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Structure and Dielectric Properties of BSKNN

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Ferroelectric Ceramic Compositions of $(Ba_{1-y}Sr_y)_4$ $(K_xNa_{1-x})_2$ $Nb_{10}O_{30}$ where $x = 0.6$, 0.4, 0.5, 0.75 and $Y = 0.4$, 0.6, 0.75 and 0.25 have been prepared and characterized by XRD and SEM. Materials are found which belongs to tetragonal structure. The optimum sintering temperature is found to be 1225 °C to achieve maximum physical properties. Compositions at morphotropic phase boundary (MPB) region are shown to have enhanced dielectric properties and anomalous resistivity behaviour which is explained by Heywang's model.

I. INTRODUCTION

Since 1981, the single crystalline ferroelectrics $(Ba_{1-y}Sr_y)_{0.8}(K_xNa_{1-x})_{0.4}Nb_2O_6$ where $0.5 \leq x \leq 0.75$ and $0.3 \leq y \leq 0.9$ (BSKNN) with tetragonal tungsten bronze type structure in which the A sites are all occupied has been developed and studied by XU *et al.* [1–7]. BSKNN exists [8] in the quaternary system $BaNb_2O_6$-$SrNb_2O_6$-$KNbO_3$-$NaNbO_3$. Further it has been reported [9] that a morphotropic phase boundary (MPB) region exists between the ceramic composition of BSKNN-2 ($Ba_{1.0}Sr_{3.0}K_1Na_1Nb_{10}O_{30}$) and BSKNN-3 ($Ba_{1.6}Sr_{2.4}K_{0.8}Na_{1.2}Nb_{10}O_{30}$). BSKNN solid solution crystals are based on the $Sr_2NaNb_5O_{15}$ and $Ba_2KNb_5O_{15}$ systems. Also, these crystals showed a good piezoelectric and pyroelectric properties and were useful piezoelectric transducer and pyroelectric detector materials [3–5]. Further, BSKNN was found to be a photorefractive material and a self pumped phase conjugator [10]. It has sufficient hardness to allow good machining and workability and is insoluble in ordinary solvents including water.

In view of the importance of BSKNN for device applications and since the material exhibits a MPB region, it is proposed to study the effect of sintering temperature on density, dielectric, ferroelectric and microstructural properties at MPB region to achieve enhanced properties.

II. EXPERIMENTAL

Following materials have been prepared by the conventional high temperature ceramic technique with Analar grade $BaCo_3$, $SrCO_3$, K_2CO_3, Na_2CO_3 and Nb_2O_5. Suitable proportions of the starting materials were mixed and calcinated twice at 950 °C for 6 hrs to provide homogeneous single phase.

$Ba_{2.4}Sr_{1.6}K_{1.2}Na_{0.8}Nb_{10}O_{30}$ (BSKNN-1)
$Ba_{1.6}Sr_{2.4}K_{0.8}Na_{1.2}Nb_{10}O_{30}$ (BSKNN-2)
$Ba_{1.0}Sr_{3.0}K_{1.0}Na_{1.0}Nb_{10}O_{30}$ (BSKNN-3)
$Ba_{3.0}Sr_{1.0}K_{1.5}Na_{0.5}Nb_{10}O_{30}$ (BSKNN-4)

The calcined powders were then mixed with a binder PVA and pressed into disc shape of around 1.5 mm of thickness and diameter of 11 mm. The discs were sintered at different temperatures 1175 °C, 1200 °C, 1225 °C and 1250 °C for 8 hrs. More than 85−94% of the theoretical density has been achieved in the prepared materials. The samples are polished and electroded with silver paste and then cured at 600 °C for the dielectric and resistivity studies. The phase identification in the above materials have been made by using a diffractometer (JEOL-JDX-8P) with X-ray CuK_α radiation and Nickel filter. Scanning electron microscopic studies have been made on the materials coated with thin film of Au, using a SEM JEOL-330-A . Dielectric and resistivity studies have been made using a digital LCR meter (VLCR 6) and a Keithley model 614 electrometer, respectively.

III. RESULTS AND DISCUSSION

The XRD patterns obtained are of single phase and belongs to tetragonal structure. The lattice constants have been evaluated using unit weighted least square computer program. The lattice constants in BSKNN-1 are a,b = 12.53 Å and c = 3.97 Å which are well matched with literature [11] values, a,b = 12.506 Å and c = 3.982 Å. Similarly the lattice parameters in BSKNN-3 are a,b = 12.43 Å and c = 3.93 Å well agreed with reported values a,b = 12.437 Å and c = 3.935 Å.

Density in all the composition has been measured with water immersion method. No systematic behaviour in density is observed. However, the maximum density about 94 percent to that of the theoretical value has been observed for the composition BSKNN-1 which is at MPB sintered at 1225 °C. The density data is given in

Table 1. Lattice Parameters.

Comps.	a=b (Å)	c (Å)
BSKNN-1	12.53	3.97
BSKNN-2	12.46	3.95
BSKNN-3	12.43	3.93
BSKNN-4	12.45	3.93

Table 2. Grain diameter have been computed from the SEM photograph. No systematic behaviour is observed in grain growth. Values of grain diameters (GD, μm) in the composition has been given in Table 2.

The typical response of dielectric constant at 1 kHz with temperature on BSKNN sintered at 1225 °C and 1250 °C has been shown in Fig. 1. A broad dielectric response has been observed in all the compositions sintered at four different temperatures. This broadness may be due to compositional fluctuations. The room temperature dielectric constant (KRT) maximum dielectric constant observed at curie temperature (KTC) and transition temperature (TC) for the composition sintered at different temperatures are given in Table 2. The curie temperatures obtained shows a little increase with increasing sintering temperature.Transition temperatures

Table 2. Density, grain diameter and dielectric data.

Sin. Temp. (°C)	Comp. No.	D (g/cm^3)	GD (μm)	KRT	KTC	TC (°C)
1175	BSKNN-1	5.08	1.212	430	638	195
	BSKNN-2	4.40	1.590	200	269	142
	BSKNN-3	4.95	1.248	370	510	164
	BSKNN-4	4.33	1.174	260	380	162
1200	BSKNN-1	4.44	1.401	650	1050	198
	BSKNN-2	4.36	1.553	310	452	152
	BSKNN-3	4.33	1.022	150	227	168
	BSKNN-4	4.53	1.590	375	478	139
1225	BSKNN-1	5.32	1.181	800	1090	201
	BSKNN-2	4.50	1.098	325	520	157
	BSKNN-3	4.30	1.401	230	285	174
	BSKNN-4	4.63	1.287	780	1020	127
1250	BSKNN-1	4.43	1.098	575	897	205
	BSKNN-2	4.53	1.893	265	430	157
	BSKNN-3	4.87	1.212	140	210	177
	BSKNN-4	4.86	1.590	375	447	147

Table 3. Resistivity data: Sint. Temp: 1225 °C.

Comp. No.	ρ_{RT} ($\times 10^6$ Ωcm)	ρ_{max} ($\times 10^7$ Ωcm)	ρ_{TC} (°C)	E_a, ev +ve	E_a, ev −ve
BSKNN-1	1.1	3.2	201	0.22	0.11
BSKNN-2	3.2	0.6	—	0.49	—
BSKNN-3	1.6	3.3	174	0.12	0.02
BSKNN-4	1.6	1.7	—	0.32	—

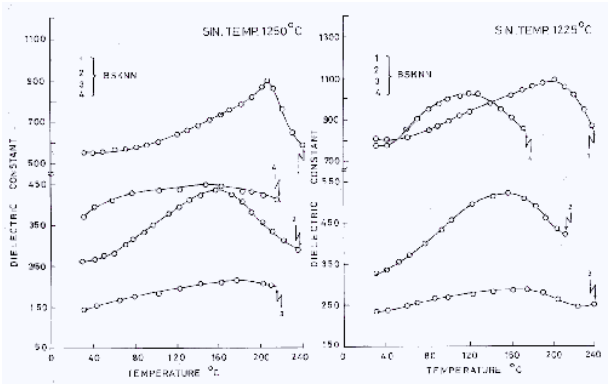

Fig. 1. Dielectric constant vs. temperature.

obtained in BSKNN-1 and BSKNN-3 which are at MPB region are found to be around 200 °C and 170 °C. The values are well matched with the literature values [8]. The values of KRT and KTC for BSKNN-1 and BSKNN-3 are much higher than BSKNN-2 and BSKNN-4 indicating MPB behavior of enhanced physical property. A curie-weiss law has been obeyed in para region and curie-Weiss constant has been computed and found to be in the order of 10^5 K. This indicated the materials are belong to oxygen octahedra ferroelectrics [11].

The trend in DC resistivity with the temperature in compositions sintered at 1225 °C has been depicted in Fig. 2. It is evident that the resistivity response both in BSKNN-1 and BSKNN-3 is anomolous, i.e., as the temperature increases, the resistivity also increases, resistiv-

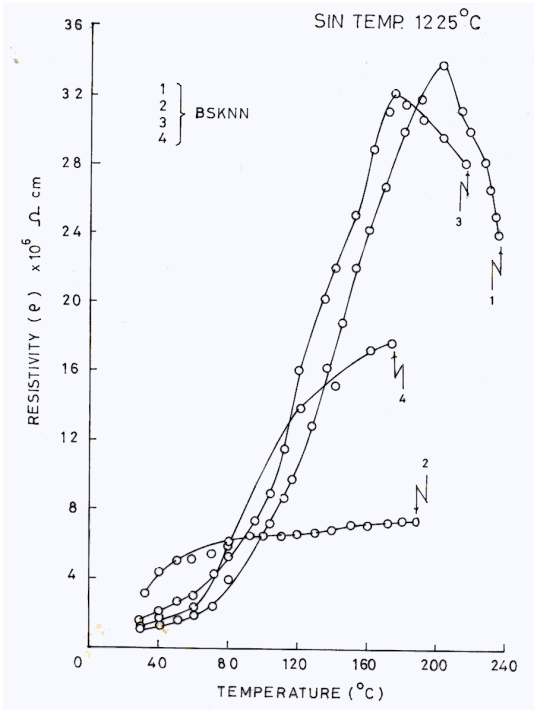

Fig. 2. Resistivity vs. temperature.

ity gives a maximum (ρ_{max}) at a particular temperature (ρ_{tc}). Even after the increasing temperature resistivity shows a decrease. This type of behaviour is also called as positive temperature co-efficient of resistivity (PTCR). Similar behaviour [12] has been observed in strontium titanium niobate ceramics. This type of behaviour can be explained by Heywang's model [13,14]. According to this model barrier layers are formed between ceramic grain which will increases the resistivity near transition temperature of the material. The values of maximum resistivity corresponding temperature (ρ_{tc}) are found to be comparable to that of ferroelectric curie temperature obtained from dielectric measurements. The behaviour of BSKNN-2 and BSKNN-4 is simply a metallic behaviour.

It is concluded that BSKNN materials belong to tetragonal structures. As the sintering temperature increases the ferroelectric curie temperature also increases. The KRT and KTC are found to be much higher values in BSKNN-1 and BSKNN-3 compared with BSKNN-2 and BSKNN-4 indicating the former materials at MPB region. Also anomolous resistivity behaviour has been found in MPB region composition of BSKNN.

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