Ferroelectric Characterization of Vanadium doped SBN

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Abstract : *SBT and vanadium doped SBT have been synthesized at 1000 °C and 900 °C respectively by using mixed oxide solid state reaction method according to the compositional formula $SrBi_2(Ta_{1-x}V_x)_2O_9$ where x=0.00 and 0.15 with approximately 4 wt% excess Bi_2O_3.. Post sinter annealing was performed on both virgin and Vanadium doped SBT samples and an effort have been made to investigate the mechanism of formation of oxygen vacancy in a systematic and detailed structural, and electrical study of SBT ceramics upon vanadium doping under fast heating rate and different annealing times, since the electrical properties are strongly influenced by processing parameters including the precursor preparation, pyrolysis temperature, and final annealing temperature. XRD analyses indicated that a single phase layered perovskite structure was observed without any detection of secondary phases up to 15% of vanadium doping in SBT. Low temperature synthesis of SBT could minimize the high temperature bismuth losses in the material and provide a better profile of high temperature dielectric loss and dielectric permittivity without even vanadium doping. Annealing also had a significant impact on ferroelectric hysteresis of doped SBT ceramics. The PE loop analysis of annealed sample of virgin SBT does not have any effect on hysteresis parameters and a good ferroelectric hysteresis loop was developed in as sintered samples of SBT. Furthermore, the polarization switching could not be possible within the applied voltage range even after 7.5 h annealing in case of vanadium doped samples. Polarization could only be switched after performing 24 h annealing on vanadium doped SBT sample. Hysteresis behavior was quite in agreement with the observed dielectric properties of the ceramics.*

Key Words :

1. Introduction

Ferroelectrics are excellent candidates for the applications in data storage in digital memory systems. Among them bismuth oxide layered perovskite materials, such as $SrBi_2Nb_2O_9$ (SBN) and $SrBi_2Ta_2O_9$ (SBT) have attracted an increasing attention for FeRAM applications, because they are fatigue-free and lead free and possess ferroelectric properties independent of film thickness. Recently, efforts have been made to enhance their properties by the addition or substitution of alternative cations. In particular, partial substitution of niobium by pentavalent vanadium cations in SBN (SBNV) has been reported[1-6] to enhance the ferroelectric properties. Although there are several reports on the dielectric and ferroelectric properties of Va –doped SBN system[7-12] for variable Va-doping, the data pertaining to the frequency dependence over a wide temperature range (40^0C to 500^0C) which is of practical importance has not been reported yet. In this article, we report the frequency dependent electrical properties of Va-doped SBN system using complex impedance spectroscopy.

2. Experimental

The Polycrystalline samples of strontium bismuth vanadium niobates with a compositional formula $SrBi_2(Nb_{1-x}V_x)_2O_9$ (SBNV) for x= 0.0, 0.05, 0.10 and 0.15 were prepared by solid state reaction method using high purity $SrCO_3$, Bi_2O_3, Nb_2O_5 and V_2O_5 as starting materials. All the powders were weighed in a desired weight ratio with approximately 3 wt% excess bismuth.

Powders were preheated at 850^0C for pure SBN and at 800^0C for 2h for vanadium doped ceramics in a tubular furnace. These powders were ground and re-calcined at 900^0C for 1 Hr and 850^0C for 2 h temperature for SBN and vanadium doped SBN ceramics respectively. Pellets were prepared using a uniaxial hydraulic press at a pressure of 5×10^5 N/m^2. Pellets of samples without vanadium doping were sintered at 900^0C for 2 hr, while the sintering temperature was kept at 850^0C for vanadium doped samples. This lower sintering temperature for SBN was to prevent the bismuth loss at high temperatures. The X-Ray Diffraction (XRD-Bruker D8 Advanced) patterns of sintered pellets were recorded at room temperature using Cu K_α radiation (λ= 1.5418Å) in the wide range of Bragg's angle lying between $10^0 < 2\theta < 80^0$ to confirm the phase purity of the material. Dielectric measurements were carried out on silver electrode samples in the temperature range 40^0C - 500^0C on a computer controlled HIOKI LCR–Hi Tester 3532, at various frequencies ranging from 100 Hz to 100 KHz.

3. Results and Discussion

XRD analysis indicated that single phase layered perovskite were formed within the composition range studied. The presence of excess bismuth is beneficial to a certain extent because it tends to bring down the formation temperature of the desired material. Too much of excess bismuth could lead to segregation of Bi_2O_3 from the rest of the matrix, and result in degradation of properties. In our study, however, we did not observe any Bi_2O_3 peaks in XRD. The experimental density of the samples was found to lie in the range 92% to 97% of the X-ray density of the materials.

Some of the structural and dielectric parameters are given in *Table-1*. The complex impedance spectroscopy enables us to separate out the contribution of grains, grain boundaries and polarization effects to the electrical properties of the materials in frequency and time domain as well. Using the complex impedance spectrum the electrical conduction behaviour and its frequency and temperature dependence can also be studied with the relation $\sigma_{ac} = 2\pi f \varepsilon \varepsilon_0 \tan\delta$, where f, ε and ε_0 are the frequency, dielectric permittivity and the vacuum permittivity respectively. The real and imaginary part of impedance can also be given in terms of resistance and capacitance of grain and grain boundaries.

$$Z' = \frac{Rg}{1+(\omega RgCg)^2} + \frac{Rg}{1+(\omega RgbCgb)^2} \quad (1)$$

$$Z'' = Rg\left(\frac{\omega RgCg}{1+(\omega RgCg)^2}\right) + Rgb\left(\frac{\omega RgbCgb}{1+(\omega RgbCgb)^2}\right) \quad (2)$$

where $\omega = 2\pi f$ is the angular frequency and Cg, Rg, Cgb and Rgb are the capacitance and resistance of grains and grain boundaries respectively. *Figure-1-4* shows the typical Z′ Vs Z″ plots of SBN and vanadium doped SBN samples at various temperatures starting from 100 ^{o}C to 500 ^{o}C in the frequency span lying between 100 Hz to 1 MHz. As shown in Fig 1-4 up to 250 ^{o}C there is only one semicircle like arc corresponding to each temperature for all the samples. This indicates that the electrical process in the material arise basically due [13-16] to the contribution from bulk (grain interior) and can be modeled as an equivalent electrical circuit comprising of parallel combination of Rg and Cg. In vanadium doped Fig. 2-4 sample there is also a noticeable dispersion in the Z′ Vs Z″ curves as temperature goes from 100 ^{o}C to 250 ^{o}C and the Z′ shifted towards lower values, indicating the reduction in the grain resistance and a possible enhancement in the bulk conduction upon vanadium doping.

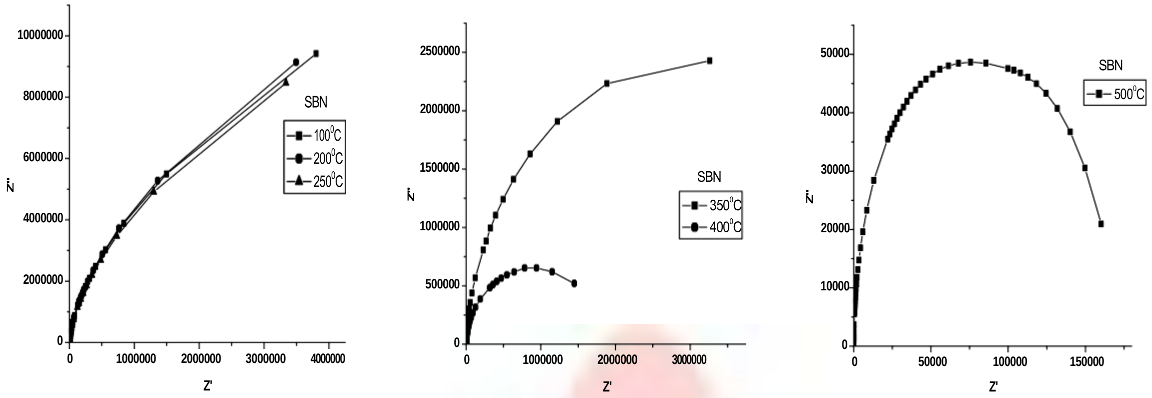

Fig. 1 Complex Impedance Plots at Different Temperatures for as Sintered SBN(X=0)

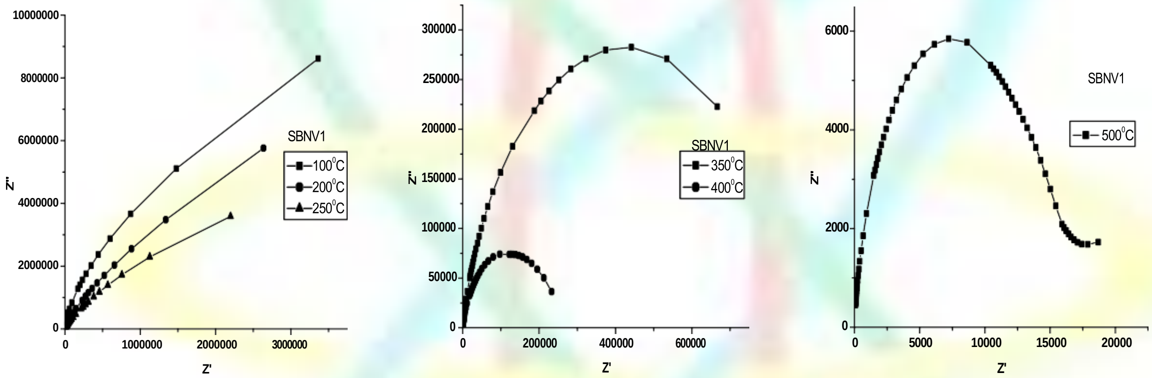

Fig. 2 Complex Impedance Plots at Different Temperatures for as Sintered SBNV(X=0.05)

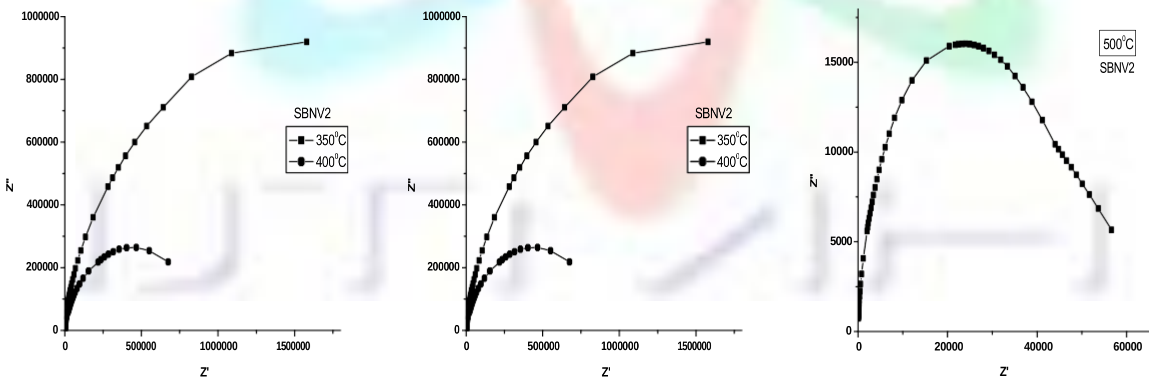

Fig. 3 Complex Impedance Plots at Different Temperatures for as Sintered SBNV(X=0.10)

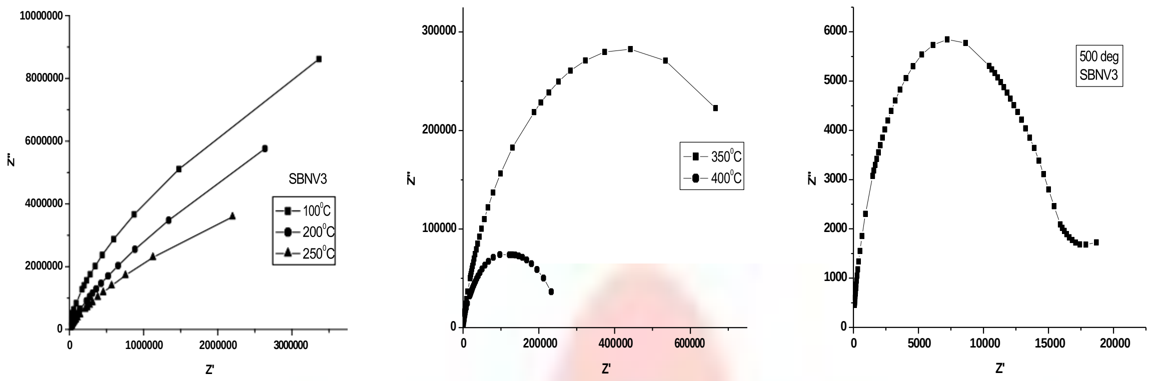

Fig. 4 Complex Impedance Plots at Different Temperatures for as Sintered SBNV(X=0.15)

No such dispersion could be observed in SBN (Fig.1) up to 250 °C temperature. On higher temperatures (> 250 °C) these arcs become circular. No trace of second semicircle was detected up to 500 °C for un doped SBN samples (Fig.1). However, there occurs another semicircular arc in the vanadium doped sample at 500 °C which is attributed to the intragranular activities starting in the material. No contribution from the interfacial polarization effect could be extracted from the complex impedance spectrum in the entire temperature range studied over here.

Table1. Structural and Dielectric Parameters of $SrBi_2(Nb_{1-x}V_x)_2O_9$

Composition	ε_{max} at 1KHz frequency	T_c(°C) at 1 KHz frequency	Lattice parameters		
			a (Å)	c (Å)	V(Å³)
SBN; x=0	2032	455	3.898	25.249	383.643
SBNV; x=0.05	2085	460	3.901	25.290	384.250
SBNV; x=0.10	1686	465	3.890	25.026	378.690
SBNV; x=0.15	1482	475	3.881	25.123	378.406

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