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Pyroelectric and dielectric properties of lead-free ferroelectric $Ba_3Nb_2O_8$ ceramic

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ABSTRACT

The present study highlights ferroelectric phase transition, dielectric, pyroelectric properties and conduction mechanism of highly crystallized barium orthoniobate ($Ba_3Nb_2O_8$) ceramic, prepared by a solid-state reaction technique. X-ray diffraction studies show the formation of a single-phase compound in hexagonal crystal system. Detailed studies of dielectric parameters (ε_r and $\tan\delta$) of the compound as a function of temperature and frequency reveal their independence over a wide range of temperature and frequency. An anomaly in ε_r suggests the possible existence of a ferroelectric–paraelectric phase transition of diffuse-type in the material. The low dielectric loss and moderate relative permittivity make this material (with certain modification) a potential candidate for microwave applications. Studies of pyroelectric properties reveal that the materials have reasonably high figure of merit useful for fabrication of pyroelectric detectors. The low-leakage current and negative temperature coefficient of resistance (NTCR) behavior of the sample have been verified from *J–E* plots. The nature of variation of dc conductivity with temperature confirms the Arrhenius and NTCR behavior of the material.

1. Introduction

The discovery of ferroelectricity and other allied phenomena in Rochelle salt by Valasek [1] in 1921 started a new era for the extensive investigation of dielectric materials of different structural families for possible industrial applications. Out of the large number of ferroelectric materials investigated so far, barium titanate ($BaTiO_3$) of perovskite family has drawn much attention of researchers because of its unusual non-linear properties useful for devices. Some of the simple and complex oxides, derived from perovskite structure, are extensively studied for their greater structural stability [2,3] required for devices. Among all the oxides studied so far, some lead-based perovskites such as $Pb(MgNb)O_3$ (PMN) and $Pb(ZrTi)O_3$ (PZT) were extensively studies to get their excellent dielectric, ferroelectric and pyroelectric properties useful for multilayer capacitors, sensors and actuators [4–8]. However, these lead-based ceramics exhibits compositional fluctuations due to evaporation of PbO. As a result, the mechanical and electrical properties of these materials are greatly affected, and at the same time they create environmental pollution. In order to answer these functional limitations several rare-earth ions-based lead-free oxides such as calcium oxa-metallate have extensively been investigated [9]. In the process of searching new non-toxic oxides, orthometallates of alkaline earth metals with a general formula of $M_3\,(BO_4)_2$ (M = divalent metal and B = pentavalent metal), have attracted much attention of the scientists for their non-toxic nature and promising transport and ferroelectric properties useful for solid-state devices [9]. Recently various metal orthoniobates such as $Ba_3Nb_2O_8$ and $Ba_4Nb_2O_9$ are found to be more interesting because of their structural stability, promising characters and low loss for micro-wave applications [10–12]. These cation-deficient hexagonal (perovskite based) materials with a general formula $M_nB_{n-\delta}O_{3n-x}$ ($\delta \geqslant 1$, $x \geqslant 0$) are prepared by varying the ratio of cubic (c) and hexagonal (h) stacking of (MO_3) layers. With the cationic ratio (*M:B*) as 3:2 (i.e., $n = 3$, $\delta = 1$), one of every three B-sites remain unoccupied and different structures can be formed depending on the composition and extent of anion deficiency [13,14]. Further, with $x = 1$ along with the above condition, the oxygen-deficient cubic (MO_2) layers are formed that force a change in coordination of B atoms from octahedral to tetrahedral. As a result the palmierite structure is expected to be formed from that of the 9R polytypes [15]. Further study on BaO-rich part of the BaO–Nb_2O_5 binary system (i.e., $Ba_3Nb_2O_8$ and $Ba_4Nb_2O_9$) reveals that such compounds decompose at ambient atmosphere and temperature because of their compositional variation with experimental conditions [16]. The defect structure and the presence of Nb^{5+} ions account for its high-temperature ferroelectric and high-electronic conductivity [15].

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Apart from several structural studies on $Ba_3Nb_2O_8$ and other similar compounds, Vanderah et al. [16] reported the phase equilibria and crystal chemistry in the BaO–Nb_2O_5 systems and alumina modified same system. Further Gonzalez et al. [17] studied the cation deficient molybdenum modified BaO-rich system using Raman spectroscopy. The high frequency dielectric properties of $A_5B_4O_{15}$ microwave ceramics was reported by Kamba et al. [18]. Recently, we have reported the structural and electrical properties of $Ba_3V_2O_8$ and $Ba_3Nb_2O_8$ [19,20] of this family.

It is very much clear from the above literature survey that except some work on structural properties, electrical properties and phase equilibria of $Ba_3Nb_2O_8$ and other similar BaO-rich systems [16–20], not much work have been reported on ferroelectric phase transition and pyroelectric properties of the compound. In view of the importance of the material for possible device applications, the present work is an attempt to synthesize lead-free complex perovskite, $Ba_3Nb_2O_8$, by a standard solid-state reaction route and to study its ferroelectric phase transition, pyroelectric properties and conduction mechanism for better understanding of the material.

2. Materials and methods

The lead-free ferroelectric ceramic $Ba_3Nb_2O_8$ was prepared by a high-temperature solid-state reaction route as per the chemical equation: $3(BaCO_3) + Nb_2O_5 \rightarrow Ba_3Nb_2O_8 + 3(CO_2)$. The AR grade precursors; $BaCO_3$ (99%, M/s LOBA Chemie Pvt. Ltd., India) and Nb_2O_5 (99.9%, M/s LOBA Chemie Pvt. Ltd., India), taken in proper stoichiometry, were mixed first mechanically in an agate-mortar and pestle for an hour. This was followed by wet grinding (in methanol) for another hour to get a homogeneous mixture of the constituents. This mixture was finally calcined at 1425 °C (as decided by repeated firing/mixing) for 4 h in air. The formation and quality of the desired compound were checked from the X-ray diffraction (XRD) pattern of the material, recorded at room temperature using a X-ray powder diffractometer (XPERT-PRO, DISIR) with Cu Kα radiation (λ = 1.5405 Å) in a wide range of Bragg angle θ ($0 \leqslant 2\theta \leqslant 60$) at a scanning rate of 2°/min. The calcined powder of the compound was cold pressed into cylindrical pellets (10 mm diameter and 1–2 mm thickness) using polyvinyl alcohol (PVA) as the binder and applying an isostatic pressure of 4×10^6 N/m^2. The pellets were then sintered in oxygen atmosphere at an optimized temperature 1450 °C for 4 h followed by furnace cooling. To perform electrical measurements, both the flat and parallel surfaces of the sintered pellet were electroded with air-drying conducting silver paste and then dried at 150 °C for 8 h to remove moisture (if any). The dielectric and other related parameters were measured as a function of temperature (30–500 °C) and frequency (100 Hz–1 MHz) using a computer-controlled phase sensitive meter (PSM LCR 4NL, Model: 1735, UK), a laboratory-designed sample holder and a small vertical pit furnace. An input signal of constant voltage amplitude ~1 V was applied across the sample for the measurement. The polarization (hysteresis loop) of the poled sample (electric field = 7 kV/cm, time = 8 h) was obtained at different temperatures using a workstation of hysteresis loop tracer (M/S Marine India, New Delhi). The pyroelectric current of the pellet sample was measured at different temperature (30–500 °C) by an electrometer (Keithley Instruments Inc., Model 6517B) at the heating rate of nearly 2 °C/min. A constant voltage was applied across the sample to measure the dc conductivity using the same electrometer.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows XRD pattern of $Ba_3Nb_2O_8$ calcined powder at room temperature. The diffraction pattern shows a number of sharp peaks, different from those of the ingredients. The pattern also reveals better homogeneity and crystallization of the material and thus confirms the formation of a single-phase compound without any significant trace of pyrochlore and any other phase. The well-resolved sharp peaks in the XRD pattern indicate the material is highly crystallized. All observed diffraction peaks of the pattern could be assigned to the hexagonal phase which is in good agreement with the crystallographic data of earlier reported works [16,18]. The lattice parameters of the selected unit cell were refined using the least-squares sub-routine of the standard computer program package "POWD" [21]. These refined lattice parameters are: a = 4.4104(4) Å and c = 21.336(4) Å, where the number in the parenthesis denotes the standard deviation of unit cell parameters. Using refined lattice parameters, each peak was again indexed, and interplanar spacing (d) of reflection planes of the compound was calculated, and compared with its observed value (Table 1). The refined unit cell parameters with proposed crystal structure (hexagonal) of the sample are very much consistent with those reported earlier [16,18]. The contributions of strain and other effects in the broadening of XRD peaks and crystallite size calculation have been ignored due to the use of powder sample [22].

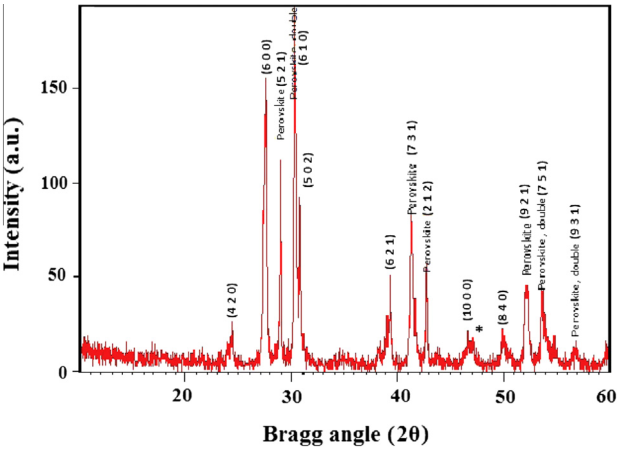

Fig. 1. XRD pattern of $Ba_3Nb_2O_8$ at room temperature.

3.2. Dielectric properties

The basic study on electrical properties of materials reveals that their dielectric parameters are not only dependent on their geometry and temperature, but also on the frequency of applied electric field. Fig. 2(a) shows the variation of dielectric constant (ε_r) of $Ba_3Nb_2O_8$ with temperature at some selected frequencies (10 kHz and 500 kHz). The decrease in ε_r with increasing frequency is a general feature of dielectric materials [23]. For a given frequency the value of ε_r is almost constant over the low temperature range (from room temperature to about 150 °C). With further increase in temperature, it increases gradually to its maximum value (ε_{max}) and then decreases. This dielectric anomaly observed at 357 °C suggests the transition from the ferroelectric to paraelectric phase and usually referred as transition temperature (T_c) [20,24]. Above T_c, the increase of ε_r (at lower frequencies) may be attributed to space charge polarization arising from mobility of ions/imperfections in

Table 1
Comparison of d_{obs}, d_{cal} and Miller indices of XRD peaks.

Sl. no.	2θ (degree)	Miller indices			d-Spacing	
		h	k	l	d_{obs}	d_{cal}
1	24.36	4	2	0	3.6508	3.6555
2	27.61	6	0	0	3.2280	3.2239
3	28.86	5	2	1	3.0909	3.0974
4	30.26	6	1	0	2.9510	2.9498
5	30.85	5	0	2	2.8959	2.9083
6	39.25	6	2	1	2.2933	2.2918
7	41.40	7	3	1	2.1791	2.1763
8	42.76	2	1	2	2.1129	2.1113
9	46.91	10	0	0	1.9352	1.9343
10	49.86	8	4	0	1.8274	1.8278
11	52.21	9	2	1	1.7505	1.7496
12	53.62	7	5	1	1.7077	1.7082
13	57.14	9	3	1	1.6472	1.6470