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Preparation and Ferroelectric Studies on Strontium Barium Sodium Niobate Ceramics

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Solid solutions of $Ba_{1-x}Sr_xNa_2Nb_{10}O_{30}$ where x = 2.0; 2.4; 2.8 and 3.2 have been prepared and characterized by maximum dielectric and resistivity properties for the compositions sintered at 1225 °C for the composition at morphotropic phase boundary region (MPB). An anomalous resistivity behaviour has been observed for the same compositions. The optimum sintering temperature 1225 °C is found to achieve enhanced physical properties in this system.

I. INTRODUCTION

The search for increased electro-optic, pyroelectric and piezoelectric effects in the tungsten bronze ferroelectric crystal family has stimulated interest in a number of potential morphotropic phase boundary (MPB) systems. The tungsten bronze system [1] binary join from (1-x)$Ba_2NaNb_5O_{15}-xSr_2NaNb_5O_5$, (1-x)BNN-xSNN is attractive because it doesn't contain lead. Although, the end members of both are weakly orthorhombic, they possess different space group symmetries, (Ccm_2 for BNN Bbm_2 for SNN) [2,3] and therefore potential for morphotropic phase boundary (MPB) behaviour in a binary system. In the BNN-SNN system, it has been found that the ferroelectric phase transition temperature decreased and then increased, indicating the possibility of morphotropic phase boundary [4,5] region near the composition $Ba_{1.6}Sr_{2.4}Na_{2.0}Nb_{10}O_{15}$.

In view of tungsten bronze ferroelectrics, which have morphotropic boundary, can have a number of enhanced dielectric, piezoelectric and electro-optic properties when compared to more conventional ferroelectric materials. It is proposed to study the effect of sintering temperature on density, dielectric, ferroelectric, and microstructure in the composition in and around MPB region of BNN-SNN system.

II. EXPERIMENTAL

Samples of BNN-SNN system with the following compositions have been prepared with the usual high temperature technique, by taking suitable proportion of $BaCO_3$, $SrCO_3$, Na_2CO_3 and Nb_2O_5 of AR grade purity as starting materials, yield the compositions.

- $Ba_{1.6}Sr_{2.4}Na_{2.0}Nb_{10}O_{30}$ - BSNN - 1
- $Ba_{1.2}Sr_{2.8}Na_{2.0}Nb_{10}O_{30}$ - BSNN - 2
- $Ba_{0.8}Sr_{3.2}Na_{2.0}Nb_{10}O_{30}$ - BSNN - 3
- $Ba_{2.0}Sr_{2.0}Na_{2.0}Nb_{10}O_{30}$ - BSNN - 4

The physical mixtures were dry ground into fine powders and these were further mixed thoroughly in presence of methanol to improve homogeneity. The mixture were calcined twice at 950 °C for 6 hrs in air. The calcined samples were pressed into pellets with 5% PVA as binder using a pressure of 5 tons per square inch, after burning the binder at 600 °C for 1 hr.

The phase identification has been carried out by XRD using CuK_α radiation. The microstructural studies were carried out by using SEM 330-A JEOL. Dielectric and resistivity measurements were carried out by using a capacitance bridge, Digital LCR meter type VLLR-6 and Keithley model 614 electrometer, respectively, on silver coated pellets of 11 mm diameter, around 13 mm thickness cured at 600 °C for 1 hr. Density is measured by water immersion method.

III. RESULTS AND DISCUSSION

The XRD patterns in the compositions indicated the structure to be orthorhombic. The lattice parameters of the same computed from their XRD patterns and given in table 1. It is obvious that the lattice constants in BSNN-1 (which is at MPB region) are a = 17.59 Å, b = 17.56 Å and c = 3.93 Å. The values obtained are very much close to the literature values [4]. Similarly the lattice constants in rest of the three compositions obtained are closed with the reported value [4]. Densities in the compositions has been measured and tabulated in Table 2. The density (D, gr/cm^3) values are of nearly 90% to that of theoretical values. However, no systematic variation in densities has been observed. The values of grain diameter (GD, μm) of compositions sintered at different temperatures are given in Table 2. It is obvious that there is no systematic behaviour of grain growth observed. However, there is a decrease in the grain size

Table 1. Lattice constants

Comps	a (Å)	b (Å)	c (Å)
BSNN-1	17.59	17.65	3.93
BSNN-2	17.58	17.59	3.91
BSNN-3	17.52	17.59	3.93
BSNN-4	17.58	17.75	3.93

with increasing of sintering temperature. Also, within the composition at a particular sintering temperature the maximum grain diameter has been found for BSNN-1.

Dielectric constant versus temperature for typical sintering temperature at 1225 °C and 1250 °C were shown in Fig. 1. The dielectric response in all the compositions at four different sintering temperatures has been observed to be broad. This behaviour may be due to compositional fluctuations. The Curie temperature for the composition BSNN-1 for all the sintering temperatures found to be around 200 °C, which is well matched with the literature value [4]. As strontium content increases T_c found to increase, up to 70% of strontium content. Even after further increase in strontium contents the Curie temperature found to decrease. The maximum values of room temperature dielectric constant (K_{RT}), and dielectric constant at Curie temperature (K_{Tc}) are found for the composition, BSNN-1, at the sintering temperature 1225 °C. Therefore 1225 °C is the optimum sintering temperature for the MPB composition of BSNN-1. The Curie-Weiss law has been observed in the para-region, and Curie-Weiss constant computed and found to in the order of 10^5 K, indicating the materials are to be oxygen octahedra ferroelectrics.

D.C. resistivity measurements have been made with 2-probe method by applying a constant voltage of 5 volts for all compositions. As the sintering temperature, 1225 °C is found to be optimum temperature from the dielectric measurements, therefore the resistivity response with temperature in the compositions performed at the same temperature. The variation of resistivity with temperature has been shown in Fig. 2. It is obvious that the resistivity behaviour both in BSNN-1 and BSNN-3 is anomalous, i.e., as the temperature increases resistivity also increases, resistivity gives a maximum (ρ_{max}) at a particular temperature (ρ_{Tc}) even after the increase in temperature resistivity shows a decrease, this type of behaviour is also called positive temperature coefficient of resistivity (PTCR). This type of behaviour is similar to modified $BaTiO_3$. Similar behaviour [6] has been observed in strontium titanium niobate. This behaviour can be explained by Heywang's model [7,8]. According to this model, barrier layers are formed between ceramic grains which will increases the resistivity near T_c of the material. The values of ρ_{Tc} are found to be comparable that of T_c obtained from dielectric measurements. Where as the resistivity behaviour in BSNN-2

Table 2. Density, grain diameter and dielectric data

Sin. Temp. °C	Comp No.	D g/cm^3	GD μm	K_{RT}	K_{Tc}	T_c °C
1175	BSNN-1	4.54	1.818	160	365	202
	BSNN-2	4.67	1.439	250	350	128
	BSNN-3	5.02	1.022	340	510	162
	BSNN-4	4.76	1.439	530	800	128
1200	BSNN-1	4.43	1.401	160	620	196
	BSNN-2	4.58	1.666	280	335	102
	BSNN-3	4.64	1.590	660	753	124
	BSNN-4	4.40	-	140	210	122
1225	BSNN-1	4.56	1.439	315	760	202
	BSNN-2	4.57	1.477	320	388	107
	BSNN-3	4.38	1.363	240	257	117
	BSNN-4	4.71	-	325	415	117
1250	BSNN-1	4.98	1.704	180	475	202
	BSNN-2	5.00	-	190	290	122
	BSNN-3	5.03	1.287	110	175	152
	BSNN-4	5.03	-	175	982	117

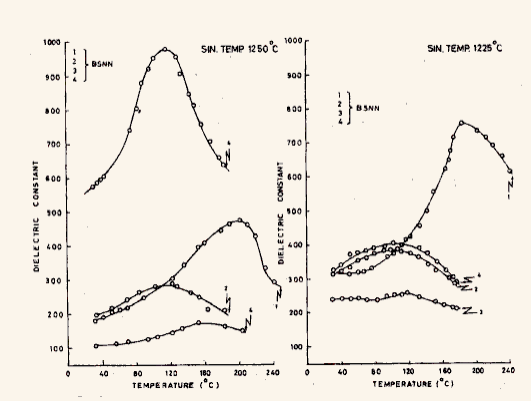

Fig. 1. Dielectric constant vs temperature.

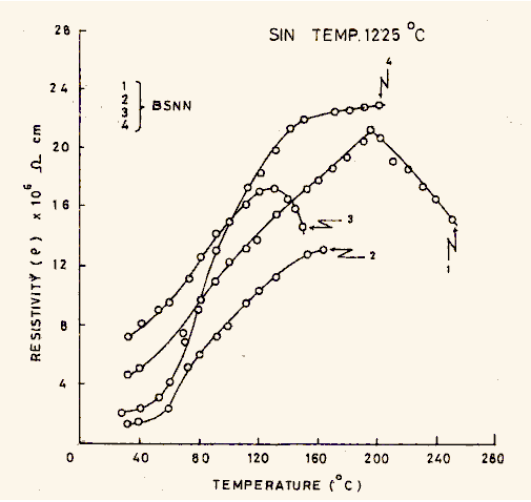

Fig. 2. Resistivity vs temperature.

Table 3. Resistivity data at sintering temperature : 1225 °C

Comp. No.	$\rho_{RT}\times$ Ω-Cm	$\rho_{max}\times10^7$ Ω-Cm	ρ_{Tc} °C	E_a, eV +ve	E_a, eV -ve
BSNN-1	4.5	2.4	198	0.17	0.02
BSNN-2	1.4	1.3	-	0.23	-
BSNN-3	5.2	1.7	127	0.29	0.03
BSNN-4	1.8	2.2	-	0.19	-

and BSNN-4 has been found to be metallic. The values of activation energies (E_a) have been computed and given in Table 3 along with ρ_{eT}, ρ_{max} and ρ_{Tc}.

It is concluded that the compositions are belongs to orthorhombic structure and the maximum density varies from 85-94% to that of theoretical values has been found. The maximum K_{RT} and K_{Tc} have been found for the composition BSNN-1 at MPB sintered at 1225 °C. Therefore, it is concluded that 1225 °C is the optimum sintering temperature to achieve enhanced physical properties in BSNN system. Finally an anomalous resistivity behaviour which can be explained by Heywang's model has been found in BSNN-1 and BSNN-3 which is at MPB region for BSNN system.

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