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Induced anisotropic behavior and enhanced electrical properties on hot-pressed strontium barium niobate ceramics

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ABSTRACT

$Sr_{0.30}Ba_{0.70}Nb_2O_6$ (SBN30) ferroelectric ceramics were fabricated by conventional sintering (CS) and by hot-pressing sintering (HP) and their crystal structure, microstructure, dielectric, ferroelectric and pyroelectric properties were studied and compared. Preferred orientation of the HP ceramics was detected through X-ray diffraction. Dense microstructure virtually free of pores has been achieved in HP samples. Moreover, the HP samples manifested prominent anisotropy in electrical properties. Besides, the relative permittivity (ε_r), saturated polarization (P_s), pyroelectric coefficient (p) in the direction perpendicular to the pressing axis were much higher than those of the randomly oriented CS samples. The HP samples sintered under 200 MPa show excellent pyroelectric properties in the direction perpendicular to the pressing axis, with pyroelectric coefficient of 2.38×10^{-8}C/cm^{2}K and pyroelectric figure of merit of F_i=1.13 pm/V, F_v=1.89 m^2/C and F_d=0.63 μPa$^{-1/2}$, which roughly triple the values obtained in CS samples. These results indicate that hot-pressing is a viable option for accessing single-crystal-like anisotropy as well as enhanced electrical properties in polycrystalline ceramics, thus unveiling the distinctive potential of HP SBN30 ceramics for infrared detector applications.

1. Introduction

$Sr_xBa_{1-x}Nb_2O_6$ (SBN) is a solid solution with the tetragonal tungsten bronze (TTB) structure, for x=0.25–0.75 [1]. It has been widely studied for its excellent electro-optic, piezoelectric, pyroelectric, and photorefractive properties [2–4]. The TTB structure is characterized by the general formula $(A1)_2(A2)_4(C)_4(B1)_{12}(B2)_{18}O_{30}$ which features BO_6 octahedra sharing corners to form a complex array so that three types of interstitial sites (A1, A2, and C sites) are accessible for different cations. In SBN, the Ba^{2+} ion (1.35 Å) predominantly occupies the 15-fold-coordinated A2 sites, the Sr^{2+} ion (1.13 Å) are found to migrate between A2 and 12-fold-coordinated A1 sites depending on the material's composition [5], whereas the 9-fold-coordinated C sites are too small to be taken up and remains empty. As a whole, there are five Sr^{2+} and Ba^{2+} ions distributed over the six available A1 and A2 positions, one of the A-sites remains unoccupied. The compositional flexibility and the crystallographic non-equivalent A1 and A2 sites of TTB structure enable researchers to modify the physical properties of SBN. Therefore, this material can be utilized for various applications.

Considering the global restrictions to lead-based compounds in recent years, SBN has received increasing attention as a potential alternative for lead-based materials for application in pyroelectric infrared detectors. SBN crystals and textured ceramics have been reported to exhibit high pyroelectric coefficient of 5.5×10^{-8} C/cm^{2}K [6] and 4.1×10^{-8} C/cm^{2}K [7] respectively, which are comparable to lead zirconate titanate (PZT) ceramics. Nevertheless, conventionally sintered SBN ceramics have relatively low pyroelectric coefficient due to random orientation and abnormal grain growth. Hence, Doping and utilizing various synthetic techniques have been widely carried out for SBN systems in order to improve their electrical properties [7–11]. Previously, our group found Ca-substitution is capable of enhancing the pyroelectric properties of SBN ceramics [12]. Duran et al. improved SBN ceramics' electrical properties distinctly via templated grain growth method [9]. However, the majority of the research work were concentrated on SBN systems with relatively high Sr/Ba ratio. One of the major drawbacks of these high performance materials is their limited Curie temperature (T_C < 120 °C). Apart from the requirement of excellent electrical properties, higher Curie temperature is also the prerequisite for practical application to prevent the material from depoling during the manufacture and operation processes. Therefore, how to achieve outstanding electrical properties as well as desirable

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high Curie temperature in SBN-based materials deserves further research.

As the Sr/Ba ratio decreases, the transition temperature T_C increases linearly at the expense of its electrical properties [4]. Additionally, it has been reported that hot-working techniques, such as hot-forging and hot-pressing, are effective ways to obtain dense ceramics with preferential orientations and the process is much more simplified than texturing techniques (i.e. templated grain growth or reacted templated grain growth technique).

In the present study, the crystal structure, microstructure, dielectric, ferroelectric, and pyroelectric properties of higher Ba content composition $Sr_{0.30}Ba_{0.70}Nb_2O_6$ (SBN30) ceramics synthesized by conventional sintering (CS) and by hot-pressing sintering (HP) have been studied and compared. And their potential for application in uncooled infrared detectors were further evaluated.

2. Experimental procedure

Powders with the nominal composition $Sr_{0.30}Ba_{0.70}Nb_2O_6$ (SBN30) were prepared using a standard oxide mixture method, with Nb_2O_5 (99.3%), $BaCO_3$ (99%), $SrCO_3$ (99%), and $CaCO_3$ (99%) as raw materials. Stoichiometric amounts of the starting powders were thoroughly mixed by ball milling. The mixture then was calcined at 1200 °C for 3 h to obtain the SBN compound. The calcined powder was ball-milled again, and then mixed with a binder, after which the powders were uniaxially pressed into disks 15 mm in diameter and 2 mm in thickness for the CS samples and cylinders 18 mm in diameter and 18 mm in height for the HP samples. These two types of samples were heated to 800 °C for 2 h to remove binder. Then CS samples were sintered at 1360 °C for 4 h in air and HP samples were placed in a SiC die and surrounded by ZrO_2 powders to sinter at 1260 °C for 4 h under the pressure of 100 ~ 200 MPa.

The natural surface and the optically polished and thermally etched surface of the ceramics were observed by scanning electron microscopy TM3000 (Tabletop Microscope; Hitachi, Japan) and FESEM (S-4800, Hitachi, Japan) respectively. The crystal structures of the CS and HP samples were characterized by X-ray diffraction (XRD, D/MAX-2550V; Rigaku, Tokyo, Japan) using Cu Kα radiation. The bulk density of the sintered samples was measured by Archimedes method. Electric measurements for CS and HP samples were carried out after the samples were polished to 0.5 mm thick and coated with silver electrode on both sides by screen-printing. Particularly, the HP samples were coated in two ways: (i) by applying an electrical field perpendicularly to the pressing axis (labeled as HP⊥), and (ii) by applying an electrical field parallel to the axis (labeled as HP∥). Measurements of the dielectric constant and dielectric loss as a function of temperature were performed in the temperature range from 20 °C to 350 °C using a Hewlett Packard LCR meter. The hysteresis loops of polarization versus electric field (*P-E*) were characterized by applying an electric field of sinusoidal waveform at 1 Hz using a TF Analyzer 2000 (aixACCT Systems GmbH; Dennewartstrasse, Aachen, Germany) assisted with high-voltage power supply (Trek Inc, Medina, NY). A poling treatment was conducted on samples in silicone oil under an electric field of 7 kV/mm at 210 °C for 60 min, and then cooled down to room temperature with the electric field maintained at 7 kV/mm. The pyroelectric properties were studied with a Keithley 6517 A electrometer/high resistance meter while the polarized samples were subjected to heating (at a constant rate of 2 °C/min) inside an oven, similar as the evaluation method reported earlier [4,12].

3. Results and discussion

3.1. Phase and microstructure

Fig. 1 shows XRD patterns of the CS and HP ceramics sintered under different pressures. The diffraction peaks were indexed according to JCPDS39-0265. The patterns revealed that a pure tetragonal tungsten bronze (TTB) structure was formed in all cases. Moreover, many diffraction peaks, such as (001) and (002) exhibited preferred orientation in HP ceramics. We normalized all the diffraction peaks of CS and HP samples and then used the intensity of CS samples as norm to evaluate the preferred orientation degree of HP samples in perpendicular and parallel directions for the convenience of comparison. Detailed results are listed in Table 1. It elucidates that the (001) and (002) clearly been enhanced with higher pressure and the perpendicular direction facilitated the (001) and (002) compared with the parallel direction.

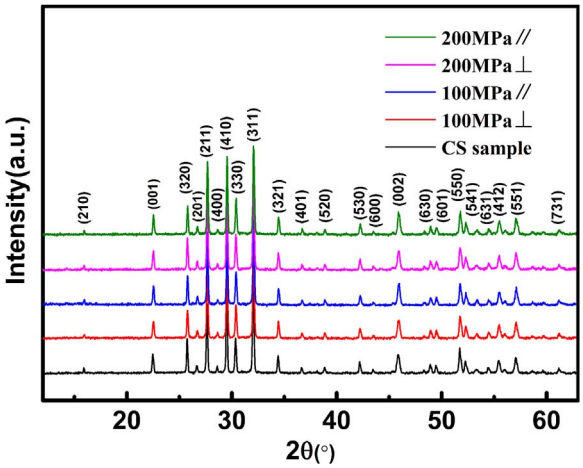

Fig. 1. X-ray diffraction patterns of the CS and the HP SBN30 ceramics.

Since the SBN grains have non-equiaxial shape and grow along the [001] direction [13], the applied pressure restricted the grain growth in the pressing direction and favored the arrangement of [001] oriented grains in the plane perpendicular to the pressing axis, leading to a texture structure to some degree.

Fig. 2 shows a fine microstructure with well-grown grains and clear crystalline boundaries formed both in CS and HP samples. Besides, the shape and size of the grains obtained by the two different sintering processes were similar. However, it is evident that the HP ceramics sintered under higher pressure have a more compact structure than the CS ceramics. The microstructure of 200 MPa⊥samples are virtually free of pores. The relative density of all the samples are listed in Table 2. Overall, hot-pressing increased the ceramic density of SBN70 samples which all reached above 95% of the theoretical density. And it is noted that higher pressure resulted in larger relative density. Such a phenomenon could be ascribed to the strengthened diffusion driving forces provided by the pressure applied during high-temperature sintering.

3.2. Dielectric and phase transition properties

Not only is there a tremendous improvement in the microstructure of these ceramics due to HP sintering, but there is also a considerable enhancement in their electrical performance. Fig. 3 shows the temperature dependence of the dielectric constant (ε_r) and dielectric loss

Table 1
Intensity ratio of diffraction peaks of the CS and the HP SBN30 ceramics.

Samples	Intensity ratio of diffraction peaks I_{HP}/I_{CS}			
	(001)	(211)	(002)	(550)
100 MPa //	0.91	1.01	0.96	0.76
100 MPa ⊥	1.00	1.05	1.15	0.87
200 MPa //	1.02	1.02	1.03	0.90
200 MPa ⊥	1.04	1.05	1.20	0.94