

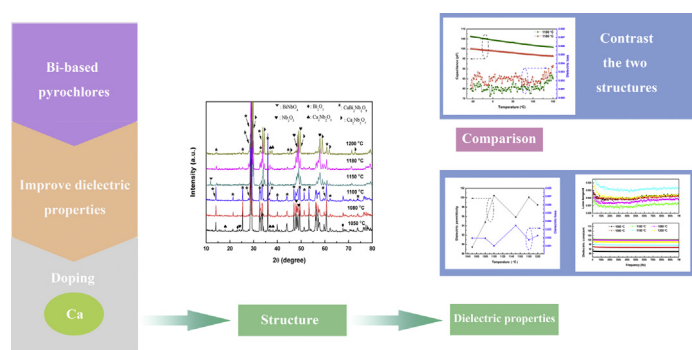


Crystal structure and dielectric properties of $\text{Bi}_2\text{O}_3\text{-CaO-Nb}_2\text{O}_5$ compounds

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GRAPHICAL ABSTRACT



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ABSTRACT

The $\text{Bi}_2\text{O}_3\text{-CaO-Nb}_2\text{O}_5$ (BCN) materials were prepared by solid-state reaction. The BCN pyrochlores exhibited a layered structure with general formula of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ when the sintering temperature below 1100 °C, and the sample in a nearly pure phase at 1100 °C. The structure of BCN ceramics was gradually transformed into $\text{Ca}_2\text{Nb}_2\text{O}_7$ pyrochlore structure with further increasing the sintering temperature. The dielectric properties varied with structures. The BCN ceramic sintered at 1100 °C exhibited excellent dielectric properties with a dielectric constant of ~110 and a dielectric loss of ~0.001. The dielectric constants of all the ceramics were independent with the measurement frequency (100 Hz–1 MHz) at room temperature. However, the dielectric loss decreased dramatically at low frequency and then increased slightly with increasing frequency. The temperature dependence of dielectric properties of BCN ceramics was also investigated. The BCN materials with a $\text{Ca}_2\text{Nb}_2\text{O}_7$ pyrochlore structure were more sensitive to the temperature than that with a $\text{CaBi}_2\text{Nb}_2\text{O}_9$ structure.

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1. Introduction

Bismuth based pyrochlore oxides have attracted considerable attentions due to their high dielectric permittivity combines with low dielectric loss, which are promising candidate materials for microelectronic applications [1–6]. Moreover, the bismuth based pyrochlore materials

usually have low sintering temperatures and a chemical compatibility with Ag electrodes. Therefore, bismuth based pyrochlore materials are also potential candidates for low temperature co-fire ceramic (LTCC) technology towards development of multilayer components and devices [7–10].

The bismuth based $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore structure can be described as two interpenetrating networks of $\text{A}_2\text{O}'$ tetrahedral network and corner-shared B_2O_6 octahedral network. In the $\text{A}_2\text{O}'$ tetrahedral sub-structure, the A cations are randomly displaced from the eight-fold coordinated

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positions. The dielectric properties of materials are closely related to the polarizability in the structures. In the bismuth based pyrochlore structures, the random fields and interactions between the disordered ions on the A-site are the major sources of polarizability [11]. Furthermore, some of bismuth pyrochlores such as $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ (BZN) and $\text{Bi}_{1.5}\text{MgNb}_{1.5}\text{O}_7$ (BMN) have electric field dependence of dielectric permittivity [12–16]. In these materials, Zn^{2+} or Mg^{2+} ions can occupy both A-site and B-site, which would increase the disorder degree of the structure. The dielectric tunability is believed to be concerned with the applied fields effectively clamp out the polarizability from the field-forced ordering [12,17]. Due to this flexible structure, substitution with highly polarized cations may enhance the dielectric properties of bismuth-based pyrochlores.

In this paper, the highly polarizable Ca^{2+} ions were introduced to substitute Mg^{2+} ions in the BMN materials. The detailed phase composition variation of Bi_2O_3 -CaO- Nb_2O_5 (BCN) pyrochlores was described. Besides, the relationship between dielectric properties and structure variation was systematically investigated.

2. Experimental procedure

The conventional solid-state method was applied in BCN sample synthesis with Bi_2O_3 (99.9%), CaO (99%), and Nb_2O_5 (99.9%) as starting materials. The mixtures of starting materials in stoichiometry were ball milled in sufficient alcohol media with polyethylene bottles for 12 h, and then dried and calcined at 950 °C for 2 h. The calcined samples were remilled with the same conditions to obtain BCN powders. After remilling, the dried powders were grinded with a polyvinyl alcohol (PVA) binder. The granulated powders were pressed into disks with a diameter of 15 mm and a thickness of 1 mm at a pressure of 150 MPa. The samples were baked at 650 °C for 6 h to remove PVA, the green compacts were placed in sealed Al_2O_3 crucibles and fully surrounded by the powders of matching compositions with the sintering temperature ranging from 1050 °C to 1180 °C for 2 h.

The crystalline structure of samples with polished surface was characterized by X-ray diffraction (XRD, BeDe D1) instrument. The microstructure observation of the sintered ceramics was performed by scanning electron microscope (SEM, FEI, Inspect F). For dielectric measurement, samples were machined and polished to the right size besides post-fired silver electrodes were pasted on the both major surfaces of the disk pellets. Dielectric properties were investigated at room temperature as a function of the frequency (100 Hz–1 MHz) by using an Agilent 4294A precision impedance analyzer with a 500 mV oscillation voltage. The temperature coefficient of capacitance in the temperature range of –55–150 °C was measured by an Agilent 4284A precision impedance analyzer in conjunction with a temperature chamber at 1 MHz with a 500 mV oscillation voltage. The temperature was controlled by a LakeShore temperature controller. Temperature varied from 77 K to 310 K using liquid nitrogen with a cooling rate of 5 K/min. The permittivity of the BCN materials was calculated from the sample thickness and electrode areas.

3. Results and discussion

The XRD patterns of BCN ceramics sintered at a temperature ranged from 1050 °C to 1200 °C are shown in Fig. 1. The BCN ceramics sintered below 1100 °C showed a layer-structured $\text{CaBi}_2\text{Nb}_2\text{O}_9$ with an orthorhombic phase, which were different from that of the desired structures as the BMN/BZN with cubic pyrochlore phase. The structure of bismuth-based pyrochlores depends on the ratio of oxides and sintering temperature [18–22]. Although, the starting compositions of BCN pyrochlores are similar to the stoichiometry of cubic pyrochlore BMN materials. The long-rang coupling of the $6s^2$ long-pair electrons of Bi^{3+} cations and the larger ionic radius of Ca^{2+} cations made it hard to form the pyrochlore structure and induced the orthorhombic distortion in BCN layered structure. The samples sintered at 1050 °C consisted the

secondary phases of $\text{Ca}_4\text{Nb}_2\text{O}_9$, Bi_2O_3 , and Nb_2O_5 as shown in Fig. 1. During the sintering process, CaO preferentially reacted with Nb_2O_5 to form $\text{Ca}_4\text{Nb}_2\text{O}_9$ solid solution first, and then reacted with the Bi_2O_3 to form less-volatile components. The reaction cannot totally complete at this temperature, therefore, some of secondary phases remain in the form of unreacted raw materials. The samples sintered at 1100 °C presented a nearly pure $\text{CaBi}_2\text{Nb}_2\text{O}_9$ orthorhombic phase except the raw materials, which cannot fully reacted in this stoichiometry. The major crystalline structure of BCN ceramics transferred to the $\text{Ca}_2\text{Nb}_2\text{O}_7$ pyrochlore phase with the further increasing sintering temperature. However, the secondary phases of Bi_2O_3 , Nb_2O_5 , and bismuth niobate oxide were detected in these samples.

To further describe the phase transition in BCN ceramics with sintering temperature, the diffraction peaks were fitted to profile shape functions by Jade 6 software in order to get full width at half maximum (FWHM), peak areas, and peak heights of the strongest characteristic peaks of each detected phase in the BCN ceramics are shown in Fig. 2. The intensity heights and areas of all the studied peaks exhibited the same variation with the temperature. The presence of the (115) $\text{Ca}_4\text{Nb}_2\text{O}_9$ peak and (400) Bi_2O_3 peak indicated there were always small amounts in the BCN samples, especially the Bi_2O_3 only existed in the samples sintering under 1100 °C. The (222) $\text{Ca}_2\text{Nb}_2\text{O}_7$ peak was first detected at 1150 °C, and its peak intensity increased with increasing sintering temperature, which revealed the main structure of BCN ceramics began to transfer to $\text{Ca}_2\text{Nb}_2\text{O}_7$ pyrochlore phase. Moreover, the FWHM of $\text{Ca}_2\text{Nb}_2\text{O}_7$ peaks showed the largest value at 1150 °C and then decreased with further increasing temperature, indicating the smaller crystal size of new formed $\text{Ca}_2\text{Nb}_2\text{O}_7$ crystals at 1150 °C and crystal size increased with further increasing temperature. Meanwhile, the largest FWHM of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ phase and Nb_2O_5 phase at 1150 °C were also confirmed $\text{CaBi}_2\text{Nb}_2\text{O}_9$ begun to decompose and newly formed $\text{Ca}_2\text{Nb}_2\text{O}_7$ pyrochlore phase.

Fig. 3 displays the surface morphologies of BCN ceramics with different sintering temperatures by SEM. The samples sintered at 1050 °C already presented a dense and homogenous microstructure with an average grain size of 6 μm , which were spherical grains. The columnar grains began to form at sintering temperature of 1080 °C. With the increase of sintering temperature, the larger grains consumed the smaller grains resulted in the obviously increasing of the average grain size. All the samples sintered above 1050 °C exhibited uniform well-densified surface morphologies with almost no porosity. Moreover, the large agglomerated clusters with dimension of thousands nanometers were observed in the samples sintered above 1100 °C. The samples sintered at higher temperature have more energy for grain boundary diffusion and thus enhanced the grain growth.

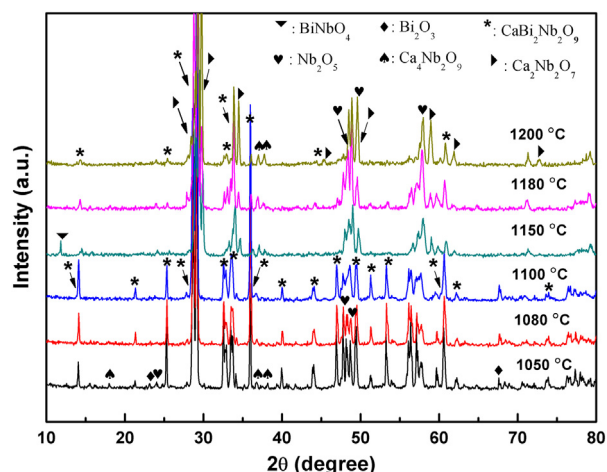


Fig. 1. XRD patterns of BCN ceramics with different sintering temperatures.

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