powders heat treated at 500 °C for 2 h. It is shown that the BFN particles with a single perovskite phase in the space group $Pm\overline{3}m(221)$ was obtained without visible signal of secondary phases. All peaks of BFN@xSiO_2 core-shell heterostructure corresponded to that of BFN structure. It can also be seen that the amorphous SiO_2 shows a steamed bun shape curve in the XRD patterns from 15° to 30°. For the coated BFN@SiO_2 composite powders, there is no crystallization peak of SiO_2, instead it shows typical amorphous feature of SiO_2 from 15° to 30° (Fig. 2b) which is 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. As shown in Fig. 2c, the BFN particles prepared by the conventional solid-state method have a uniform morphology and good dispersity with grain sizes of around 200–300 nm.

The TEM images of BFN and BFN@xSiO_2 core-shell powders are shown in Fig. 3. As can be seen in Fig. 3a, the surfaces of pure BFN powder have smooth edge lines without any coating layers, especially from the enlargements of the surface region. From Fig. 3b–d, it is clearly observed that a compact thin translucent layer with a nanoscale thickness covered the surface of the core BFN particle, which confirms the nanoscale size of SiO_2 shell. What's more, it can be seen the coated layers are continuous, especially when the content of SiO_2 is more as shown in Fig. 3d. The thicknesses of SiO_2 shell gradually increase with increasing weight ratios of SiO_2 layers. The selected-area electron diffraction (SAED) pattern taken from the SiO_2 shell region of BFN@SiO_2 core-shell powder heat treated at 500 °C suggests a noncrystalline and amorphous structure of SiO_2 shell, which is consistent with the XRD results and will be beneficial to the sintering behavior of ceramics.

In order to further confirm the successful uniform coating of the insulating SiO_2 shell on the surface of particle, EDS analysis of