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Dielectric properties of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ [$X = 0.1$ and 0.2] ceramics

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Abstract

The results of systematic studies on the dielectric properties of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ [$X = 0.1$ and 0.2] ferroelectric ceramics are reported. X-ray diffraction (XRD) studies on $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ revealed that the single-phase layered perovskites was formed without any detectable secondary phase. However, with $X = 0.2$ in addition to the major layered perovskite phase, a minor unknown phase was noticed. An enhancement in the dielectric properties of $SrBi_2Nb_2O_9$ (SBN) was observed with the increase in partial substitution of pentavalent niobium ions (0.68 Å) by smaller pentavalent vanadium ions (0.59 Å) in the B sites along with the deficiency of strontium ions in the A site.

Keywords: C. Dielectric properties; Aurivillius family; Layered oxides; Ceramics

1. Introduction

$SrBi_2Nb_2O_9$ (SBN) and $SrBi_2Ta_2O_9$ (SBT) have attracted great interest in recent years as potential candidates to replace lead zirconate titanate (PZT) in ferroelectric random access memories (FeRAMs) application. Large remanent polarization, low coercive field, high Curie temperature and lowering the synthesizing temperature are highly desirable to make SBN an alternative to PZT in FeRAM applications. The SBN belong to the Aurivillius family of layered oxides and the crystal structure is built up of two perovskite-like layers, infinite in two dimensions, alternating with a layer of $(Bi_2O_2)^{2+}$ along the *c* direction. The presence of the Bi_2O_2 layers has been thought to serve as the shock absorber for enduring the fatigue of polarization. The influence of substituting effect in SBN was widely reported in literature aimed at improving the dielectric and ferroelectric properties [1–5]. In particular, substitution of V^{5+} with Nb^{5+} in SBN found to have significant enhancement in ferroelectric properties [6–9]. Bismuth layer structured ferroelectrics (BLSFs) synthesized with Sr-deficient and Bi-excess compositions were found to show significant enhanced ferroelectrics properties [10–12]. In this paper we report the results of systematic studies on the dielectric properties $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ [$X = 0.1$ and 0.2] ferroelectric ceramics.

2. Experimental

$Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ [$X = 0.1$ and 0.2] ceramic samples were prepared by two step solid state reaction sintering. The starting materials $SrCO_3$, Bi_2O_3, V_2O_5 and Nb_2O_5 (all with 99% purity) were admixed with a desired weight ratio with 4 wt.% excess Bi_2O_3. Excess Bi_2O_3 was added to compensate the weight loss of Bi_2O_3 during sintering. The admixed powders were ball milled in acetone media, dried and then fired in air for 6 h at 800 °C. The fired powders were ground and admixed with 2 wt.% polyvinyl alcohol as a binder and pressed into disks at 250 MPa. The disks were sintered for 6 h at 900 °C.

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Phase formation and crystallinity of the sintered samples were characterized by X-ray diffraction (XRD, Philips Analytical diffractometer). For the electrical property measurements, the sintered disks were polished and coated with silver paste on both sides. The dielectric measurements were carried out at frequencies 20 Hz to 1 MHz using LCR meter (HP 4284A) with a signal voltage of 50 mV in the temperature range from 30 to 600 °C.

3. Results and discussion

The calculated powder X-ray diffraction (XRD) pattern of SBN based on $A2_1am$ structure and the measured powder XRD pattern of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ and 0.2 are shown in Fig. 1a–c, respectively. The XRD pattern of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ shown in Fig. 1b matches very closely both the positions and relative intensities of the diffraction peaks with the calculated powder XRD pattern of SBN and confirms that the single-phase layered perovskites were formed without any detectable secondary phase. The structural refinement

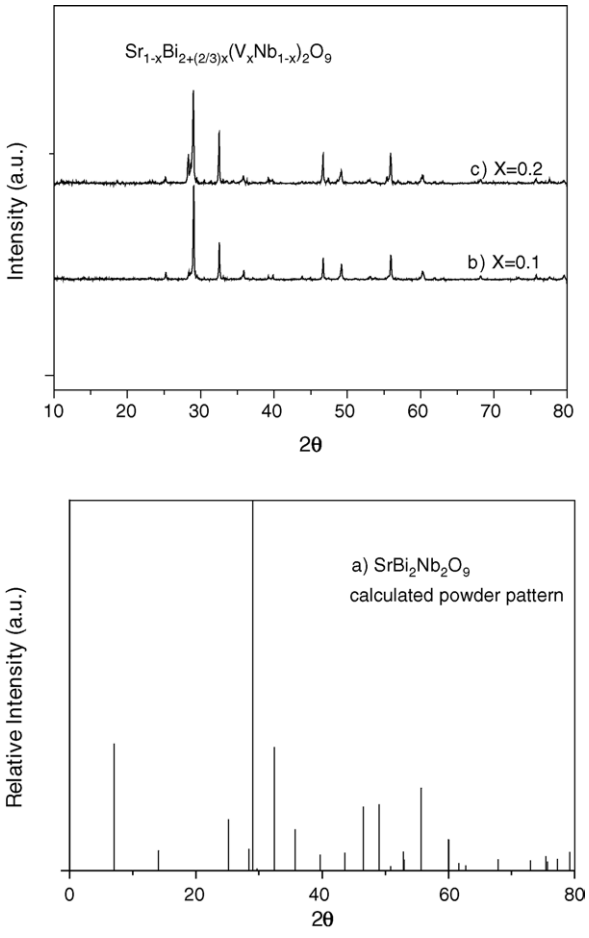

Fig. 1. (a) Calculated XRD pattern of $SrBi_2Nb_2O_9$ and the measured XRD patterns for the composition $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with (b) $X = 0.1$ and (c) $X = 0.2$.

indicated that there is no noticeable change in the lattice constant between SBN and $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$. However, the XRD pattern for $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.2$ shown in Fig. 1c indicated a clear split in the dominant diffraction peak observed at around $2\theta = 29°$ corresponding to SBN. The XRD pattern of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.2$ also indicated the formation of new weak diffraction peaks at $2\theta = 47$ and 54° and slight changes both in the positions and relative intensities of the dominant diffraction peaks compared to XRD pattern of SBN and these changes revealed that in addition to the major layered perovskite phase, a minor unknown phase was formed.

$SrBi_2Nb_2O_9$ exhibits usual ferroelectric transition at around 425 °C with a peak dielectric constant value of around 500. Wu et al. reported the Curie temperature at 457 °C with maximum dielectric constant of 1300 [6] and Ezhilvalavan et al. reported the Curie temperature at 477 °C with maximum dielectric constant of 779 for $SrBi_2(V_{0.1}N_{0.9})_2O_9$ (SBVN) ceramics [13]. Higher dielectric constant at the transition temperature observed for SBVN compared to SBN was attributed to the partial substitution of pentavalent niobium ions (Nb^{5+}: 69pm) by smaller pentavalent vanadium ions (V^{5+}: 59pm) in the B site of layered perovskite structure, which leads to an increased ''rattling space'' for the cations inside the oxygen octahedron.

Thin films synthesized with Sr-deficient and Bi-excess composition $Sr_{0.8}Bi_{2.2}Ta_2O_9$ exhibits transition at 400 °C and approximately eight times higher dielectric constant at the transition temperature compared to its room temperature dielectric constant value [10]. Nanocrystalline $Sr_{0.7}Bi_{2.2}Ta_2O_9$ sample prepared by Panda et al. by solution based method exhibited transition at 396 °C with maximum dielectric constant of 1766 at the measured frequency of 1 kHz [11]. The non-stoichiometric $Sr_{1-X}Bi_{2+2X/3}Ta_2O_9$ ceramics prepared from sol–gel-derived powders by Jain et al. observed the phase transition temperature at 378 and 455 °C and maximum dielectric constant of 810 and 1230, respectively, for $X = 0.15$ and 0.30 at the measured frequency of 10 kHz [12]. Recently Sridarane et al. reported higher Curie temperature and enhanced dielectric constant at the transition temperature for $Sr_{1+X}Bi_{2-(2/3)X}(V_XTa_{1-X})_2O_9$ [$X = 0.1$ and 0.2] [14]. However, few works have been carried out on SBN synthesized with Sr-deficient and Bi-excess composition.

The temperature-dependent dielectric constant of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ [$X = 0.1$ and 0.2] samples prepared in this work measured at 100 kHz with an oscillation amplitude of 50 mV are displayed in Fig. 2. The ferroelectric transition temperature of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ and 0.2 were observed at 420 and 493 °C, respectively. The peak dielectric constant measured at transition temperature for $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ were at 1169 and 2782, respectively, with $X = 0.1$ and 0.2. Higher transition temperature and enhanced

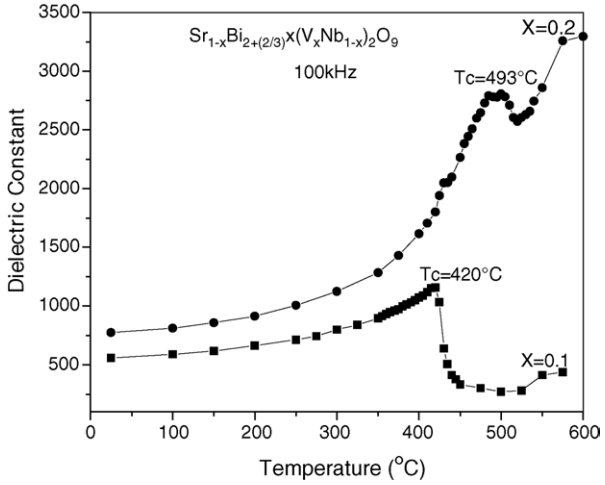

Fig. 2. Temperature-dependent dielectric constant of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ and 0.2 measured at 100 kHz.

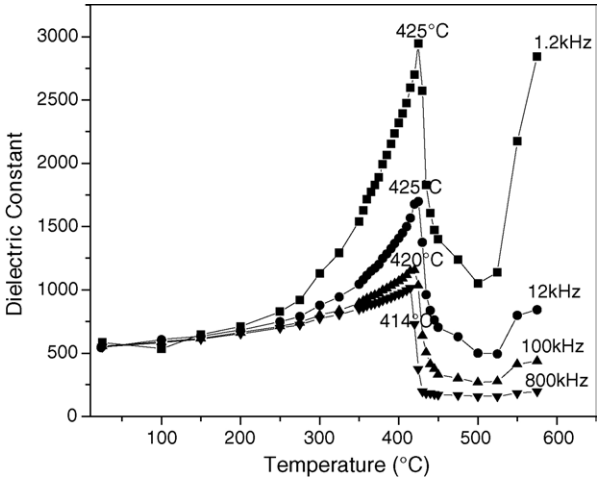

Fig. 3. Temperature-dependent dielectric constant of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ measured at various frequencies.

dielectric constant at the transition temperature were clearly observed with the increase in partial substitution of pentavalent niobium ions (0.68 Å) by smaller pentavalent vanadium ions (0.59 Å) in the B sites along with the deficiency of strontium ions in the A site.

The XRD patterns shown in Fig. 1b indicated that there was no noticeable shift of XRD peaks with the calculated powder XRD pattern of SBN and suggesting no appreciable change in the lattice constant. In the layer-structured perovskites the crystal structure may not change to a larger extent unlike in the case of non-layered perovskites with doping because of the structural constraint imposed by $[Bi_2O_2]^{2+}$ interlayer. Therefore, there would be an increased ionic polarization with doping of vanadium ($X = 0.1$), due to a combination of almost unchanged crystal structure and reduced ionic radius. The enhancement in the peak dielectric constant for $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ ceramics with $X = 0.1$ at the transition temperature related to the larger polarizability attained through increased ''rattling space'' for the cations inside the distorted $Nb(V)O_6$ oxygen octahedral of the perovskite block.

However, a higher concentration of vanadium ($X = 0.2$) doping and increase in Sr-deficient lead to a huge increase in peak dielectric constant to 2782 and Curie temperature to 493 °C. The reason for this might be due to the larger distortion in $Nb(V)O_6$ octahedra compared to $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$. In addition to the major peak observed at 493 °C a small hump has been noticed at 430 °C in the temperature-dependent dielectric constant measurement as shown in Fig. 2 might be due to the larger diameter of the cation.

Figs. 3 and 4 show the dielectric constants of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ ferroelectrics measured as a function of temperature at frequencies 1, 12, 100 and 800 kHz, with $X = 0.1$ and 0.2, respectively. At all measured frequencies $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ exhibits sharp peak for $X = 0.1$ and broad peak for $X = 0.2$ at the transition temperature. The dielectric constants measured at low temperatures for both $X = 0.1$ and 0.2 are the same regardless the frequencies used for the measurements, however, at higher temperature $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.2$ exhibits increase in dielectric constant with increase of temperature. The transition temperature for $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ and 0.2 systems were found to be decreased slightly with increase of frequencies. The transition temperature was found to be shifted from 425 to 415 °C for $X = 0.1$ and similarly shifted from 510 to 485 °C for $X = 0.2$ when the frequency changes from 1 to 800 kHz. Strong frequency dispersion of dielectric constant and Curie temperature shifting towards higher temperature with an increasing frequency are characteristic of relaxor ferroelectrics. However, the observed small negative shift of Curie temperature as a function of frequency might be a result of an overlap of the true paraferroelectric transition peak with the defect induced dielectric relaxation observed at high temperature.

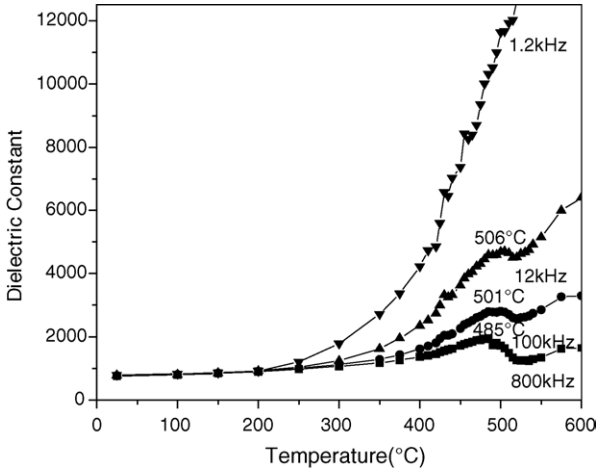

Fig. 4. Temperature-dependent dielectric constant of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.2$ measured at various frequencies.

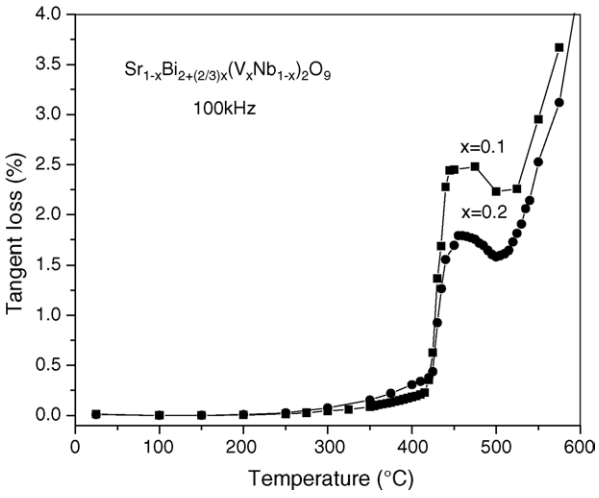

Fig. 5. Temperature-dependent dielectric loss of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ and 0.2 measured at 100 kHz.

Fig. 5 describes the temperature-dependent loss tangent of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ and 0.2 measured at 100 kHz. $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.2$ exhibits slight reduction in the dielectric loss compared to $X = 0.1$. In general the tangent loss increases with increase of temperature might be due to larger distortion in $Nb(V)O_6$ octahedron of the perovskite block and shows a peak near the transition temperature.

4. Conclusion

$Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ and 0.2 were prepared by solid state reaction route. XRD results on $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ with $X = 0.1$ revealed that the single-phase layered perovskites was formed without any detectable secondary phase, however, with $X = 0.2$ in addition to the major layered perovskite phase, a minor unknown phase was noticed. A clear enhancement in the peak dielectric constant at the Curie temperature were noticed for $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ ceramics with $X = 0.1$ and 0.2 compared to SBN. Enhancement in the dielectric constant observed at the transition temperature of $Sr_{1-X}Bi_{2+(2/3)X}(V_XNb_{1-X})_2O_9$ ceramics with $X = 0.1$ and 0.2 related to the larger polarizability attained through increased ''rattling space'' for the cations inside the distorted $Nb(V)O_6$ oxygen octahedron of the perovskite block.

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