



Structural distortion and phase transition studies of Aurivillius type $\text{Sr}_{1-x}\text{Pb}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ ferroelectric ceramics

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Abstract

In this paper, effects of lead doping on the lattice response and phase transitions of $\text{Sr}_{1-x}\text{Pb}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ ($x=0.0-0.5$ in steps of 0.1) ferroelectric ceramics are reported. It is observed that structure attains more tetragonality with doping of lead up to 40%. Increased orthorhombic distortion is observed for undoped SBN and 50 at.% lead substituted SBN. Phase transitions for all samples were studied using Curie temperature measurements and are explained in terms of lattice response of these ceramics. Sample with $x=0.5$ shows decreased tetragonal strain and Curie temperature. Relationship of polarization with lattice response is discussed.

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1. Introduction

Layered ceramics have received a lot of attention because of their applications in non-volatile random access memories, ceramic multilayer capacitors, etc. [1–3]. In 1950s, Aurivillius synthesized a new series of layered ceramics, which contained bismuth layer as a structural constraint. These ceramics have advantage over lead based zirconia ceramics as the later undergo degradation in charge storage properties with the application of electric field. Bismuth layered ceramics show degradation in storage properties after about 10^{12} cycles whereas lead based ceramics suffered loss in switching charge after about 10^6 cycles. The role of bismuth layer in influencing the electrical and ferroelectric properties of these ceramics has been

found to be crucial. This layer is reported to be paraelectric in nature while perovskite unit cell structures are ferroelectric. Modifications in these ceramics by doping to improve the properties of Aurivillius type of ceramics have been a matter of interest. These ceramics show high value of Curie temperature and fatigue resistance, but suffer from high dielectric loss and low dielectric constant for which presence of free charges in the structure is believed to be the cause. Among bismuth layer ceramics, $\text{SrBi}_2\text{Nb}_2\text{O}_9$ and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ have drawn special attention of researchers because of their high fatigue resistance and less distorted structure as compared to those of other bismuth layer Aurivillius ceramics [4]. The authors felt a need for detailed investigation of the influence of the structural properties like tetragonal strain (c/a ; strain along c -axis), orthorhombic distortion (b/a) (deviation from tetragonal structure, i.e. $b/a=1$; minimum distortion) and orthorhombicity [$2(a-b)/(a+b)$] which is a measure of orthorhombic nature of a structure, on the phase transitions of Aurivillius ceramics [5–7,22]. In the present work, $\text{Sr}_{1-x}\text{Pb}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ ceramics

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are studied for doping concentrations of lead up to $x=0.5$ (in steps of 0.1). Curie temperature (T_c) of all the prepared samples is measured and is explained in terms of obtained structural properties. Spontaneous polarization (P_s) is calculated using the difference in lattice constants calculated from observed d-values through X-ray diffractograms. Possibility of linearity between Curie temperature and Spontaneous polarization values proposed by Desu et al. [8] have been examined.

2. Experimental

Samples were prepared using solid-state reaction method taking SrCO_3 , PbO , Bi_2O_3 and Nb_2O_5 (all from Aldrich) in stoichiometric proportions. Mixtures were calcined at 900°C in air. Powdered samples were mixed with polyvinylalcohol (Aldrich) solution in two wt. percentage proportions and then molded into disc shape pellets by applying a pressure of 270 MPa. Pellets were sintered at 1150°C for 2 h. X-ray diffractograms were taken for all the calcined and sintered samples on Philips X-ray diffractometer PW 1710 using Cu K_α radiation of wavelength 1.54439 \AA in the range $10^\circ \leq 2\theta \leq 70^\circ$ at a scanning rate of $0.05^\circ/\text{s}$. All the pellets were coated using silver paste and cured at 600°C for half an hour. Curie temperature measurements at a frequency of 100 KHz were taken on an HP 4192A Impedance Analyzer operating at oscillation level of 1 V.

3. Results and discussion

Analysis of the powder X-ray diffraction patterns, collected using a diffractometer, confirmed that all samples coexist in tetragonal and orthorhombic symmetry and the peaks could be indexed in space group $14mmm$ [9]. The position and intensity of intense peaks in X-ray diffractograms suggested the formation of perovskite structure in all the sintered samples. X-ray diffractograms of sintered samples with $x=0.0, 0.3, 0.4$ and 0.5 are shown in Fig. 1. Some variation in the intensities of peaks and the shifts in the positions of certain peaks have been observed which can be attributed to the variation in lattice distortions in the

samples [10]. Lattice parameters, shown in Table 1, are calculated from the obtained d-values and are used to calculate structural distortion parameters such as orthorhombicity, tetragonal strain and orthorhombic distortion. For these calculations, unit cell was treated as orthorhombic [11] and peaks (200), (0010) and (110) were chosen for this purpose. No systematic variation in lattice parameters is observed, which may be attributed to the structural inhomogeneity. Such behavior has also been reported by others [12,14]. All the doped samples are observed to possess lower values of lattice constants a and c as compared to those for undoped $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN). The value of b , however, is higher for all the doped samples. The site occupancy of lead atoms in the studied structure can be explained on the basis of the ionic radius of atoms, coordination number and bond strengths. The values of these parameters are given in Table 1. It can be assumed that due to very small difference in the ionic radius of lead and strontium and due to their identical coordination number, substitution of lead onto strontium sites is most favourable. Possibility of substitution onto the niobium sites, i.e. on the octahedral sites is unlikely because of greater bond strengths of niobium with oxygen [13]. Also, consideration based on coordination number does not favour lead occupying bismuth sites. Lead not going to the bismuth or niobium sites is further supported by the observation that lattice constants a and c show an overall decrease with increasing lead concentration.

Structural properties are studied through the calculations of tetragonal strain and orthorhombicity. Tetragonal strain increases slowly with doping up to 40 at.% and decreases rapidly for 50 at.% concentration (Fig. 2). Cohen and others [14,16] explained that incorporation of lead onto A-sites in perovskite structures should increase tetragonality of the structure, the reason for which has been attributed to the covalent nature of Pb–O bond, which is hybridizing. In these structures, strontium forms ionic bond with neighbouring oxygens. This according to Cohen and others favours orthorhombicity of crystal system. The same is observed in present work, samples with 10–40 at.% lead content show more tetragonal strain and less orthorhombicity. Therefore, it can be assumed that incorporation of lead increased tetragonality of structure up to 40 at.% substitution. Whereas for 50 at.% substitution, structure possibly suffer

Table 1
Ionic radius (IR), coordination number (CN), bond energy (B.E.) of elements [15] with oxygen and lattice parameters with composition x

	IR (\AA)	CN	B.E. (kJ/mol)	Composition (x)	a (\AA)	b (\AA)	c (\AA)
Sr^{2+}	1.44	12	426	0.0	3.945	3.798	25.475
Pb^{2+}	1.49	12	382	0.1	3.919	3.941	25.336
Nb^{5+}	0.64	6	771	0.2	3.920	3.931	25.350
Bi^{3+}	0.96	5	337	0.3	3.923	3.950	25.405
				0.4	3.912	3.916	25.409
				0.5	3.940	3.860	25.209

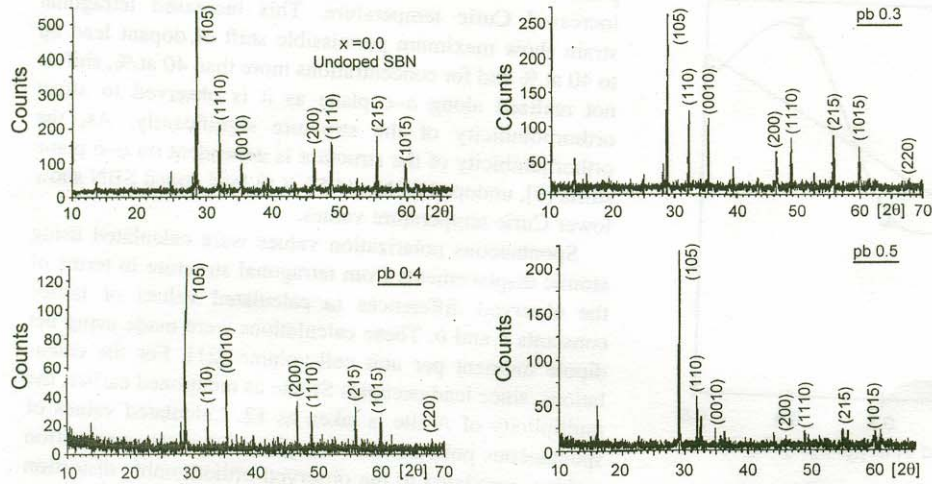


Fig. 1. X-ray diffractograms of stoichiometric SBN and 30–40–50 at.% lead doped samples.

equivalence of hybridization (Pb–O) with ionic interaction (Sr–O) in structure. For $x=0.5$ substitution lattice strain is released possibly due to two opposite interactions of equal magnitudes. Samples with 10–40 at.% lead samples show almost tetragonal nature, whereas undoped and 50 at.% samples are found to possess maximum orthorhombic nature. As these bismuth layered ceramics are known to coexist in tetragonal phase (elongated structure along the $a-c$ plane) and orthorhombic phase (elongated structure along $a-b$ plane) [17], it is, therefore, concluded that $x=0.1, 0.2, 0.3, 0.4$ lead doped samples had dominant tetragonal nature whereas undoped and 0.5 doped samples are primarily orthorhombic.

Phase transitions of all the sintered samples are studied by finding the Curie temperature from the dielectric constant versus temperature curves at 100 KHz (Fig. 3). The temperature at which the phase transition occurs corresponds to Curie temperature of the sample. At 100 KHz frequency, dielectric constant is the result of only ionic and

electronic contributions and space charge and dipolar polarization are saturated [18]. Room temperature dielectric constant value increases from 116 for SBN to 172 for 0.5 sample. This suggests that probably hybridizing nature of Pb–O bond promotes electronic polarization in the structure, which results in ordering in the lattice. Further dielectric studies of these ceramics are in progress and will be reported soon. As evident from Fig. 3, all the samples undergo only one phase transition in the studied temperature range. It is observed that Curie temperature increases from 437 °C (for undoped SBN) to 476 °C for 40 at.% doped sample. Slight decrease in Curie temperature 468 °C is observed for 50 at.% doped SBN (Fig. 4). This decrease in Curie temperature can be explained on the basis of reduced tetragonal lattice strain discussed earlier. Lattice strain is known to restrict the domain wall motion thereby effecting

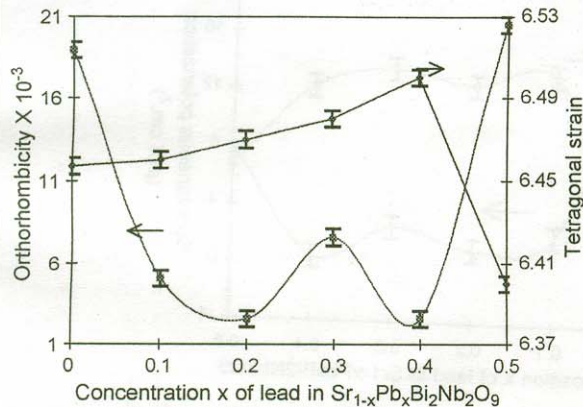


Fig. 2. Orthorhombicity and tetragonal strain of undoped and lead doped SBN.

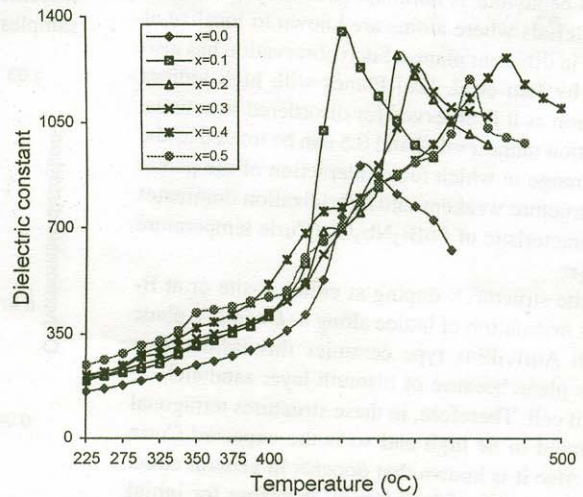


Fig. 3. Dielectric constant versus temperature plots of $Sr_{1-x}Pb_xBi_2Nb_2O_9$; ($x=0.0-0.5$).

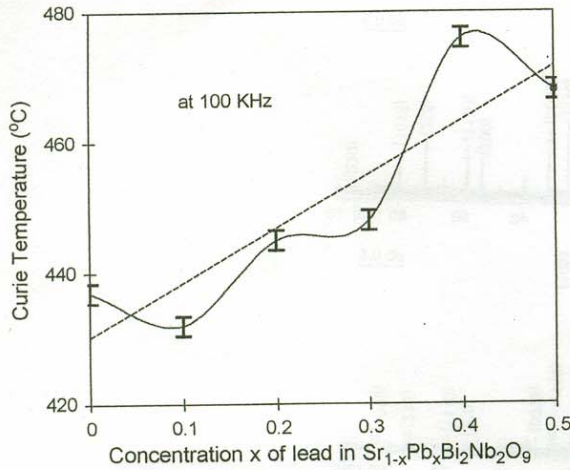


Fig. 4. Compositional variation of Curie temperature.

the phase transition. Therefore, during phase change greater thermal energy is required to carry out the phase transition. The variation of Curie temperature with composition is shown in Fig. 4, which is similar to tetragonal strain behaviour (Fig. 2) with composition and justifies the explanation. Large value of tetragonal strain and Curie temperature for 40 at.% lead content is possibly due to its maximum permissible change in rattle space available between the octahedrons and in this condition the bismuth layer is highly constrained [19]. No explanation is obvious at the moment for the observed decrease in Curie temperature for $x=0.5$ sample. However, if the trend is studied in Fig. 4 then an increase in Curie temperature should have been observed. A decrease in homogeneity of $x=0.5$ sample can also be estimated from the X-ray diffractogram where X-ray peaks at higher 2θ values are almost suppressed and intensity of low 2θ peaks is increased. This behaviour is normally shown by disordered amorphous materials where atoms are known to localize at particular sites in different planes. Such observation has also been reported by Jain et al. [20] Planes with high indices show suppression as it is observed for disordered structures. The concentration range $x=0.4$ and 0.5 can be treated as the concentration range in which ionic interaction of the parent $\text{SrBi}_2\text{Nb}_2\text{O}_9$ structure weakens and hybridization dominates which is a characteristic of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (Curie temperature is 527°C [10]).

In perovskite structures, doping at either A-site or at B-site influences orientation of lattice along $a-b$ and $a-c$ plane equally but in Aurivillius type ceramics this influence is limited to $a-c$ plane because of bismuth layer sandwiching perovskite unit cell. Therefore, in these structures tetragonal strain is observed to be high and so is the expected Curie temperature. Also it is known that dopants in general affect the electrical properties of host lattice, therefore for initial concentrations of lead up to 40 at.% role of bismuth layer is significant as the alignment of atoms is observed along $a-c$

plane in terms of the increased tetragonal strain, i.e. the increased Curie temperature. This increased tetragonal strain show maximum permissible shift of dopant lead up to 40 at.% and for concentrations more than 40 at.%, shift is not realized along $a-c$ plane as it is observed to affect orthorhombicity of the structure significantly. As, the orthorhombicity of the structure is dependent on $a-b$ plane shifts [9], undoped SBN and 50 at.% lead doped SBN show lower Curie temperature values.

Spontaneous polarization values were calculated using atomic displacements from tetragonal structure in terms of the observed differences in calculated values of lattice constants a and b . These calculations were made using net dipole moment per unit cell-volume [21]. For the calculations, since lead occupies Sr-site as mentioned earlier, the multiplicity of A-site is taken as 12. Calculated values of spontaneous polarization were plotted against composition and are correlated to the observed orthorhombic distortion (Fig. 5). Good agreement is observed for the above two parameters. In addition, these calculations support the phase transition studies. It follows from the present work that Curie temperature does not vary linearly with spontaneous polarization as has been suggested by others [8] for SBN ceramics because of high degree of structural inhomogeneity offered by the octahedrons. Similar observation was reported by Shimakawa et al. [22] in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ for different A-site cation substitution and Ismunandar et al. [14] in $\text{PbBi}_2\text{Nb}_2\text{O}_9$.

4. Conclusions

It is concluded from the present work that lead doping onto the sites of strontium reduces lattice distortions of $\text{Sr}_{1-x}\text{Pb}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ (SPBN) as the value of x increases up to 0.4. Orthorhombic state is favoured in $x=0.0$ and 0.5 samples. Increase in tetragonal strain and Curie temperature of samples up to 40 at.% concentration of lead is attributed to

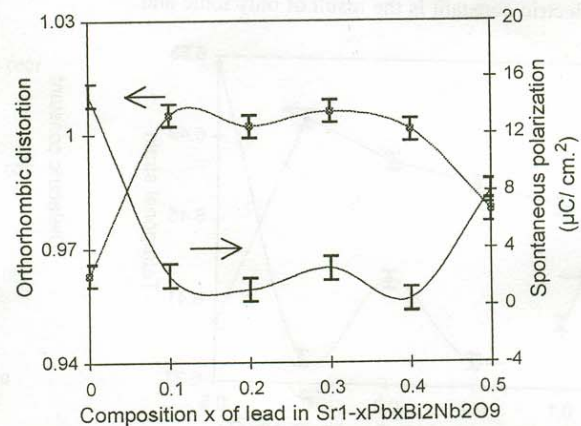


Fig. 5. Orthorhombic distortion and spontaneous polarization P_s of $\text{Sr}_{1-x}\text{Pb}_x\text{Bi}_2\text{Nb}_2\text{O}_9$; ($x=0.0-0.5$).

reduced lattice distortions. Calculated values of spontaneous polarization are higher for undoped and 50 at.% doped samples for which increased orthorhombic distortion is believed to be the cause.

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