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Influence of lone pair on structural and electrical properties of Sb substituted Bismuth layered $SrBi_2Nb_2O_9$ ceramics

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HIGHLIGHTS

- Enhanced stereochemistry effect of $5s^2$ lone pair electron on dielectric property.
- The increase in lattice parameter 'c' due to structural rearrangement is discussed.
- Reduced grain growth results in decreased density due to secondary phases.
- Decreased dielectric constant due to atomic size effect and secondary phases.

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ABSTRACT

Antimony (Sb) substituted Strontium Bismuth Niobate ceramics with chemical formula $SrBi_{2-x}Sb_x Nb_2O_9$ (SBSN) have been prepared through conventional solid state reaction method with varying Sb content in the range ($x = 0.0$ to 0.5). Limited solubility of Sb content in SBN ceramics were revealed through X-ray diffraction studies which indicates secondary phases of Sb_2O_3 in prepared ceramics for Sb content $x > 0.2$. Formation of single phase with orthorhombic structure were confirmed for compositions having $x = 0.0$ to 0.2. Increase in *c*-axis of lattice crystal are analyzed and correlated to the ionic structure and existence of lone pair in Sb. Dielectric properties of all SBSN ceramics compositions are studied as a function of temperature over the frequency range of 100 Hz–1 MHz. Increase in Sb incorporation shows insignificant shift in Ferroelectric to Paraelectric Phase transition Temperature in SBSN ceramics. Sb substitution results in the increase in ferroelectricity ($2P_r = 15.4\ \mu C/cm^2$) and poiezoelectric coefficient ($d_{33} = 20$ pC/N) for composition having $x = 0.1$ in SBSN ceramic. Sb substitution results in increase of piezoelectric coefficients (d_{33}) whereas piezoelectric charge coefficient values for composition $SrSb_{0.1}Bi_{1.9}Nb_2O_9$ was found to be comparable to that of PZT at room temperature. Existence of lone pair of electron in Antimony were correlated with high piezoelectric coefficient in SBSN ceramics.

1. Introduction

Bismuth Layered Structured Ferroelectric (BLSF) materials display high temperature tolerance properties which are technologically important for various device application such as thermally stable capacitors, microwave applications, positive temperature coefficient devices, piezoelectric transducers, actuators and photonic devices [1–3]. Strontium Bismuth Niobate (SBN) is a potential candidate which belong to BLSF and is harnessed for non volatile random access memory applications and fine frequency tolerance resonators applications [2,4,5]. There are precedence that display the tailoring of material properties of these BLSF materials by prudently selecting an element to be replaced and substitute another element. Goldschmidt introduced tolerance to predict the stability of the perovskite layers [6]. Armstrong and Newnham [7], Subbarao [8] and Dorrian et al. [9] found that the ions at perovskite A position can be substituted with various alkaline, alkaline earth and rare-earth ions with greater solubility limits. The B-site presents the lower tolerance to substitution and can accept ions with ionic radii between 0.58 and 0.65 Å [7]. However, it has been recently observed that cations with lone electron pairs, like Pb^{2+}, can replace Bi^{3+} because the substitution at this position is more

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favorable for asymmetric cations [10,11].

Wu et al. studied the influence of various A-site dopants (Ca^{2+}, Ba^{2+}) and B-site dopants (W^{6+},V^{5+}) on the dielectric properties of SBN ceramics and correlated the observations with the difference in the ionic radii [12–14]. Substitution of host cations by dopant having smaller ionic radius result in increased rattling space leading to a higher transition temperature and a large dielectric constant at transition point, while dopants having larger radius will result in lower transition temperature with lower dielectric constant at transition temperature. Venkataraman et al. [15] reported the effect of vanadium doping at B site on the dielectric, ferroelectric and pyroelectric properties, and correlated these properties with the change in grain size. Ando et al. [16] investigated the effect of substitution of Ba and Ca at A-site on the temperature coefficient of frequency (TCF) for fine tolerance resonator devices.

Bi^{3+} has an electronic configuration of [Xe] $4f^{14}5d^{10}6s^2$ and $6s^2$ electrons are commonly referred to as the lone pair electrons. Hybridization of the 6s and 6p orbitals, and the resulting lone electron pair yields some very interesting stereochemistry and steric related properties. Bismuth environments commonly have seven-fold coordination with some long and some short bonds due to the stereo active lone pair of electrons. These arrangements are found in solid-state materials and organometallics. Millan et al. [17] reported for the first time that substitution into the Aurivillius Bi_2O_2 layer by Pb^{2+} ion is possible and the basic structure can be retained. Cations with a stereo-chemical active lone pair of electrons, like Pb^{2+}, Sb^{3+} or Te^{4+}, substitute for Bi^{3+} without destroying the crystal network [17,18].

Castro et al. [19] reported that antimony atom exhibits the typical one sided coordination with a stereo-active lone pair. They are strongly bonded to three oxygen atoms, a fourth oxygen being at a longer distance. Sb_2WO_6 or $WO_2Sb_2O_4$ appear as an interesting model to imagine the possible ways for the $[Bi_2O_2]_{2n-n}$ layers distortion. Castro et al. [18] reported the slight decrease of parameter '*a*' due to substitution of smaller Sb cation. Castro et al. [20] reported the synthesis of the partly substituted Aurivillius phase $Bi_{2-x}Sb_xSrNb_2O_9$ in the range $0 \leq x \leq 1$, but did not observe an Aurivillius phase for $x > 1$. Fruth et al. [21] suggested the possible substitution of Bi^{3+} by the smaller ions of Sb^{3+} which enters into the bismuth layer, due to its similar stencil behaviour, by the presence of a $5s^2$ lone pair associated with Sb^{3+} and $6s^2$ associated with Bi^{3+}. Although several reports show that cations such as Pb^{2+}, Sb^{3+} having lone pair electrons may substitute for bismuth without destroying its basic structure, still there is a lack of clear information about the changes in the microstructure, dielectric and piezoelectric response about the Sb doping in SBN or other BLSF compositions. Antimony has a lone pair electron attached similar to that of bismuth, thus substitution of Antimony would helped to analyze the key role of lone pair (if any) in giving rise to ferroelectricity and piezoelectricity in BLSF compounds. No reports are available in the literature regarding such studies like changes in structural and electrical properties due to Antimony substitution in SBN ceramics. In the present study single phase Sb substituted SBN ceramics were prepared from solid state reaction route and effect of Sb substitution were analyzed on structural and electrical properties of Strontium Bismuth Niobate ceramics and attempt has been made to correlate the existence of lone pair with piezoelectricty and dielectric properties for SBN ceramics.

2. Experimental

Ceramic samples of $SrBi_{2-x}Sb_x$ Nb_2O_9 (SBSN) were prepared by conventional solid state reaction technique. Reagent-grade oxide or carbonates powders of Bi_2O_3, $SrCO_3$, Nb_2O_3, Sb_2O_3 with 99% purity were weighed and mixed in stoichiometric ratio. The materials were thoroughly mixed and ball milled for 24 h with ZrO_2 balls using distilled water as mixing media. After calcining at 1000 °C, ball milled powder were mixed with binder (5% PVA). Dry powder was pressed into circular disks of 10 mm diameter using hydraulic press and pellets were reactively sintered at 1200 °C for 1 h using conventional muffle furnace. Densities of pellets were measured from Archimedes buoyancy principle. Crystallographic structure were analyzed by X-ray diffractometer (XRD) (Philips PW 1830) using CuK radiation. A JEOL scanning electron microscope (MODEL JSM - 840) was used to study the microstructure of prepared ceramics. Both faces of pellets were polished with fine emery paper and coated with platinum film by RF sputtering. The dielectric properties of SBSN ceramics were studied in metal-ferroelectric-metal (MFM) configuration using Agilent 4284A LCR meter as a function of frequency in the range 100 Hz -1 MHz. DC conductivity measurement was done with Keithley 610C Electrometer source measure unit. Temperature dependent studies were made using specially designed sample cell over the wide range of temperature from room temperature to 500 °C. Piezoelectric properties were studied using d_{33} Piezotest (Piezometer). Hysteresis loop were measured at 200 °C from automated PE loop tracer (M/s Arimagetronics, India) at 50 Hz based on Sawyer tower circuit.

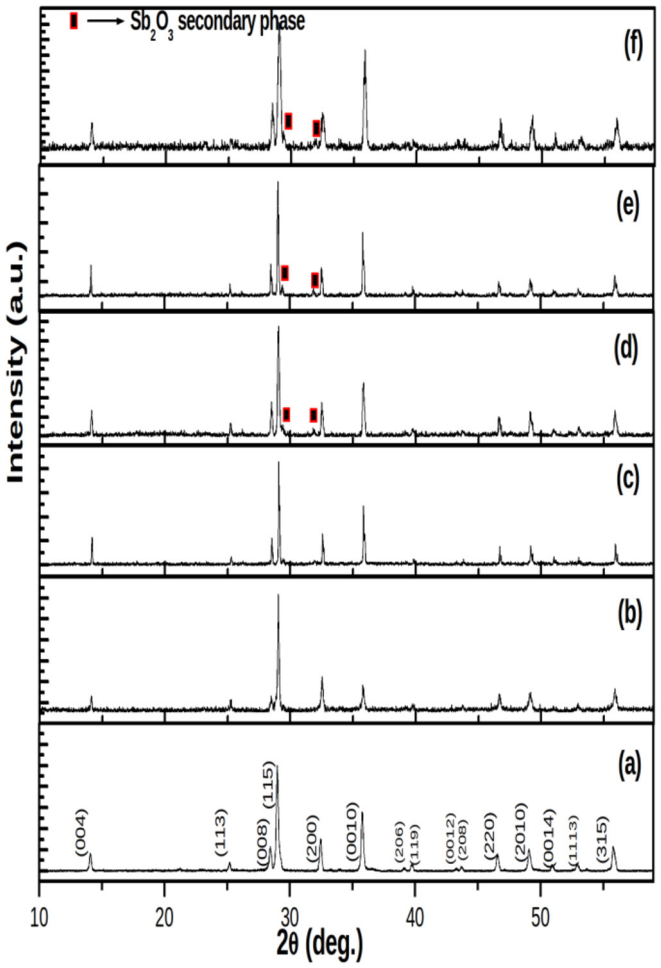

Fig. 1. X-Ray Diffraction spectra of Sb substitution in $SrBi_{2-x}Sb_xNb_2O_9$ ceramic compositions.