Microstructural, dielectric, impedance and electric modulus studies on vanadium—doped and pure strontium bismuth niobate ($\text{SrBi}_2\text{Nb}_2\text{O}_9$) ceramics

B. H. VENKATARAMAN, K. B. R. VARMA*

Materials Research Centre, Indian Institute of Science, Bangalore-560012, India

E-mail: kbrvarma@mrc.iisc.ernet.in

$\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) and $\text{SrBi}_2(\text{Nb}_{0.9}\text{V}_{0.1})_2\text{O}_9$ (SBVN) ceramics were fabricated from the powders consisting of μm sized grains, obtained via the solid state reaction route. V_2O_5 was found to be an effective microstructure modifier and grain growth truncator for SBN ceramics. X-ray structural studies carried out on SBVN ceramics confirmed the existence of preferential orientation (*c*-planes) of the grains. V_2O_5 addition has substantially improved the sinterability of SBN and enabled to achieve high density (95%) which was otherwise difficult in the case of pure SBN. The dielectric properties of SBN ceramics were significantly enhanced by the partial replacement of Nb ions by pentavalent vanadium ions. The complex impedance diagrams of dense SBVN ceramics exhibited only one semicircle indicating a significant contribution from the grains. In contrast, the impedance plots for the porous (density 88%) SBN ceramics show an additional low-frequency semicircle which was attributed to the blocker (pore) size effects. The dielectric behavior of SBN and SBVN ceramics was rationalized using the impedance and modulus data.

1. Introduction

Strontium bismuth niobate, $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) has been recognised to be an increasingly important material for ferroelectric based device applications which include non-volatile random access memory devices [1, 2]. This material belongs to a non-centrosymmetric polar crystal class at room temperature and undergoes a ferroelectric to paraelectric transition around 700 K [3]. A structural scheme of this material is simple though the chemical formula appears to be complicated. It has a layered structure with two NbO_6 octahedra sandwiched between Bi_2O_2 layers. This sequence of structural arrangement was categorized as the Aurivillius family of ferroelectric oxides belonging to the general formula $[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$. These materials have a tendency to grow mostly in the *ab*-plane and as a consequence one ends up in getting extended plates with their *c*-axes perpendicular to them. Similar trend has been observed in the grain growth when one attempts to sinter the powders into dense ceramics. Because of the rapid growth that is involved in the *ab*-plane, a significant percentage of porosity is invariably found to be associated with these ceramics. It appears to be difficult to obtain dense ceramics of SBN which are desired for many studies. It is with this background we have been making attempts to add a few sintering aids/dopants to obtain dense ceramics. In the process, we made an attempt to dope SBN with V_2O_5 . Interest-

ingly, partial replacement of niobium ions by vanadium ions has not only helped in obtaining dense SBN ceramics associated with a uniform microstructure, but also with improved dielectric and ferroelectric properties. In this paper, the details with regard to the effect of V_2O_5 doping on the structural, microstructural, dielectric and impedance characteristics of SBN ceramics are elucidated.

2. Experimental

Polycrystalline strontium bismuth niobate, $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) and strontium bismuth vanadium niobate $\text{SrBi}_2(\text{V}_{0.1}\text{Nb}_{0.9})_2\text{O}_9$ (SBVN) powders were prepared by solid state reaction route. For this, high purity (99.99%) starting materials, SrCO_3 , Bi_2O_3 , Nb_2O_5 and V_2O_5 (Aldrich Chemicals) were mixed and ground well in acetone medium for 1 h. The mixture was then heated in air for 12 h at 1270 K for vanadium doped SBN samples and at 1370 K for the samples without vanadium, with intermediate grinding and heating stages. The formation of the monophasic compound was confirmed via X-ray powder diffraction (XRD) using $\text{CuK}\alpha$ radiation. The as-prepared powder was then cold-pressed at 300 K for a few minutes at the pressure of 300 kg/cm². The pressed pellets were subjected to the conventional sintering process in air at 1420 K for 10 h. Prior to the structural characterization and physical property

* Author to whom all correspondence should be addressed. (Fax: +91-80-3600683)

measurements, all the samples (SBN and SBVN) were annealed at 1073 K for 3 h in flowing oxygen in order to stabilize V^{5+} ions. The sintered flat pellets were subjected to XRD studies for phase identification. The XRD patterns of the sintered pellets were compared with that of the as-prepared polycrystalline powder to examine whether there is any grain-orientation. The degree of grain orientation (f) was calculated [4] by using the Lotgering's method.

$$f = \left(\frac{P - P_0}{1 - P_0} \right) \quad (1)$$

where $P = \Sigma I_{00l} / \Sigma I_{hkl}$ for the given oriented sample and $P_0 = \Sigma I_{00l} / \Sigma I_{hkl}$ for the non-oriented sample.

The densities of the sintered pellets were determined by the liquid displacement/Archimede's method. Xylene, the density of which is 0.87 gm/cm³ was used as the liquid media. The densities obtained for SBN and SBVN were 88 and 95% of the theoretical values. The microstructural studies were carried out on these sintered pellets using a Leica 440I Scanning Electron Microscope. The impedance measurements were done on the polished pellets as a function of the frequency (100 Hz–1 MHz) and temperature (573–823 K), using an impedance analyzer (HP 4194A) at a signal strength of 0.5 Vrms.

3. Results and discussion

3.1. Structural studies and degree of grain-orientation

Fig. 1(a) and (b) shows the XRD patterns obtained for the randomly oriented polycrystalline SBN and SBVN (10 mol% V_2O_5 added SBN) powders. Careful analyses of the X-ray data confirm the formation of single phase layered perovskites without any impu-

Figure 1 The XRD patterns recorded for the polycrystalline powders of (a) SBN and (b) SBVN.

Figure 2 The XRD patterns obtained on the single surfaces sintered at 1150 °C/10 h of (a) SBN and (b) SBVN.

rity/secondary phase. In order to find out whether V_2O_5 doping brings in any preferential orientation in the grain growth, XRD has been done on the well sintered flat discs. The XRD recorded for the ceramic discs of SBN and SBVN are shown in Fig. 2(a) and (b). It is evident from these patterns that the positions of the Bragg peaks are not different from those of the powdered patterns shown in Fig. 1. However, the X-ray intensities corresponding to c-planes (i.e) (004), (006), (008), (0010) and (0012) of SBVN (Fig. 2(b)) are stronger than those of pure SBN. The degree of grain orientation (f) in the sintered pellet of SBVN ceramics is found to be 54%. This finding confirms that the addition of V_2O_5 results in obtaining partially c-oriented plates of SBN unlike in the case of undoped SBN ceramics in which extended grain growth in random is encountered.

3.2. Microstructural studies

3.2.1. Microstructures of SBN and SBVN

Fig. 3(a)–(b) shows the scanning electron micrographs recorded for the polished surfaces of SBN and SBVN ceramics. The SEM recorded for pure SBN pellets indicate the presence of elongated plate shaped grains associated with inter and intra porosity (Fig. 3(a)).

On the other hand one would see tightly packed equiaxed plate shaped grains in the micrographs recorded for SBVN (Fig. 3(b)). The grains are well packed and the major planes are parallel to the c-planes (e.g., {001}), which is considered to be a preferential growth in the layered perovskites. One of the reasons for this microstructural modification is that the addition of V_2O_5 promotes the formation of a low melting phase at the grain boundaries and facilitates the easy rotation of the grains to attain their normal growth habit during sintering. The liquid phase would effectively increase the diffusion distance between the grains, resulting in obtaining dense ceramics (95% of the theoretical density) associated with uniform microstructure as observed in the present case. Growth that is slow normal

Figure 3 The scanning electron micrographs obtained for the polished surfaces of (a) SBN and (b) SBVN ceramics.

to and rapid parallel to a low energy surface leads to plate like grains. SBN crystals have a tendency to grow in the *ab*-plane perpendicular to the *c*-axis. This justifies the abnormal growth that is observed in the case of pure SBN ceramics. Growth planes that are strikingly seen in Fig. 3(b) are those of low surface energy and the transfer of the material from the matrix grains occurs through a thin layer of intergranular material, often liquid, in which the diffusion coefficient is relatively high. The variation in the morphology of the grains triggered by the dopant would also lead to the preferred orientation.

3.3. Dielectric studies

Fig. 4 shows the temperature dependent dielectric constants (ϵ_r) for both porous SBN and dense SBVN ceramics at 100 kHz. The ϵ_r in both cases increases with increasing temperature and undergoes a maximum around 720 K. Subsequently it decreases with increasing temperature till 800 K. However, the magnitude of ϵ_r right from room temperature to 800 K is higher for SBVN ceramics. The ϵ_r at 720 K for SBVN is 1000 and that for SBN is 740. The excessive porosity associated with SBN ceramics had led to the lower values of dielectric constant. The higher ϵ_r of SBVN samples indicates an increase in polarizability, arising out of the increased rattling space owing to the incorporation

Figure 4 The temperature dependence of ϵ_r at 100 kHz for SBN and SBVN ceramics.

of much smaller vanadium ions in Nb sites apart from higher connectivity as these are very dense. The significant porosity that is associated with pure SBN ceramics has prompted us to invoke the dielectric mixture formulae that are normally employed to predict the dielectric constants of two phase composites. In the present work, various formulae are used in order to predict the dielectric constant of the ceramic, which is considered to be diphasic material with pores of volume fraction V_1 (having dielectric constant $\epsilon_1 = 1$) uniformly distributed in the matrix of SBN of volume fraction V_2 (dielectric constant ϵ_2). The effective dielectric constant of this composite is given by the expression

$$\epsilon_{\text{eff}} = \epsilon_2 \left[1 + 3V_1 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \right] \quad (2)$$

The effective dielectric constant (ϵ_{eff}) calculated using Clausius-Mossotti relation [5] for the volume fraction ($V_1 = 0.115$) is 84 (at 100 kHz, 300 K), but the experimentally measured value is 100.

The most commonly used dielectric mixture rule is Lichtenecker's [6] which is

$$\log \epsilon_{\text{eff}} = V_1 \log \epsilon_1 + V_2 \log \epsilon_2 \quad (3)$$

The above equation is the intermediate form of the series and parallel combination laws for dielectric mixtures. The effective dielectric constant obtained using this formula is 70 (at $V_1 = 0.115$), which is also not in agreement with the experimental value. The reason for this is based on the fact that these formulae do not take the shape of the pores into the consideration.

According to Wiener [7, 8] the formula that takes into account the spherical shape of the phase 1 (pores) is

given by the equation

$$\left(\frac{\varepsilon_{\text{eff}} - \varepsilon_2}{\varepsilon_{\text{eff}} + 2\varepsilon_2} \right) = V_1 \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \right) \quad (4)$$

The effective dielectric constant calculated using this formula is 97, which is close to that of the experimentally measured value, 100.

The effect of vanadium doping (10 mol%) on the T_c (Curie temperature) of SBN ceramics is less significant though there is an increasing trend in T_c with increasing vanadium content. The Curie temperatures of these samples (SBN and SBVN) are around 720 K and is slightly higher than that reported for SBN ceramic in the literature [3] (700 K). The higher T_c that is observed in the present studies for pure SBN ceramics is attributed to the difference in their microstructures. It is well known that for ferroelectric ceramics the dielectric constant and the Curie temperature are grain size dependent.

3.4. Impedance and modulus spectroscopic studies

3.4.1. Background theory

Complex impedance analysis is a well known and powerful tool which has been effectively used for probing into the dielectric materials. This analyses enable one to resolve the contributions of various processes such as the electrode effects, bulk effects and the interfaces viz the grain boundaries etc in the frequency domain. In general the data in the complex plane could be represented in any of the four basic formalisms. These are complex impedance (Z^*), complex admittance (Y^*), complex permittivity (ε_r^*) and complex modulus (M^*) which are related. When the relaxation times of various processes differ as a consequence of different capacitive components, the complex impedance representation is made use of. In the complex impedance plot (Cole-Cole; Z' vs. $-Z''$ plotted in a linear scale), depending on the relative values of their relaxation times, they give rise to three semicircular arcs. Generally, the arc at the high frequency end refers to the bulk electrical conduction, the intermediate arc corresponds to conduction by the grain boundaries and the arc at the low frequency end arises from electrode processes. Each of these semicircles could be represented by a single RC combination. A depressed semicircle whose center lies below the real axis suggests the departure from the ideal Debye behavior. The semicircle passes through a maximum at a frequency f_0 (relaxation frequency) and satisfies the condition.

$$\omega\tau = 1 \quad (5)$$

On the other hand complex modulus or permittivity plane plots are used to represent the response of dielectric systems [9].

The classical model to describe the impedance behavior is that of Debye and it is written in the form

$$Z^* = Z' - jZ'' \quad (6)$$

$$= R/(1 + i\omega\tau) \quad (7)$$

where $\tau = RC$. This equation implies a simple RC circuit in parallel which gives rise to a semicircle whose center lies on the real axis in the complex plane (Z'' vs. Z' ; M'' vs. M') or a Debye peak in the spectroscopic plots of the imaginary component (Z' , M'' vs. $\log f$), where

$$Z' = \frac{R}{1 + (\omega RC)^2} \quad (8)$$

$$Z'' = R \left(\frac{\omega RC}{1 + (\omega RC)^2} \right) \quad (9)$$

Similarly the real and imaginary parts of modulus functions are expressed by the following

$$M^* = j\omega C_0 Z^* \quad (10)$$

$$M' = \frac{C_0}{C} \left(\frac{(\omega RC)^2}{1 + (\omega RC)^2} \right) \quad (11)$$

$$M'' = \frac{C_0}{C} \left(\frac{\omega RC}{1 + (\omega RC)^2} \right) \quad (12)$$

In the above equations ω is the angular frequency ($= 2\pi f$), C_0 is the vacuum capacitance of the measuring cell and electrodes with an air gap of the dimensions of the sample thickness.

$C_0 = \varepsilon_0 \times A/d$, where ε_0 is the permittivity of free space (8.85×10^{-12} F/m), d is the thickness and A is the area of the specimen. However, in reality, this is most often not the situation, the center of the semicircle lies off the real axis by an angle θ ($= \beta\pi/2$). It is described by the following equation

$$Z^* = R/(1 + i\omega\tau)^n \quad (13)$$

$n = 1 - \beta$, where β is the angle of deviation from the ideal semicircular arc. The simple Debye equation for the relaxation is the case for $\beta = 0$, i.e., $n = 1$. Complex impedance plane plots of Z' versus Z'' (where Z' and Z'' are the real and imaginary parts of the complex impedance plane, respectively) are useful for determining the dominant resistance of a sample but are insensitive to the smaller values of resistances. Similarly, complex modulus plots are useful in determining the smallest capacitance. Sinclair and West [10] suggested the combined usage of impedance and modulus spectroscopic plots to rationalize the dielectric properties. The peak heights are proportional to R for the Z'' versus frequency plots and to C^{-1} for the M'' peak. However the power of combined usage of both impedance and modulus spectroscopy is that the Z'' plot highlights the phenomenon of largest resistance whereas M'' picks up those of the smallest capacitance [11].

3.4.2. Impedance characteristics of porous SBN and dense SBVN ceramics

Fig. 5(a) and (b) shows the complex plots between the real and imaginary components of the impedance for SBN and SBVN at different temperatures in the 100 Hz–1 MHz frequency range. The striking

Figure 5 Complex impedance plots at different temperatures for (a) SBN and (b) SBVN.

difference between the impedance plots of SBN and SBVN is the stability of the high frequency semicircle due to the dense microstructure of the SBVN throughout the temperature range and on the other hand there is a variation in magnitude (frequency distribution) of these semicircles in the case of porous sample (pure SBN). In the case of SBN ceramic, (Fig. 5(a)), all the three plots show overlapping of the semicircles which could be resolved into two and it is very clear in the one which is recorded at 823 K (inset of Fig. 5(a)) that the contributions are from both grains (at the high frequency side) and the grain boundaries (on the lower frequency side). This is represented in the form of two parallel RC elements in series (inset of Fig. 5(a)). The additional contribution in the low frequency part to the specific semicircle is attributed to the blocking effect of the pores. Also the poor separation of this overlapped semicircle is ascribed to the blocker (pore) size. It is known [12] that, in electroceramics, if the blocker size is greater than $1 \mu\text{m}$, [as is the case in the present study Fig. 3(a)] it would lead to the overlapping of the semicircles. The influence of the blocker size or in other words blocker thickness on the impedance plot is discussed briefly in Section 3.4.4.

Vanadium doped SBN sample, shows only one peak in the entire range of temperatures covered in the

present study indicating a single relaxation process originating from the grain (bulk). However the one obtained at 823 K (inset of Fig. 5b) has exhibited a semicircle with symptoms of another one at low frequency end. Unfortunately because of the experimental limitation that we had on the frequency range, particularly on the low frequency end we could not demonstrate the incidence of the other semicircle.

As expected, all the semicircles of SBN and SBVN samples became smaller with increase in temperature and shift towards lower Z' values indicating a reduction in the resistance of both the grain and grain boundary. The impedance diagram in the temperature 573–823 K range could be modelled by an equivalent circuit comprised of a parallel resistance and capacitance. The low frequency intercept made by the semicircle on the real impedance axis could be used to determine the bulk resistance of the sample while the capacitive values are obtained from the frequency corresponding to the highest point in each semicircle. The value of the bulk resistance calculated from the impedance plot for the SBN ceramic is found to be higher by one order of magnitude, than that of SBVN ceramic. On the other hand, the bulk capacitance of SBVN ceramic is higher than that of SBN and thus accounting for higher ϵ_r . The values of grain resistance (R_g), grain boundary resistance

TABLE I Relaxation frequency (f_o), grain resistance (R_g), grain boundary resistance (R_{gb}) and bulk capacitance (C_b) of SBN ceramics

Temperature (K)	f_o (Hz)	R_g (ohm)	R_{gb} (ohm)	C_b (Farad)
573	500	2.5×10^6	—	1.3×10^{-10}
673	1500	9.8×10^5	—	1.0×10^{-10}
723	2000	2.7×10^5	—	3.0×10^{-10}
773	6000	1.2×10^5	—	2.4×10^{-10}
823	11085.41	6.4×10^4	1.2×10^5	2.0×10^{-10}

TABLE II Relaxation frequency (f_o), grain resistance (R_g), and bulk capacitance (C_b) of SBVN ceramics

Temperature (K)	f_o (Hz)	R_g (ohm)	C_b (Farad)
573	500	1.0×10^6	1.4×10^{-10}
673	800	6.0×10^5	3.3×10^{-10}
723	2080	7.0×10^4	1.09×10^{-9}
773	12611.67	3.6×10^4	3.52×10^{-10}
823	105952.8	6.7×10^3	1.2×10^{-10}

(R_{gb}), bulk capacitance (C_b) and relaxation frequency (f_o) through which the semicircles pass for both SBN and SBVN ceramics are listed in the Tables I and II.

3.4.3. Variation of the blocking factor

It is known in the literature that ionic carriers could be blocked at internal interfaces due to the microstructural defects such as grain boundaries, cracks and pores. This phenomenon is visualized in impedance spectroscopy as a separate semicircle at the lower frequency side. The micrographs of SBN ceramic show a porous microstructure (compared to that of SBVN) which is reflected in the impedance diagram at the low frequency end (Fig. 5(a)).

Normally, the ion blocking by the pores will quantitatively be characterised by the blocking factor α_R

$$\alpha_R = \frac{\Sigma_{\text{bulk}} - \Sigma_{dc}}{\Sigma_{\text{bulk}}} \quad (14)$$

where Σ_{bulk} and Σ_{dc} are the bulk and blocked conductances.

The parameter, α_R measures the fraction of electric carriers blocked by the microstructural defects. The blocking factor (α_R) vs temperature plot for the SBN ceramic is depicted in Fig. 6. It is evident from this figure that the blocking effect of the blockers is independent of temperature in the 573–823 K temperature range. One of the reasons for this is due to the lower value of the matrix (grain) conductivity. It is observed [13] that if the matrix conductivity is greater than 10^{-3} S/cm, blocking effect becomes negligible and the corresponding displacement current is sufficient to ensure a short circuit. In the present study as the matrix conductivity is lower than 10^{-3} S/cm (in all the ranges of temperatures under study), the current lines around the blockers isolate electric charge carriers on each side of the blocker within the blocked spaces. This leads to the lower

Figure 6 Variation of the blocking factor with temperature.

conductivity value of the SBN ceramic than that of SBVN.

3.4.4. Influence of the average blocker thickness on the impedance plot

Dessemond [14] described the influence of the blocker size on the interference between the semicircles arising out of the contributions from the bulk and the blockers, in other words on the relative values of their relaxation

Figure 7 Variation of the blocker (pore) size thickness with temperature.

frequencies. As mentioned earlier in the Section 3.4.2 of this paper, the blockers in the present study are referred to the pores that exist at the grain boundaries.

The overlapping of the relaxation frequencies of the bulk and the blocked semicircles is characterized by the frequency factor α_F , given by

$$\alpha_F = f_{bd}^0 / f_{bulk}^0 \quad (15)$$

where f_{bd}^0 and f_{bulk}^0 are the blocked and bulk semicircle relaxation frequencies. Dessemond further developed this model to relate the relaxation frequency with the average blocker thickness for better understanding of the impact of blocker on the impedance plot. He made some assumption to derive this relation. The numerical expression is given by the following equation

$$\alpha_F = 0.09^{f_{br}} / \varepsilon_{br} \quad (16)$$

Fig. 7 shows the variation of the average thickness of the blocker (evaluated from the above expression) as

a function of temperature. It decreases with increasing temperature. The effect of the same is reflected in the impedance plot of SBN ceramic as a overlapped semicircle. On the other hand the SBVN ceramics show a well stabilized bulk semicircle throughout the range of temperatures under study.

The effect of a decrease in blocker thickness associated with the other microstructural defects is reflected in the impedance spectrum (Fig. 5(a)) as a overlapped semicircle in SBN ceramic. The overlapping as expected is found to be extensive in all the diagrams and the resolution is not good, as the value of the blocker size is greater than $1 \mu\text{m}$ in the entire range of temperatures under study. A good separation between the semicircle due to the bulk and that due to the presence of blockers is expected as in the case of yttria stabilized zirconia when the blocker size is less than $1 \mu\text{m}$ [12].

3.4.5. Variation of the depression angle

The depression angles (β) for the porous SBN and dense SBVN ceramics were determined at various

Figure 8 The frequency dependence of imaginary part of the impedance at various temperatures for (a) SBN and (b) SBVN.

TABLE III Variation of the depression angles (β) with temperature

Temperature (K)	β (deg) porous SBN	β (deg) dense SBN
573	23	14
610	32	18
630	38	23
670	43	27
720	48	32
750	40	28
770	35	22

temperatures using the following relation.

$$\beta = (1 - n)\pi/2 \quad (17)$$

In both cases, the β increases with increasing temperature till 720 K ($\approx T_c$). Subsequently, in the paraelectric phase it decreases with increasing temperature and the values are listed in the Table III. The variation in β implies an increasing heterogeneity with increasing temperature. The values of the depression angles for the dense SBVN ceramics are lower (14° – 32°) than those of porous SBN ceramic (23° – 48°) indicating that the porosity leads to higher values of the depression angle. The larger depression angles of the porous SBN ceramics are as a consequence of two competing contributions of very close relaxation frequencies.

3.4.6. Variation of the imaginary part of the impedance with frequency

Fig. 8(a) and (b) shows the variation of the imaginary part of impedance as a function of frequency at three different temperatures for both SBN and SBVN ceramics. The frequency of the peak maximum shifts towards higher frequencies with increasing temperature and the relaxation occurs over several decades of frequency for both SBN and SBVN. Also, it is clear from the figures that, irrespective of the temperatures at which the measurements are made, all the curves merge at higher frequencies. At higher frequencies, the contribution from the grain predominates owing to the absence of the space charge effects. The relaxation times associated with each peak obtained from the frequencies at which the maxima (f_0) occurred, and satisfying the condition $\tau = \frac{1}{2\pi} f_0$ are used to determine the activation energies. The following equation has been used to evaluate the activation energies (E_a)

$$\tau = \tau_0 e^{\frac{E_a}{KT}} \quad (18)$$

where τ_0 is the pre-exponential factor, and K and T have their usual meaning. It is clear from the figure (Fig. 9) that a linear relation between $\ln \tau$ and $1/T$ is obtained in the 573–823 K temperature range. A straight line fit to Equation 18 yielded the activation energies of the grains for SBN and SBVN samples in the range of 1.10 and 1.21 eV. These activation energies are close to that of oxygen vacancy motion through the SBN lattice, which is found to be in agreement with the earlier reports [15].

Figure 9 Arrhenius plot for relaxation time (τ) of SBN and SBVN ceramics.

In the case of SBN ceramic, the plots of f vs. Z'' show only one peak till 723 K after that there is an indication of the appearance of two peaks and it is very clearly demonstrated in the one recorded at 823 K (inset of Fig. 8(a)). At 823 K, the SBN ceramic shows two distinct peaks akin to those of Z' vs. Z'' plots indicating that the contributions are from the grain (at the high frequency side) and the grain boundaries (on the low frequency side) respectively (inset of Fig. 8(a)). The SBVN samples exhibit a different behavior as depicted in Fig. 8(b). The weaker contributions from the grain boundary are not observed in these plots. There is only one distinct peak in the 573 to 823 K temperature range. This peak, corresponding to the bulk of the sample, shifts to higher frequencies as the temperature is increased. The plot of f vs Z'' at 823 K is shown as the inset in Fig. 8(b). We believe that the grain boundary contribution is minimized due to the closely packed uniform microstructure of the SBVN ceramics.

3.4.7. Variation of the imaginary part of the modulus with frequency

Figs. 10(a) and (b) show the variations in the imaginary part of the complex modulus with frequency at different temperatures for both SBN and SBVN ceramics respectively. In both cases the peaks shift systematically towards higher frequencies with increasing temperature. The f vs M'' plot obtained for SBN ceramic at 573 K undergoes a maximum at 800 Hz. The magnitude of the peak decreases with increasing temperature as one approaches the Curie temperature which is a direct indication of increase in the dielectric constant and thereafter the magnitude goes up with further increase in temperature. Similar trend has been observed in the

Figure 10 Variation of the imaginary part of the modulus with frequency at different temperatures for (a) SBN and (b) SBVN.

case of SBVN ceramics. However, the values of M'' are slightly lower than that of the SBN ceramics as the dielectric constants of these samples are higher. Since the change in the dielectric constant of the grain boundary phase is relatively small (almost constant) with temperature, the change in the value of M'' indicates the grain contribution. A closer observation of the imaginary parts of the impedance and modulus versus $\log f$ plots obtained at 723 K for SBN and SBVN ceramics which are shown as the insets in Fig. 10(a) and (b) reveal the following.

The frequency plots of the imaginary parts of the impedance and modulus for both SBN and SBVN ceramics in all the ranges of temperatures (573–823 K) indicate departures from the ideal Debye behavior. The width of Z'' vs. $\log f$ at half height is greater than 1.14 decades, (it should be noted that it is 1.14 decades for the ideal Debye behavior) and the peaks of Z'' and M'' are not in coincidence suggesting a deviation from the ideal Debye behavior. The Z'' plots are asymmetric and M'' are symmetric for SBN ceramic, whereas in the case of SBVN both are symmetric. A shift in $f_{\max}$ and the change in the value of $M''_{\max}$ in both samples would suggest a variation in capacitance.

Further, the inset of Fig. 10 clearly indicates the values of M'' for SBVN ceramic which are slightly lower than that of the SBN ceramic at 723 K ($\approx T_c$) as the

dielectric constant values of vanadium doped samples are higher.

3.5. Electrical conductivity

Electrical conduction (σ) is a thermally activated process and follows the Arrhenius law

$$\sigma = \sigma_0 e^{-\frac{E_a}{kT}} \quad (19)$$

where σ_0 is a pre-exponential factor and E_a , K and T are respectively the activation energy for conduction, Boltzmann's constant and the absolute temperature. The activation energy for conduction (E_a) of grains could be calculated from the slope of the straight line obtained from $\ln \sigma$ vs $1/T$ plot. Fig. 11 shows the Arrhenius plot of the dc conductivity evaluated from the impedance plots of SBN and SBVN samples as a function of temperature and the corresponding activation energies are found to be equal to 1.11 and 1.30 eV, which may be ascribed to the motion of oxygen vacancies and are consistent with those obtained by the present impedance studies and also with earlier reports [15]. Oxygen vacancies are considered to be the most mobile charge carriers in layered perovskite ferroelectrics like SBN and SBT. The evaporation of bismuth oxide in layered perovskite would lead to oxygen vacancies.

Figure 11 Arrhenius plot for d.c. conductivity (σ) of SBN and SBVN ceramics.

The conductivity value is higher for dense SBVN ceramic than that of porous SBN which may be attributed to the higher density and grain to grain contact. In the case of porous SBN ceramic, the pore acts as a blocking source which immobilizes the fraction of the matrix charge carriers because of the strong distortions in the field lines around them, which would lead to the lower conductivity.

4. Conclusions

Vanadium (10 mol%) doping on niobium sites in the SBN system resulted in obtaining partially c-oriented plates, with a dense microstructure accompanied by an

increase in dielectric constants. The low depression angles of the specific contribution in the impedance plot of dense SBVN ceramic suggest homogeneity in the electrical properties. The frequency plots of imaginary components of impedance and modulus of SBN and SBVN ceramics suggest the relaxation to be non Debye type.

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