



Synthesis of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ by Coprecipitation Method—Dielectric and Microstructural Characteristics

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Abstract. $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (SBN50) has been synthesized by coprecipitation method using $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ and Nb-oxalate as precursors and ammonium hydroxide as precipitant. Calcination at 1150°C resulted in pure SBN50 phase (XRD) and nano powder with size varying between 100–250 nm (TEM). The average grain size (SEM) in the sintered pellets ranged from 2.5 to $5\ \mu\text{m}$ as the sintering temperature varied from 1250 to 1350°C . The maximum sintered density was observed to be 93% of ρ_{th} . The plot of dielectric constant vs. temperature clearly showed a shift of dielectric maxima (ϵ_{max}) with frequency, indicating the relaxor nature of SBN50. The room temperature dielectric constant ($\epsilon_{\text{RT}} > 2300$) observed for all these samples is higher compared to the earlier reported values ($\epsilon_{\text{RT}} \sim 1500$). The T_c (for 1 KHz) varied from $47\text{--}60^\circ\text{C}$ depending on the sintering conditions. The hysteresis loops were recorded at various temperatures. The maximum saturation polarization for the unpoled pellets was found to be $2.3\ \mu\text{C}/\text{cm}^2$ when sintered at 1350°C . The improvement in dielectric and ferroelectric behavior is attributed to the enhanced homogeneity attained by the coprecipitation synthesis route used in the present study. Correlations between microstructure (sintering conditions) and dielectric behavior is explored.

Keywords: SBN, ferroelectric, relaxor, microstructure, coprecipitation, strontium barium niobate

Introduction

Ferroelectric relaxor materials are different from normal ferroelectrics due to their diffused phase transition and frequency dispersive nature. Strontium Barium Niobate is a non-lead based ferroelectric material having tetragonal tungsten bronze structure. It has the general formula of $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ($0.25 \leq x \leq 0.75$) with a unit-cell formula of $[(\text{A}1)_2(\text{A}2)_4\text{C}_4][(\text{B}1)_2(\text{B}2)_8]\text{O}_{30}$ and its physical properties change with composition [1]. In recent years it has gained much attention because of its potential application largely in electro-optic [2, 3], piezoelectric [4] and Surface Acoustic Wave (SAW) devices [5] owing to its large pyroelectric coefficient [6] and photorefractive properties [7, 8]. Due to environmental concerns, lead free materials are being

considered for many applications and SBN is among the few materials that are in the forefront of the non-lead based ferroelectric materials [9]. SBN has been synthesized using various methods and with different Sr:Ba ratio. For example, in single crystal form by Czochralski method [7], in polycrystalline form by solid-state reaction synthesis [10–12]. A number of wet chemical methods have also been implemented to synthesize SBN. Some of which are sol gel [13, 14], hydrolysis aging [15], EDTA complex chemical route [16], partial coprecipitation [17] and solution combustion [18] method. Coprecipitation method, a wet chemical method for synthesizing ceramic materials, is known to result in high homogeneity, fine grain-sized materials. This is because, the precursors are in solution medium, homogeneity is in the molecular scale.

In the present case we report the synthesis of SBN ferroelectric material by coprecipitation route.

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A detailed investigation of the microstructural and dielectric properties is presented and discussed.

Experimental Details

$\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ and NbCl_5 (Aldrich, USA, 99%), A. R. grade liq. NH_3 and H_2O_2 (Qualigen), oxalic acid (Loba, 99%) were used as the starting material. The precursor, Nb-oxalate was prepared as described elsewhere [18]. The coprecipitation reaction was carried out by drop wise addition of aqueous solution of a mixture of $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ from one burette and Nb-oxalate from another burette into a round bottomed flask containing excess ammonium hydroxide as precipitant. The coprecipitation reaction was carried out by constant stirring of the precipitant by magnetic stirrer. The precipitate was washed, dried and then calcined at different temperatures. The phase analysis of the calcined powder was done by Phillips PW1729 powder X-Ray diffractometer. Phillips CM200 Transmission Electron Microscope was used for investigating the particle size and morphology. The pure phase SBN50 powder was compacted and sintered at different temperature. Grain morphology of the sintered compacts was studied using CAMECA SU30 Scanning Electron Microscope. For dielectric measurements, the sintered pellets were gold sputtered (Technics, UK) on both sides of the circular disc. To obtain better contacts the pellets were further coated with silver paste and were oven dried before carrying out dielectric measurements. Solatron SI 1260 Impedance Analyzer was used to measure the capacitance at 1, 10, 100 KHz and 1 MHz frequencies from room temperature to 250°C. The ferroelectric hysteresis loop was recorded at the room temperature as well as higher temperature using the RT66A Ferroelectric Test System. The schematic presentation of the experimental steps is shown in Fig. 1.

Results and Discussion

Figure 2, is the X-ray diffraction pattern of powder calcined at different temperatures. It shows that the 100% SBN50 phase was formed at the calcination temperature of 1150°C. In the XRD patterns of the powder calcined at temperatures below 1150°C the peaks corresponding to intermediate phases $\text{SrNb}_2\text{O}_6/\text{BaNb}_2\text{O}_6$ were present which disappear at the temperature of 1150°C (Fig. 2).

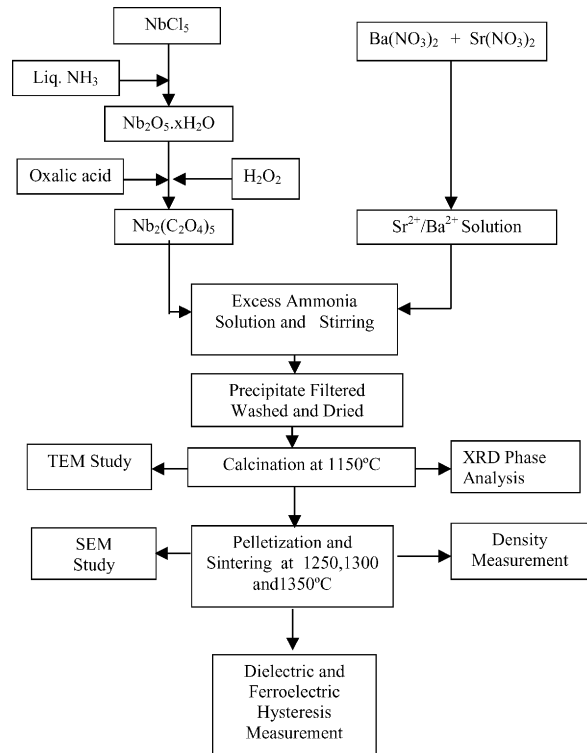


Fig. 1. Schematic flow chart of the experimental steps followed.

From the TEM investigation of the powder, the powder size was found to be in the range of 100–250 nm (Fig. 3). A fair degree of agglomeration in the powder was observed during the investigation. Figure 4(a)–(c) show the Scanning Electron Micrographs of the pellets sintered at 1250, 1300 and 1350°C respectively. Sintering at 1250°C resulted in high porosity as may be seen from the micrograph (Fig. 4(a)). It seems the necks have just formed justifying the first stage of sintering. As the temperature of sintering was increased, the grain size also increased because of broadening of the neck during sintering. Few unidirectional elongated grains can also be seen in Fig. 4(c). This may be due to Ostwald ripening of grains, where the bigger grains grow at the expense of smaller grains. Density of the sintered pellets were in the range of 86 to 93% ρ_{Th} . The variations in the average grain size and density are listed in the Table 1.

Dielectric constant was calculated from the measured parallel plate capacitance at 1, 10, 100 KHz and 1 MHz. Figures 5(a)–(c) and 6(a)–(c) show the variation of dielectric permittivity with temperature at four different frequencies. It may be noticed that a broad

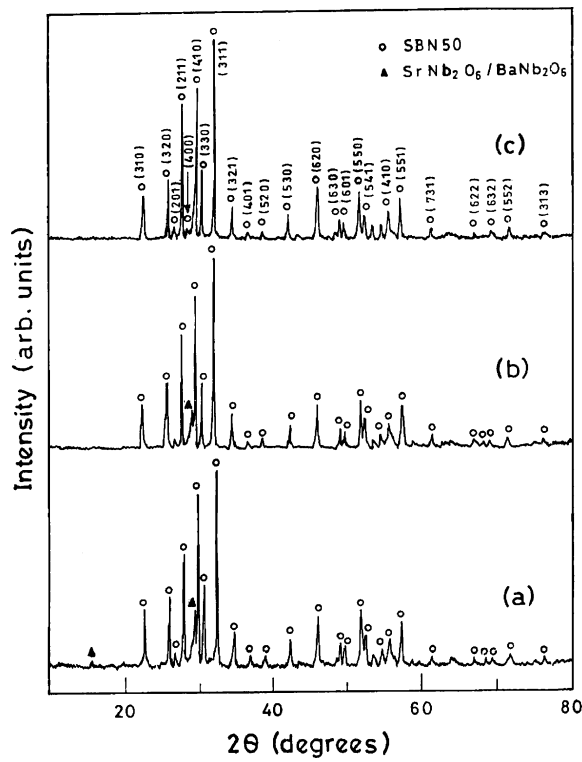


Fig. 2. X-ray diffraction patterns of the powder calcined at different temperatures ((a) 1050°C, (b) 1100°C, and (c) 1150°C).

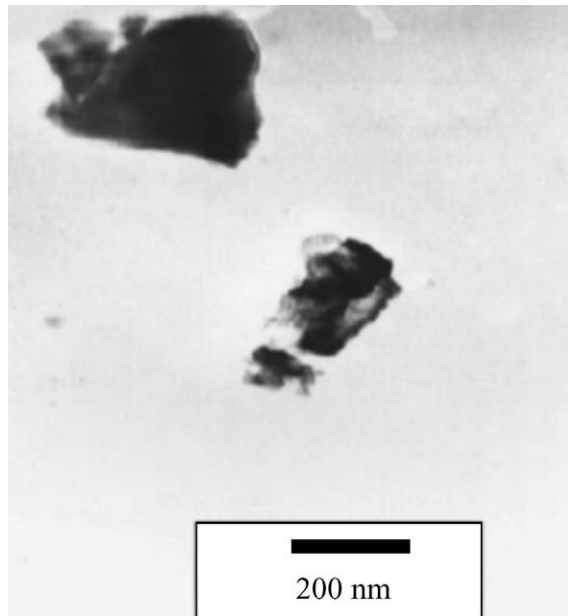


Fig. 3. Transmission Electron Micrograph of calcined powder (1150°C).

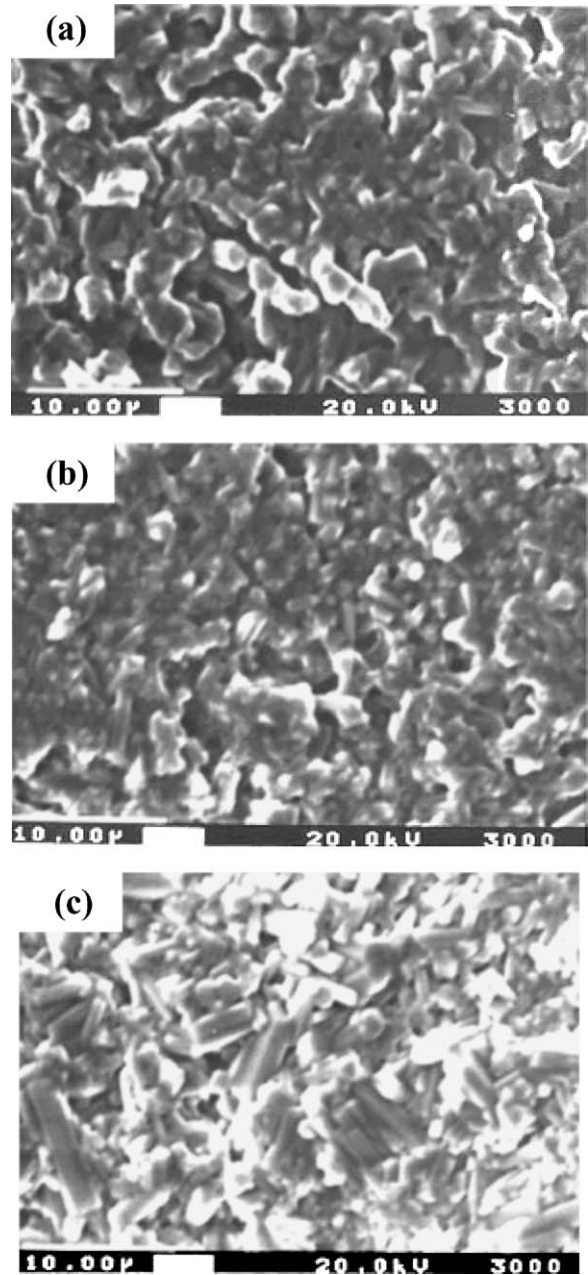


Fig. 4. Scanning Electron Micrograph of sintered pellets ((a) 1250°C, (b) 1300°C, and (c) 1350°C).

dielectric peak is present and also the maximum dielectric constant (ϵ_{max}) shifts to the right with increase in frequency. These are the characteristics of relaxor behavior of SBN50. The ϵ_{max} (dielectric constant at T_c) increases from 2717 to 3281 with the sintering temperature from 1250 to 1350°C. Similarly ϵ_{RT} (dielectric

Table 1. Variation of average grain size, density, ϵ_{\max} , ϵ_{RT} , $\tan \delta$, T_c for SBN50 sintered at different conditions.

Sintering temperature (°C)	Average grain size (μm)	Density % of ρ_{Th}	ϵ_{\max} at 1 KHz	ϵ_{RT} at 1 KHz	$\tan \delta$ (%)	T_c in °C at 1 KHz
1250	2.5	86.3	2717	2327	3.28	57
1300	3.0	90.2	2847	2779	2.46	47
1350	5.0	92.8	3281	2643	3.2	60

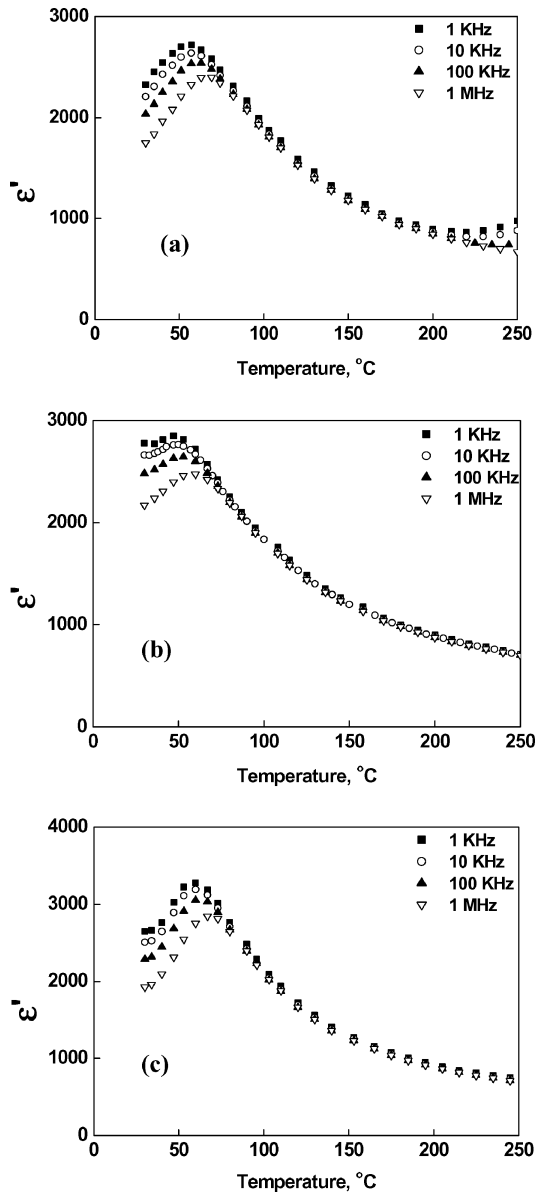


Fig. 5. Variation of dielectric constant with temperature (Sintered at (a) 1250°C, (b) 1300°C, and (c) 1350°C).

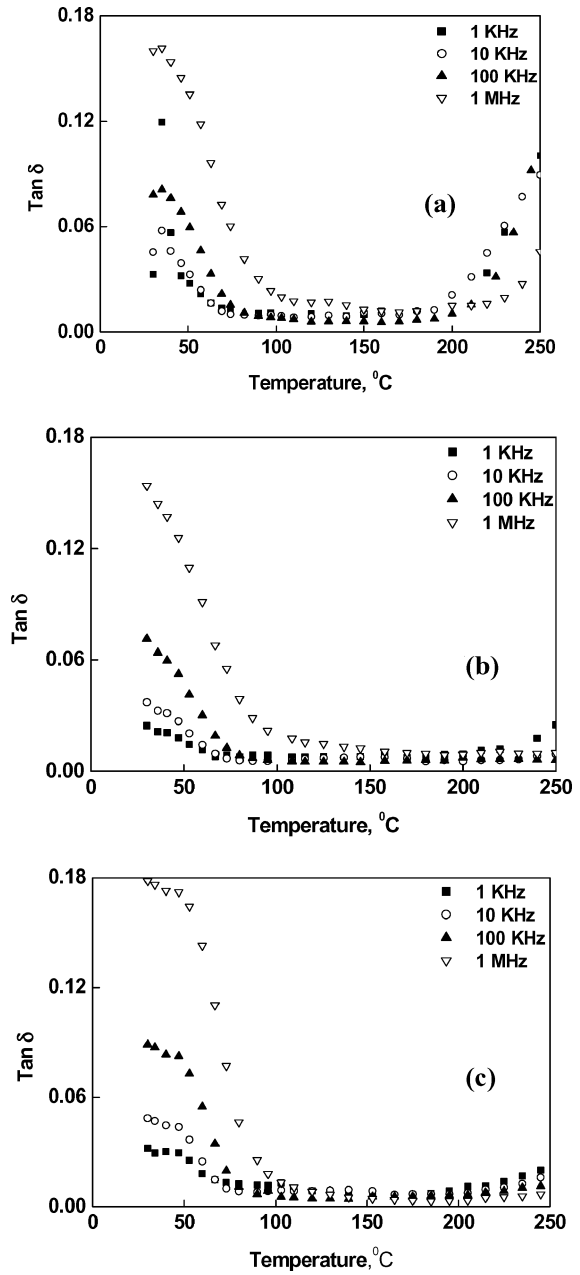


Fig. 6. Variation of dielectric loss tangent with temperature (Sintered at (a) 1250°C, (b) 1300°C, and (c) 1350°C).

constant at room temperature) increases from 2327 to 2643. The T_c was found to be 47, 57 and 60°C for sintering at 1250, 1300 and 1350°C respectively for the frequency 1 KHz. A variation in T_c , from 47 to 60°C agrees well with the reported values of T_c [$\sim 80^\circ\text{C}$ [11], 119°C [19], $50\text{--}55$ and $80\text{--}90^\circ\text{C}$ [20]] for SBN50

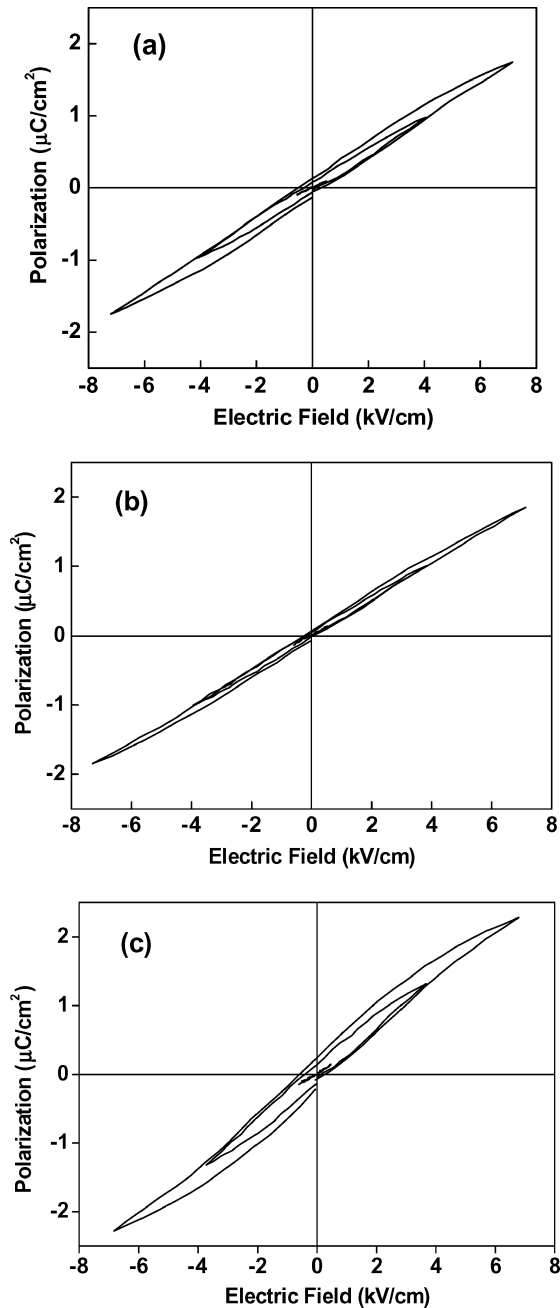


Fig. 7. Ferroelectric hysteresis loop at different field for SBN50 (Sintered at (a) 1250°C, (b) 1300°C, and (c) 1350°C).

composition. The T_c is also found to be varying with sintering temperature and method of preparation. The reason for this observed behavior still remains an unresolved issue. Maximum dielectric loss ($\text{Tan } \delta$) of $\sim 3.3\%$ was observed for the sintering temperature of

1250°C where as for 1300 and 1350°C it was ~ 2.3 and 3.2% (for 1 KHz) respectively. ϵ_{max} , ϵ_{RT} and $\text{tan } \delta$ are listed in Table 1.

The dielectric constant of SBN50 obtained by coprecipitation method described in this paper is higher than those reported, when synthesized from other routes for same sintering condition. Because all the three precursors were in the solution state it resulted in higher homogeneity in the material. Few other groups have reported different dielectric constant values at T_c for SBN50 (synthesized by solid-state methods), for example 2150 [11] and ~ 3750 [20]. Again the room temperature dielectric constant (ϵ_{RT}) at 1 KHz reported here is on the higher side as compared to the other reported values.

The ferroelectric hysteresis loop of the sintered pellets was recorded as function of polarization at different electric field. Figure 7(a)–(c) is the room temperature PE loop (hysteresis loss loop) for SBN50 sintered at 1250, 1300 and 1350°C. This clearly shows that the materials are not lossy in nature. The hysteresis loop shapes are almost elliptical in nature at low electric field where as the loop becomes nearly s-shaped with the increase in loop size with high electric field. The maximum saturation polarization (P_s) is found to be $2.28 \mu\text{C}/\text{cm}^2$ (sintered at 1350°C). This value is less than the reported value of $6.5 \mu\text{C}/\text{cm}^2$ for polycrystalline SBN50²⁰ and $25\text{--}35 \mu\text{C}/\text{cm}^2$ for single crystals⁶. The coercive field (E_c) estimated from hysteresis loop was found to be $0.595 \text{ kV}/\text{cm}$ and the remnant polarization (P_r), of the material found to be $0.236 \mu\text{C}/\text{cm}^2$ respectively when sintered at 1350°C. The resistivity is found to be in the order 10^9 to $10^{10} \Omega\text{cm}$ for all the cases. Table 2 compares the polarization values for all the sintering condition. Further to this to know the ferroelectric–paraelectric behavior, the hysteresis loss was measured at different temperatures at constant electric field. This was done by keeping the sample in between two electrodes immersed in silicone oil. The use of silicone oil ensured homogeneous heating and also avoided

Table 2. Change of P_s , P_r and E_c with sintering conditions for unpoled SBN50.

Sintering temperature (°C)	P_s ($\mu\text{C}/\text{cm}^2$)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
1250	1.963	0.136	0.609
1300	1.848	0.069	0.244
1350	2.280	0.236	0.595

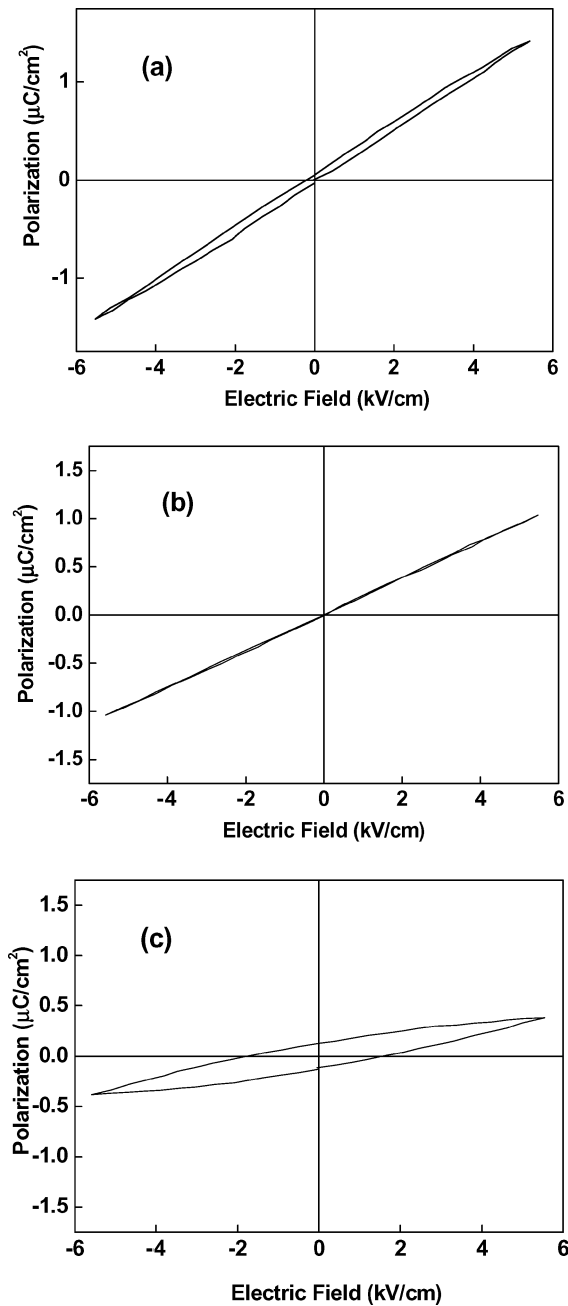


Fig. 8. Ferroelectric hysteresis loop at a constant field at different temperature for SBN 50 Sintered at 1300°C ((a) 35°C, (b) 65°C, and (c) 200°C).

sparking near contacts. Figure 8 shows the PE behavior of the pellet sintered at 1300°C, at different temperatures and at constant electric field. This shows that at 35°C, the material is ferroelectric as expected

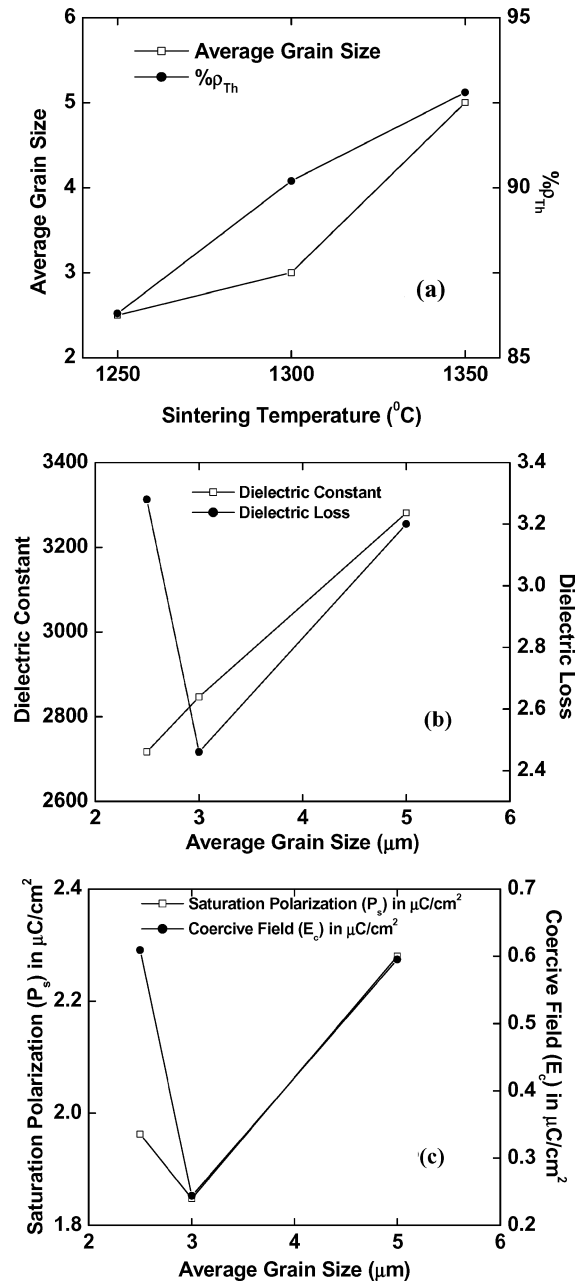


Fig. 9. (a) Variation of average grain size and $\% \rho_{\text{Th}}$ with sintering temperature. (b) Variation of dielectric constant and dielectric loss with average grain size. (c) Variation of saturation polarization and coercive field with average grain size.

with a hysteresis loop and high polarization. On increasing the temperature the material becomes paraelectric as the PE behavior becomes linear. On increasing the temperature further to 200°C, the

material shows low polarization and bulky loop indicates the lossy nature.

The relation of sintering temperature with grain size and density and the relation of grain size with dielectric behavior and spontaneous polarization with sintering temperature is shown in the Fig. 9(a)–(c). Figure 9(a) shows the steady increase of density and grain size with sintering temperature. It is also observed that the increase in dielectric constant with sintering temperature is linear in nature. However for variation of dielectric loss, saturation polarization and coercive field with sintering temperature shown in Fig. 9(b) and (c) there is no such trend is observed. Based on these results a concrete conclusion cannot be drawn at present.

Conclusions

In conclusions, SBN50 has been successfully synthesized by coprecipitation method. Superior dielectric properties have been achieved by the present method of synthesis. Room temperature dielectric constant is highest as compared to values so far reported and T_c is also close to room temperature. Grain growth is less (abnormal grain growth is totally absent) when compared to the synthesis by other methods. This resulted in absence of micro-cracks, which is a common feature when synthesized by solid-state process. This method further removes the unnecessary grinding steps, which are mandatory for solid-state reaction process. The superior properties thus obtained are expected and enhance the application potential of the material.

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