CHAPTER 3

DIELECTRIC PROPERTIES OF $\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_x\text{Nb}_{1-x})_2\text{O}_9$

$[X = 0.1 \text{ AND } 0.2]$ CERAMIC

3.1 Introduction

The fatigue free nature of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) have attracted great interest in recent years as potential candidate for ferroelectric random access memories to replace lead zirconate titanate (PZT) in ferroelectric random access memories (FeRAMs). 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 $(\text{Bi}_2\text{O}_2)^{2+}$ along the c direction. The presence of the $\text{Bi}_2\text{O}_2$ layers has been thought to serve as the shock absorber for enduring the fatigue of polarization [1]. The influence of substituting effect in SBN was widely reported in literature aimed at improving the dielectric and ferroelectric properties [2-5]. Substitution of $\text{V}^{5+}$ with $\text{Nb}^{5+}$ in SBN found to have significant enhancement in ferroelectric properties specifically [6-9]. $\text{Sr}$ - deficient and $\text{Bi}$-excess compositions were found to show significant enhanced ferroelectrics properties in Bismuth layer structured ferroelectrics (BLFS’s) [10-12]. Enhanced dielectric constant and higher Curie – temperature were reported recently [13, 14]. In this work we report the results of systematic studies on the dielectric properties of $\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_x\text{Nb}_{1-x})_2\text{O}_9$ $[X = 0.1 \text{ and } 0.2]$ ferroelectric ceramics.

3.2 Experimental

$\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_x\text{Nb}_{1-x})_2\text{O}_9[X = 0.1 \text{ and } 0.2]$ ceramic samples were prepared by two step solid state reaction sintering. The starting materials $\text{SrCO}_3$, 

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Bi$_2$O$_3$, V$_2$O$_5$ and Nb$_2$O$_5$ (all with 99% purity) were admixed with a desired weight ratio with 4 wt % excess Bi$_2$O$_3$. Excess Bi$_2$O$_3$ was added to compensate the weight loss of Bi$_2$O$_3$ 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.

Phase formation and crystallinity of the sintered samples were characterized by X-ray diffraction (XRD) (Philips Analytical diffractometer). The microstructures of the sintered samples were studied using Scanning Electron Microscopy (SEM – JSM – 5610LV, JEOL). 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 20Hz-1MHz using LCR meter (HP 4284A) with a signal voltage of 50 mV in the temperature range from 30 to 600°C.

3.3 Results and discussion

The JCPDS powder X-ray diffraction (XRD) pattern based on A$_2$lam structure and the measured powder XRD pattern of Sr$_{0.8}$Bi$_{2.2}$(V$_x$ Nb$_{1-x}$)$_2$O$_9$[X = 0.1 and 0.2] are shown in Fig. 3.1a - c respectively. The XRD pattern shown in Fig. 3.1b and c match very closely in both the positions and intensities of the diffraction peaks. The XRD pattern of Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ with X = 0.1 and 0.2 confirms that single – phase layered perovskites were formed within the composition range studied in this work without any detectable secondary phase. The XRD pattern of Sr$_{0.8}$Bi$_{2.2}$(V$_x$ Nb$_{1-x}$)$_2$O$_9$ [X = 0.1 and 0.2] could be indexed to an orthorhombic cell. The
Fig. 3.1. a) JCPDS XRD pattern of SrBi$_2$Nb$_2$O$_9$ and the measured XRD pattern for the composition Sr$_{0.8}$Bi$_{2.2}$(V$_{0.2}$Nb$_{1-x}$)$_2$O$_9$ with b) $X = 0.1$ and c) $X = 0.2$.

The structural refinement with the dominant diffraction peaks indicated that the lattice parameters of Sr$_{0.8}$Bi$_{2.2}$(V$_{0.2}$Nb$_{0.8}$)$_2$O$_9$ are $a = 5.518$ Å, $b = 5.515$ Å and $c = 25.11$ Å. The structural refinement with the dominant diffraction peaks indicated that the lattice parameters of Sr$_{0.8}$Bi$_{2.2}$(V$_{0.2}$Nb$_{0.8}$)$_2$O$_9$ are $a = 5.510$ Å, $b = 5.515$ Å and $c = 25.153$ Å when compared to the literature value for
SBN. The $\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_{0.2}\text{Nb}_{0.8})_2\text{O}_9$ shows a slight decrease in lattice constant, $a$, and a slight increase in lattice constant, $c$, in conformity with the statement in Ref. [6].

Fig. 3.2. SEM micrograph of $\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_{x}\text{Nb}_{1-x})_2\text{O}_9$ with $X=0.1$.

Fig. 3.3. SEM micrograph of $\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_{x}\text{Nb}_{1-x})_2\text{O}_9$ with $X=0.2$. 
Figures 3.2 and 3.3 show the SEM images of fracture surfaces of Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ [$X = 0.1$ and $0.2$] ceramic samples. These micrographs reveal dense structure by vanadium doping, although small voids or pores were found in the sample. The average particle size was around 3-4 \(\mu\)m. The incorporation of vanadium oxide into SBN may promote the formation of low melting point at grain boundaries during sintering. This indicates that the increasing concentration of vanadium led to a stronger packing of grains. The smaller grain size might be due to the reduced sintering temperature [9].

Figure 3.4 shows the temperature dependent dielectric constant Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ [X = 0.1 and 0.2] samples measured at 100 kHz. The SBN sample shows a typical para-ferroelectric transition at $420^\circ$C (Curie temperature) with peak dielectric constant 720. The transition temperatures of Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ ceramics with X = 0.1 and 0.2 were observed at 450 and $430^\circ$C respectively. The peak dielectric constant measured at transition temperature for non-stoichiometric composition Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ for X = 0.1 and 0.2 are 2140 and 2088 respectively. Higher dielectric constant at the transition temperature observed for SBVN, compared to SBN, was attributed to the partial substitution of pentavalent niobium ions (Nb$^{5+}$: 0.69 \(\text{Å}\)) by smaller pentavalent vanadium ions (V$^{5+}$: 0.59 \(\text{Å}\)) in the B site of layered perovskite structure, which leads to an increased “rattling space” for the cations inside the oxygen octahedron.

Wu et al [6] reported that SrBi$_2$Nb$_2$O$_9$ (SBN) exhibits usual ferroelectric transition around $435^\circ$C with a peak dielectric constant around 700 at the measured frequency of 100 kHz. Ezhilvalavan et al [15] reported the Curie temperature at $477^\circ$C with maximum dielectric constant of 779 for SrBi$_2$(V$_{0.1}$N$_{0.9}$)$_2$O$_9$ (SBVN) ceramics at the measured frequency of 100 kHz.
Recently, higher Curie temperature and enhanced dielectric constant for \( \text{Sr}_{1+X}\text{Bi}_{2+(2/3)X}\text{Ta}_{1+X}\text{O}_9 \) \( [X = 0, 0.1 \text{ and } 0.2] \) and \( \text{Sr}_{1-X}\text{Bi}_{2+(2/3)X}\text{Nb}_{1-X}\text{O}_9 \) \( [X=0.1 \text{ and } 0.2] \) ceramics were reported [13, 14].

The temperature dependent dielectric constant measured at a frequency of 100 kHz with oscillating amplitude of 50 mV is shown in Fig. 3.4. Since the ionic radius of \( \text{V}^{5+} \) is smaller than that of \( \text{Nb}^{5+} \), the incorporation of smaller ions would lead to a reduced contribution of overall atomic polarization. Curie temperature, peak dielectric constant, spontaneous polarization and coercive field of ferroelectrics are largely dependent on the ionic displacements associated with the samples. Ionic polarization is strongly dependent on the crystal structure, including density and lattice constant or unit cell volume.

The XRD patterns, shown in Figs. 3.1a and 3.1b, and the structural refinement indicate slight changes in the values of \( a \) and \( c \) of
Sr$_{0.8}$Bi$_{2.2}$(V$_{0.2}$Nb$_{0.8}$)$_2$O$_9$ compared to SBN. 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$_2$O$_2$]$^{2+}$ interlayer. The enhancement in the peak dielectric constant Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ \( X=0.1 \) and 0.2] ceramic at the transition temperature is 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.

However, a higher concentration of vanadium \( (X = 0.2) \) doping lead to a slight reduction in peak dielectric constant and in Curie temperature. The reason for this might be due to decrease in both atomic and ionic polarization. An increase in vanadium concentration \( (X=0.2) \) may be due to the slight shrinkage of the crystal lattice and further distortion of Nb(V)O$_6$ octahedra.

Figures 3.5 and 3.6 show the dielectric constants of Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$[X=0.1 and 0.2] ferroelectrics as a function of temperature measured at frequencies 1 kHz, 12 kHz, 100 kHz and 800 kHz. For all frequencies there is a gradual increase in the dielectric constant with increasing temperature for SBN with \( X=0.1 \) and 0.2 respectively. The dielectric constants at low temperatures are the same regardless of the frequencies used for the measurements, whereas at high temperatures it varies markedly. The significant enhancement of the dielectric constant at high temperatures might be due to the mobile charge carriers, which may be related to the oxygen vacancies. The transition temperature for Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ systems were found to decrease slightly with increase of frequencies. The transition temperature shifts from 465°C to 439°C for \( X=0.1 \) and from 435°C to 425°C for \( X=0.2 \) when the frequency changes.
Fig. 3.5. Temperature dependent dielectric constant of $\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_x\text{Nb}_{1-x})_2\text{O}_9$ with $X = 0.1$ measured at various frequencies.

Fig. 3.6. Temperature dependent dielectric constant of $\text{Sr}_{0.8}\text{Bi}_{2.2}(\text{V}_x\text{Nb}_{1-x})_2\text{O}_9$ with $X = 0.2$ measured at various frequencies from 1kHz to 800 kHz. Strong frequency dispersion of dielectric constant and Curie temperature shifting towards higher temperature with the increase of frequency are the characteristics of relaxor ferroelectrics. However, the
observed small negative shift of Curie temperature as a function of frequency may be due to the overlap of the true paraferroelectric transition peak with the defect induced dielectric relaxation observed at high temperature.

Figures 3.7 and 3.8 describe the temperature dependent loss tangent measured at different frequencies 1kHz, 12 kHz, 100 kHz and 800 kHz for vanadium doped Sr$_{0.8}$Bi$_{2.2}$(V$_{x}$Nb$_{1-x}$)$_2$O$_9$ samples with X=0.1 and 0.2 respectively. In general, the tangent loss for this composition decreases with increasing frequency and there is no significant anomaly near transition temperature as observed from the temperature dependent dielectric constant measurement. The tangent loss increases with increase of temperatures particularly around 375°C. The increase in tangent loss at higher temperature might be due to the formation of higher concentration of charge carriers.

3.4 Conclusions

The XRD results confirm that the polycrystalline Sr$_{0.8}$Bi$_{2.2}$(V$_x$ Nb$_{1-x}$)$_2$O$_9$ [X=0.1 and 0.2] ceramic samples prepared by two step solid state reaction sintering consisted of single-phase layered perovskites. SEM micrographs of these samples reveal dense structure by vanadium doping with the average particle size of around 3 – 4 μm. A clear enhancement in the peak dielectric constant at the Curie temperature was noticed for Sr$_{0.8}$Bi$_{2.2}$(V$_x$b$_{1-x}$)$_2$O$_9$ with [X=0.1 and 0.2] compared to SBN. Enhancement in the dielectric constant observed at the transition temperature of Sr$_{0.8}$Bi$_{2.2}$(V$_x$Nb$_{1-x}$)$_2$O$_9$ ceramics with X=0.1 and 0.2 may be correlated 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.
Fig. 3.7. Temperature dependent tangent loss of $\text{Sr}_{0.8}\text{Bi}_{2.2}(V_x\text{Nb}_{1-x})_2\text{O}_9$ with $X = 0.1$ measured at various frequencies.

Fig. 3.8. Temperature dependent tangent loss of $\text{Sr}_{0.8}\text{Bi}_{2.2}(V_x\text{Nb}_{1-x})_2\text{O}_9$ with $X = 0.2$ measured at various frequencies.
References