Structural properties of inorganic materials: tungsten bronze SBN ceramics

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MS received 29 March 1995; revised 27 September 1995

Abstract. Rare-earth doped strontium barium niobates were synthesized using usual ceramic technique. The dopants are La, Ce, Gd, Sm and Nd. The materials were characterized by XRD and density measurements. The grain sizes were determined from SEM analysis. Lattice parameters changed uniformly with rare-earth dopants in unfilled structures. Density measurements and SEM analysis confirmed only minute changes in the densities of the ceramics.

Keywords. Strontium barium niobates; rare-earth dopants; pyroelectric properties; piezoelectric properties; microstructures.

1. Introduction

There are 32 crystal classes each representing a particular type of unit cell. Out of 32, 20 have no centre of symmetry and thus are piezoelectric. Half of these 20 are polar and exhibit pyroelectric behaviour with high pyroelectric coefficient. Modified/unmodified strontium barium niobates (SBN) are the best for pyroelectric applications. Strontium barium niobate, $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ has been extensively studied by Framcombe and Lewis (1958), Jamieson *et al* (1968), Glass (1969) and Liu and Maciolek (1975) in single crystal form for pyroelectric applications using rare-earth dopants. Liu and Maciolek (1975) prepared SBN single crystals with Sr/Ba ratio of 0.49/0.51 and they reported a transition temperature (T_c) of 120°C and pyroelectric coefficient of $6 \times 10^{-8} \text{ C/cm}^2/^{\circ}\text{C}$ and other crystals doped with Pb^{2+} lowered the pyroelectric coefficient and raised the T_c to 124°C. They also reported ferroelectric and pyroelectric properties of rare-earth modified $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$. The modified materials exhibited twice the pyroelectric coefficient and four times dielectric constant of unmodified SBN materials. This clearly indicates that the modified SBN are suitable for array pyroelectric IR detector applications.

Jimanez *et al* (1976) reported the ferroelectric $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ in the ceramic form with various cations (Fe^{3+} , Mn^{4+} , Cr^{3+} and La^{3+}) as dopants. The most remarkable effect they observed was the broadening of dielectric constant i.e. ferroelectric relaxation, lowering of transition temperatures and dielectric loss. Vaivod *et al* (1977) investigated the dielectric and electro-optic properties of SBN modified with yttrium (Y), La and Ti. They observed that La^{3+} lowered the T_c while Y had hardly any effect. Another modified SBN ($\text{Sr}_{1-x}\text{Ba}_y)_{0.8}(\text{K}_{1-x}\text{Na}_x)_{0.4}\text{Nb}_2\text{O}_6$ with $x = 0.5$ and $y = 0.25$ was studied for the effect of stuffing the vacant A1, A2 and C sites. The transition temperature was observed to raise to 175°C and pyroelectric coefficient was found to be $4.3 \times 10^{-8} \text{ C/cm}^2/^{\circ}\text{C}$.

In the present study, undoped and Gd, Sm, Nd, La and Ce doped SBN were prepared and the effect of rare-earth ion substitution on the morphology of fractured surfaces of ceramic compacts have been examined.

2. Experimental

2.1 Synthesis of ceramics

The raw materials SrCO_3 , BaCO_3 , Nb_2O_5 and R^{3+} (rare-earth ion) with 99.99% purity were used for the preparation of pure and rare-earth modified SBN. The general process adopted to yield the following composition of unfilled structures was given in

Figure 1. A–C.

Figure 1. X-ray diffraction pattern of (A) $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$; (B) $\text{La}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$; (C) $\text{Ce}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$; (D) $\text{Nd}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$; (E) $\text{Sm}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$; (F) $\text{Gd}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$.

our earlier paper (Umakantham *et al* 1994):

where R = Gd, Sm, Nd, Ce, and La.

Table 1. Physical parameters of doped and undoped SBN ceramics.

Dopant	T_c (°C)	Lattice parameters		Reflections $h k l$	Volume $A \times 10^{-24}$ cc	Measured density	Theoret. density
		a (Å)	c (Å)				
Pure	94.75	12.4650	3.9438	240, 121	612.7727	5.012	5.267
La	55	12.4942	3.9343	140, 001	614.1640	4.952	5.158
Ce	70	12.4450	3.9050	140, 131	604.7986	5.132	5.239
Nd	80	12.5280	3.9433	140, 231	618.9040	5.100	5.123
Gd	110	12.5868	3.9907	240, 121	632.2367	5.112	5.158
Sm	115	12.4683	3.9578	240, 401	615.2736	4.953	5.025

According to the following solid state reaction,

the required amounts of individual carbonates and oxides were taken and mixed in ball mill for 48 h in the presence of excess of methanol to improve the homogeneity and calcined at 700°C for 3 h in alumina crucibles. The mixture was reground and pelletized into circular discs under 2–3 PSI after adding a few drops of polyvinyl alcohol as binding agent. Finally they were sintered in a closed platinum crucible at 1300°C in air for 1 h and the so formed discs were subjected to the measurement of bulk density and grain size.

2.2 Powder X-ray diffraction

The ceramic compacts were made into powder and characterized by X-ray diffraction. The diffraction patterns for all the compositions were recorded using Philips X-ray diffractometer with CuK_α radiation operating at 25–30 mA current with nickel filter at a slow scan rate of 1°/min. The patterns are shown in figure 1. The d spacings and the peak intensities were compared with the standard values of SBN material (JCPDS card no. 6–0452). (The lattice constants a and c were calculated using (1) below for tetragonal symmetry and the values obtained are (table 1)

$$1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2. \quad (1)$$

The diffraction patterns were identified as belonging to the tungsten bronze structure with tetragonal symmetry.

2.3 Density measurements

The bulk densities of the compacts were measured by the usual liquid displacement method. Theoretical densities were calculated from the cell constants using (2) below. The cell constants a and c were calculated from the XRD data.

$$D_{\text{cal}} = MZ/NV, \quad (2)$$

where M is the formula weight of the composition, N the Avogadro number, V the unit cell volume and Z the number of formula units per unit cell of the crystal structure. The

value of Z is 5 for the tungsten bronze structure. The experimental density was then compared with the literature values.

2.4 Grain size measurements

The scanning electron micrographs (SEM) were taken on fractured surfaces of the discs

Figure 2. A–C.

Figure 2. Scanning electron micrographs of (A) $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ ($\times 2000$, $10\ \mu\text{m}$); (B) $\text{La}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$ ($\times 5000$, $5\ \mu\text{m}$); (C) $\text{Ce}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$ ($\times 5000$, $5\ \mu\text{m}$); (D) $\text{Nd}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$ ($\times 5000$, $5\ \mu\text{m}$); (E) $\text{Sm}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$ ($\times 7500$, $5\ \mu\text{m}$); (F) $\text{Gd}_{0.06}\text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$ ($\times 5000$, $10\ \mu\text{m}$).

to study the morphology for the determination of the average grain size by the linear intercept method (Subbarao *et al* 1969; Umakantham *et al* 1994). The micrographs of all the six compositions are given in figure 2.

3. Results and discussion

3.1 Structural parameters

The basic requirement for the material to be ferroelectric is ferroelectric–paraelectric phase transition. This was observed (Umakantham *et al* 1987) (figure 3) by measuring the capacitance values at each temperature in all the compositions at 1 MHz frequency. All the dielectric constant vs temperature curves obeyed Curie–Weiss law in the para region (the region above the Curie temperature) and these curves have broad maxima which is a characteristic of diffuse phase transition. The curves are more broadened in rare-earth doped compositions. The diffuse nature is well observed in many relaxor ferroelectrics (RFE). The relaxor theory on ferroelectrics reveals that RFE are composed of chemically heterogeneous materials which should have a range of ferroelectric–paraelectric transition temperature. The Curie–Weiss constant depends on dimension, density and porosity of the ceramic compacts having higher values than those of single crystals. The diffraction peaks are analyzed and identified as belonging

Figure 3. Dielectric constant as a function of temperature in pure and modified SBN ceramics.

to tetragonal tungsten bronze $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (JCPDS card No 22-931972). The observed d spacings and peak intensities (I/I_0) are presented for pure sample, i.e. $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$. Both these structures are unfilled which facilitates for accommodating cations into vacant A sites. The crystallographic constants a and c calculated for all the samples are presented in table 1 against each composition. The reflections (h, k, l) used and unit cell volume are also presented.

The lattice constants of the tetragonal phase change uniformly in the unfilled structures with the doping cations. For example, the a spacing for pure SBN is $12.465 \text{ \AA}$ and for the smallest ionic radii doped, i.e. GdSBN is $12.5868 \text{ \AA}$ and further it reduces to $12.4450 \text{ \AA}$ as the ionic radii of the rare-earth increases. Similarly c value for pure SBN is $3.9438 \text{ \AA}$ and for the GdSBN $3.9907 \text{ \AA}$ decreased to a value of $3.905 \text{ \AA}$ for CeSBN. The axial ratio, i.e. $\sqrt{10}c/a$ is very close to unity which is the characteristic of SBN ceramics with tetragonal geometry in both filled and unfilled structures. But the lattice constants in filled compositions (Chandramouli 1993) do not change uniformly due to the occupancy of different ions. The monovalent cations like K^+ and Na^+ normally enter the A1 and A2 sites whereas Li^+ enters only smaller C site. The axial ratio is plotted against transition temperature in figure 4. The variation of c/a vs T_c is linear with

Figure 4. Curie temperature vs axial ratio in pure and modified SBN ceramics.

Table 2. Structural parameters of filled and unfilled compositions.

Composition	Unit cell	A	$A + RE$	Ionic radii of RE (Å)	Axial ratio $10c/a$	Average grain size (μm)
unfilled SBN compositions						
$\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ (undoped)	$\text{Sr}_{3.05}\text{Ba}_{1.95}\text{Nb}_{10}\text{O}_{30}$	5	5	—	1.0	2.4183
$\text{La}_{0.06}\text{NaK(SBN)}^u$	$\text{La}_{0.30}\text{NaK(SBN)}^u$	5.20	5.50	1.02	0.995	1.7361
$\text{Ce}_{0.06}\text{NaK(SBN)}$	$\text{Ce}_{0.30}\text{NaK(SBN)}$	5.20	5.50	1.03	0.992	1.8472
$\text{Nd}_{0.06}\text{NaK(SBN)}$	$\text{Nd}_{0.30}\text{NaK(SBN)}$	5.20	5.50	0.99	0.995	1.6891
$\text{Sm}_{0.06}\text{NaK(SBN)}$	$\text{Sm}_{0.30}\text{NaK(SBN)}$	5.20	5.50	0.96	1.004	1.2736
$\text{Gd}_{0.06}\text{NaK(SBN)}$	$\text{Gd}_{0.30}\text{NaK(SBN)}$	5.20	5.50	0.93	1.003	1.0452
filled SBN compositions						
$\text{Sr}_{0.48}\text{Ba}_{0.32}\text{Na}_{0.2}\text{Li}_{0.2}\text{Nb}_2\text{O}_6$		6	—	—	1.0002	1.95
$\text{Sr}_{0.48}\text{Ba}_{0.32}\text{Na}_{0.2}\text{K}_{0.2}\text{Nb}_2\text{O}_6$		6	—	—	1.0040	2.71
$\text{Sr}_{0.42}\text{Ba}_{0.28}\text{Na}_{0.225}\text{K}_{0.225}\text{Nb}_2\text{O}_6$		6	—	—	0.9977	2.64

$\text{NaK(SBN)}^u = \text{Na}_{0.12}\text{K}_{0.14}\text{Sr}_{0.48}\text{Ba}_{0.30}\text{Nb}_2\text{O}_6$
 $\text{NaK(SBN)}^f = \text{Na}_{0.60}\text{K}_{0.70}\text{Sr}_{2.40}\text{Ba}_{1.50}\text{Nb}_{10}\text{O}_{30}$
 A = Number of filled sites

a positive slope and similar trend was observed in alkali rare-earth niobates (Giess *et al* 1969).

Doping by cations play an important role in modifying the structure, phase transition and electrical properties. For example, in pure SBN, the transition temperature is 94.7°C . By doping with monovalent cations Na^+ and K^+ leading to a filled structure (Chandramouli *et al* 1986), the T_c is raised to 217°C . Further the T_c is drastically reduced by more than 100°C by doping with rare-earth ions in all the compositions (table 1). The rare-earth ions can also occupy the smaller C sites leading to A vacancies in TB structure. This in fact facilitates sintering by diffusion mechanism. Jimenez *et al* (1976) reported a decrease in T_c of $\sim 55^\circ\text{C}$ for $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (unfilled ceramics) with very small amounts of Mn, La and Cr.

Also it is interesting to compare these structural parameters of unfilled with filled structures corresponding to the formula $\text{A}_6\text{B}_{10}\text{O}_{30}$. The data on both filled and unfilled structures are presented in table 2.

By comparing the values in the above two tables it is understood that the extent of occupancy of A sites plays a crucial role in determining the transition temperature. Compared to the sharp decrease in T_c in substitutional solid solutions with A vacancies, the transition temperature changes only to a small extent when the A sites are filled. This difference must be attributed to the influence of stuffing excess ions into A sites. Also it may be due to the low frequency vibrations that can be naturally associated with positional disordered impurity vacancies and non-stoichiometry as observed by Burns and Burnstein (1974). Creation of A site vacancies lowers the Curie temperature at a rapid rate. This is quite a fact when the Nd^{3+} doped compositions in the two tables are seen together. The Curie point is lowered less strongly with substituents that increase the degree of filling of A sites. Similar results were observed in lead based TB ceramic structures (PbNb_2O_6) (Subbarao and Shirane 1960). These data demonstrate that the variation of number of vacancies in TB structure is a useful means of controlling the physical properties of this interesting family of ferroelectrics.

3.2 Microstructure

The microstructural study of a material can provide information regarding the morphology and distribution of phases as well as the nature and pattern of certain crystal imperfections. The nature of phase transformation has a profound influence on the microstructure of a material. The most general characteristic of a microstructure is the presence of boundaries between the phases and/or grains that comprise the material. These boundaries are very important because they affect structure-sensitive properties like dielectric, piezoelectric and pyroelectric properties. The amount of internal boundary area within a material with a reasonable degree of accuracy can be calculated by a relatively simple procedure following (3)

$$S_v = 2P_L, \quad (3)$$

where S_v is the boundary area (cm^2 per unit volume) and P_L the boundaries traversed per cm of random line across the microstructure (Saltykov 1958; Underwood 1961).

During the usual processing of ceramics, crystalline or non-crystalline powders are compacted and fired at a temperature sufficient to develop useful electrical properties. During firing, in the initial process a change may occur due to decomposition or phase transformation may take place; on further heating gradually some other changes occur commonly to give a reduction in porosity. They are (i) change in pore size and number of pores, (ii) increase in grain size, and (iii) change in pore shape. In fact, grain growth is the process by which the average grain size of strain free or nearly strain free material increases continuously during firing without change in grain size distribution.

The simplest microstructural change is grain growth in single phase materials. Grain growth occurs during densification of powder compacts (Lanze and Kellett 1989). The grain growth in dense ceramic materials is associated with grain boundary motion. The driving force is the energy reduction as an atom/ion moves across the boundary from the grain with convex surface to the grain with the concave surface (Fulrath and Pask 1966). Because of the curvature in the formation of grains, the chemical potential is greater on one side of the boundary and the potential causes atoms or ions to rearrange. In the concave location, the atom has more neighbours and therefore lowers potential energy. In turn, the boundary moves towards the centre of curvature thereby reducing its total area.

Figure 3 shows the micrographs of typical rare-earth doped (figure 2B–F) and undoped (figure 2A) ceramics processed under similar conditions. The average grain diameter (grain size) was calculated by linear intercept method. In this method a number of parallel lines are drawn across the micrograph. The number of intercepts were counted and the grain size (GS) was calculated using (4) below.

$$GS = L/I * M, \quad (4)$$

where L is the total length of line, I the number of intercepts and M the magnification. The calculated values are presented in table 2.

The average grain diameter decreases when rare-earth ion is doped. But the grain size was found to increase with increase in the ionic radii of the dopants in the unfilled structures. The micrographs indicate that there is not much change in the pore volume. It is also clear that the grains are partly smooth and partially rounded in some of the samples. This is supported by the observation of slightly larger grains here and there.

From the above observations and the morphological changes of the grains, the grain growth and smoothening of the grains may be controlled by the volume and surface diffusion mechanisms, respectively. This also supports very small changes in the specimen densities (calculated densities) in all the compositions.

4. Conclusions

- (i) Tungsten bronze ceramic materials are very useful in pyroelectric applications.
- (ii) SBN ceramics have high pyroelectric coefficients as reported by earlier researchers both in single crystal and in ceramic materials. Comparative study of filled and unfilled structures is interesting.
- (iii) Grain growth in the present SBN ceramics is uniform and sensitive to the additive cations. The electrical properties can partially be controlled by this type of growth mechanism.
- (iv) The present study can be extended to other cationic dopants for PTC and pyroelectric IR detector applications.

Acknowledgement

One of the authors (KUK) thanks the CSIR, New Delhi for awarding a Research Associateship (1990) and Pool Officer (1995).

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