# Co-Precipitation Method for the Preparation of Nanocrystalline Ferroelectric $SrBi_2Nb_2O_9$ Ceramics

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**Abstract.** A simple co-precipitation technique had been successfully applied for the preparation of pure ultrafine single phase $SrBi_2Nb_2O_9$. Ammonium hydroxide and ammonium oxalate were used to precipitate $Sr^{2+}$, $Bi^{3+}$ and $Nb^{5+}$ cations simultaneously. No pyrochlore phase was found while heating powder at 850°C and pure $SrBi_2Nb_2O_9$ (SBN) phase was formed as revealed by the X-ray diffraction (XRD) studies. Particle size and morphology was studied by transmission electron microscopy (TEM). The room temperature dielectric constant at 1 kHz is 100. The ferroelectric hysteresis loop parameters of these samples were also studied.

**Keywords:** ceramics, electronic materials, oxides, chemical synthesis, ferroelectricity

## 1. Introduction

Bismuth-based**,** layered-structured perovskites such as $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) have been investigated in recent years because of their potential application in nonvolatile ferroelectric random access memories (FRAM) [1–3]. The advantages of these materials are fatigue-free operation and the compositions are free of toxic lead. For FRAM device applications, large remnant polarization, low coercive field by high Curie temperature are required for better performance and reliable operation. This Aurivillus family of compounds [4–6] may be represented by a general formula $(Bi_2O_2)^{2+} (A_{n-1}B_nO_{3n+1})^{2-}$ where A = Sr, Ca, Ba, Pb etc is in 12-fold coordination, B = Ta, Nb etc is in 6-fold coordination and n is any integer ($n = 1, 3$ etc). Most of the early developments of FRAM were carried out using lead zirconate titanate (PZT) perovskite ferroelectric due to its large remnant polarization ($P_r \sim 40 \ \mu C \ cm^{-2}$) and well documented properties. However, because of the problems associated with high leakage current, poor retention of switched charges etc, high density FRAM devices were not yet commercially

available. SBT films were found to exhibit no fatigue up to $10^{12}$ cycles, excellent retention characteristics and very low leakage currents on Pt electrodes. Synthesis of SBN thin films is known by pulse laser deposition [7], dip coating [8], sol-gel [9], microwave process [10] and from aqueous solution [11]. The dielectric and ferroelectric properties of SBN are discussed in Ref.12. However bulk ceramic powder synthesis has no reports using aqueous solution technique other than conventional solid state method [12].

The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, reactivity, purity and chemical composition. Using chemical methods, e.g. co-precipitation [13–15], sol-gel [9], etc have been confirmed to efficiently control the morphology and chemical composition of prepared powder. Among the reports of these wet chemical techniques sol-gel, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and difficult to maintain reaction conditions. SBN was reported to be prepared by aqueous route using niobium-citrate complex [16] and combustion method [17]. Co-precipitation is one of the successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution [13–15]. The purpose of this study was to prepare ultrafine

$SrBi_2Nb_2O_9$ powder using co-precipitation technique from simple inorganic salts. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. This method was not reported for the preparation of SBN powders in the literature.

## 2. Experimental

The $SrBi_2Nb_2O_9$ powder was prepared by precipitation from aqueous solution, in which the reactants were mixed in one molar stoichiometric quantities. The starting raw materials were niobium (V) oxide, bismuth (III) nitrate and strontium chloride, which were of AR grade (LOBA cheme). The aqueous solution was mixed in the following order: first, A stoichiometric amount of $SrCl_2 \cdot 6H_2O$ was dissolved in distilled water, $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in minimum amount of dilute $HNO_3$ to avoid precipitation of Bi ions and $Nb_2O_5$ was dissolved in a heated conc. HF at 100°C for 10 hrs. After the solution was mixed, an excess of quantity of concentrated HCl is added to the above solution to dissolve the strontium fluoride formed by the mixing of $NbF_5$ and $SrCl_2 \cdot 6H_2O$. An aqueous mixture of liquid ammonia and ammonium oxalate were added with constant stirring to the above solution mixture until pH > 10 to ensure complete precipitation (Fig. 1 for flowchart of preparation). After filtration and the precipitate was washed several times and dried in an oven at 100°C for 12 hrs. The oven-dried precursor was calcined at various temperatures ranging from 700 to 900°C to get phase pure samples. For comparison, SBN samples are also prepared by the conventional method. The corresponding oxides or carbonates were taken in stoichiometric ratio and mixed, ground several times and heated at 1000°C for 72 hours. The calcined powders from both precipitate derived and ceramic method were mixed with few drops of 1 wt% solution of poly vinyl alcohol and pelletized under the load of 1–2 tons (13 mm dia, 2 mm thickness). The green pellets (prepared by both methods such as coprecipitation and ceramic techniques) were sintered at 1000°C for 2 hours. The density of the sintered pellets were measured by Archimedes method. The surfaces of the sintered pellet were polished and electroded with low-temperature curing silver paint. The ferroelectric hysteresis loop parameters were measured with aid of a home-built Sawyer-Tower circuit.
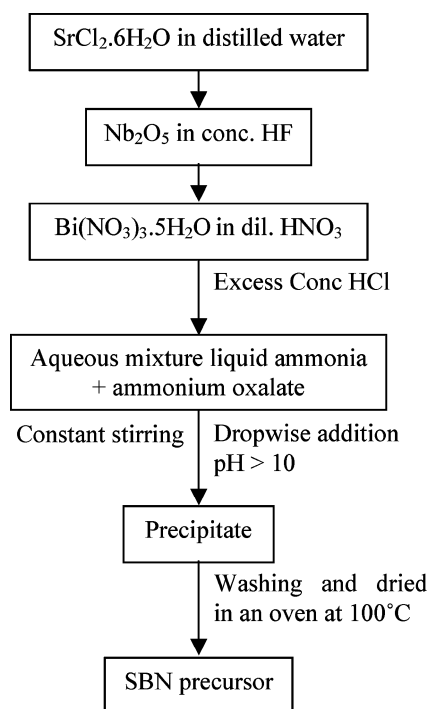


*Fig. 1.* Flowchart for the preparation SBN precursor.

The oven dried precursor of strontium oxalate and bismuth niobium hydroxide was characterized by various physico-chemical techniques. The powder X-ray patterns were recorded for oven dried and samples sintered at various temperatures by using Philips PW-1710
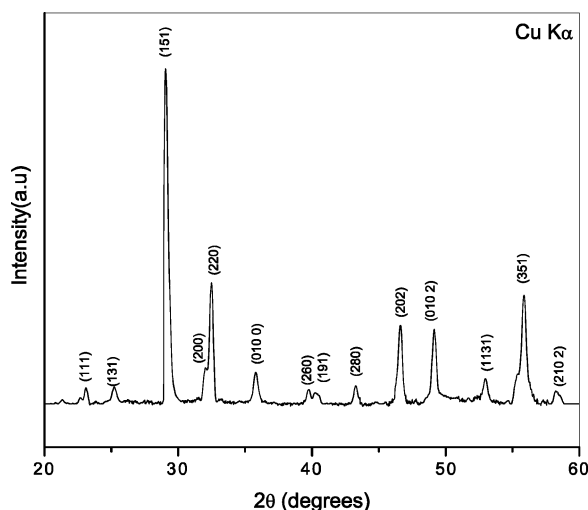


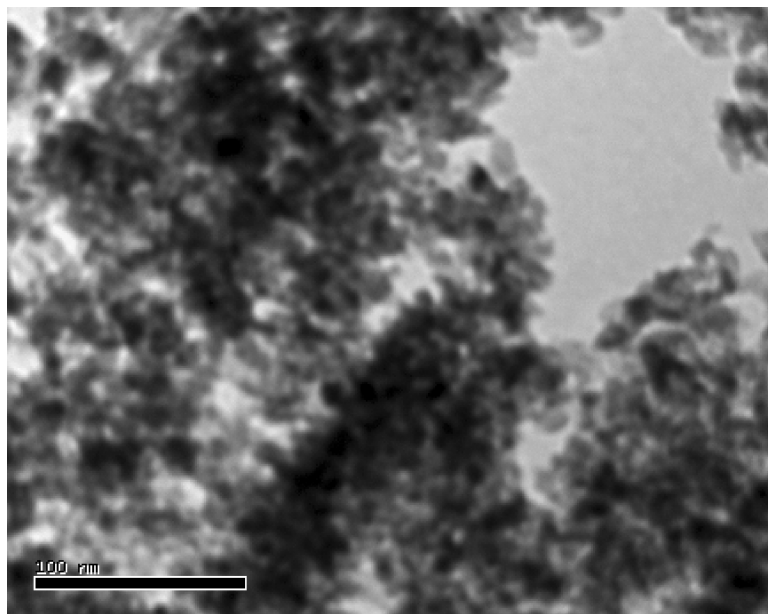*Fig. 2.* XRD of SBN precursor powder calcined at 850°C.

*Fig. 3.* TEM of SBN precursor powder calcined at 850°C.

model X-ray diffractometer using Cu-K$_\alpha$. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2$\theta$ range of 10°–80° for the period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. The fracture surface of the sintered samples are examined by Scanning electron microscope (Leica Cambridge 440 microscope) for the determination of the average grain size.

## 3.   Result and Discussion

Figure 2 shows the XRD pattern of SBN powder calcined at 850°C indicating formation of phase pure SBN powder. The crystal structure of SBN is orthorhombic and all the d-lines pattern match with reported values [18]. The calculated lattice parameters by least square fit are $a = 5.521$ Å, $b = 5.513$ Å and $c = 25.098$ Å. Conventional solid state method also forms SBN phase at 1000°C [12] after prolonged heating (72 hours) with comparatively larger particle size of $\sim 1$ $\mu$m. The parti-

cle size and morphology of the calcined powders were examined by transmission electron microscopy. Particle morphology of calcined powder (850° for 6 h) prepared by coprecipitation was irregular in shape, with an average primary particle size around 30 nm (Fig. 3). The particle size calculated from Scherrer's formula $(t = K\lambda/B\mathrm{Cos}\theta_B)$ where $t$ is the average size of the particles, assuming particles are spherical, $K = 0.9$, $\lambda$ is the wavelength of X-ray radiation, $B$ is the full width at half maximum of the diffracted peak and $\theta_B$
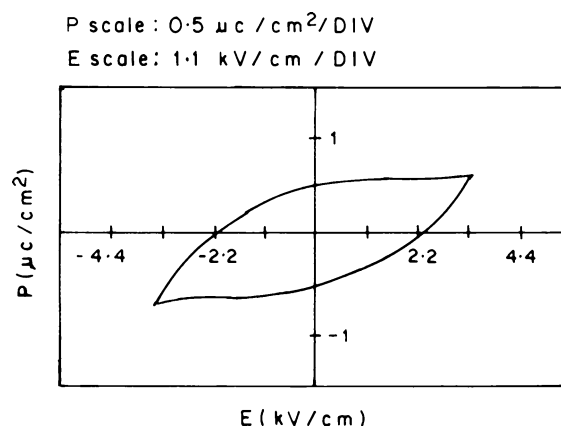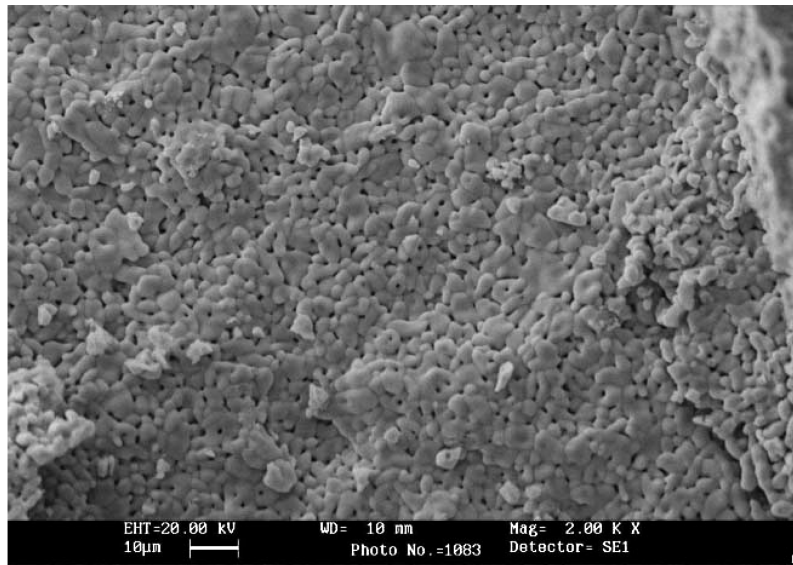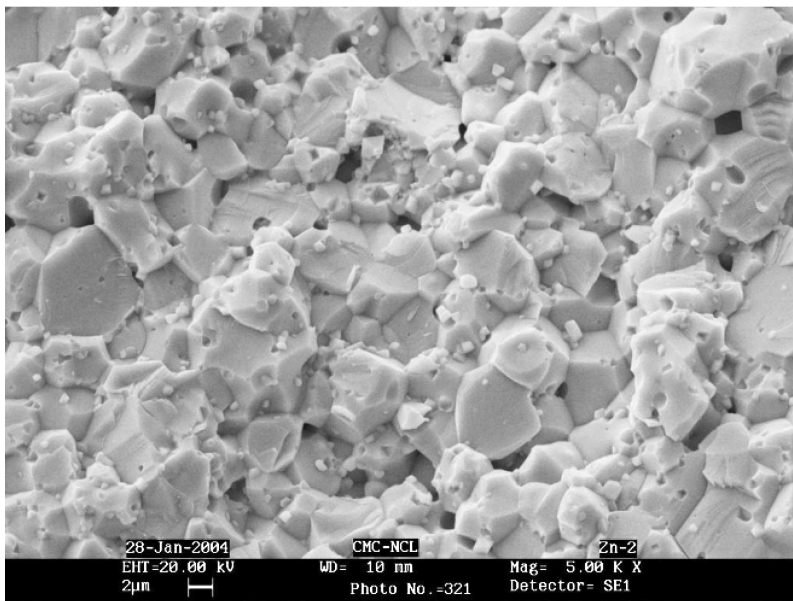
P scale : 0·5 $\mu$c / cm$^2$/DIV

E scale: 1·1  kV / cm / DIV



*Fig. 4.* Ferroelectric hysteresis loop traced by Sawyer-Tower circuit for coprecipitation derived sintered SBN samples.

(a)



(b)

*Fig. 5.* SEM of sintered (a) coprecipitation derived and (b) conventional method samples.

is the angle of diffraction) is 35 nm. The density of all the samples are above 93% of the single crystal values.

Figure 4 shows the relation between polarization ($P$) and applied electric field ($E$). The ferroelectric hysteresis loop parameters measurements of the pellet sintered at 1000°C showed the values of remnant polarization $P_r = 0.5 \ \mu C/cm^2$ and coercive field, $E_C = 2.2$ kV/cm at an applied voltage of 60 kV/cm without an electric breakdown of the sample. The

reported values of these parameters varies as $E_C \sim$ 80–120 kV/cm and $P_r \sim$ 4–10 $\mu$C/cm$^2$ depending on preparative conditions [11, 19, 20]. The Curie temperature of SBN samples is around 430°C [11, 19, 20]. It is well known that the ferroelectric properties obtained depend on sinter-density, defects present in the sample and thermal treatment given. The typical microstructure of the sintered samples are given in Fig. 5. It is found that conventional method leads to more pores and non uniform grain size. The average grain size is found to be 4 $\mu$m for coprecipitated SBN samples. The samples prepared by the conventional technique have remnant polarization $P_r = 0.3$ $\mu$C/cm$^2$ and coercive field, $E_C \sim 1$ kV/cm at an applied field of 50 kV/cm without occurring an electric breakdown. The dielctric constant is calculated using the equation

$$C = \varepsilon_r \varepsilon_o A/d \tag{1}$$

where $C$ is the capacitance measured, $A$ is the area of the pellet, $d$ is the thickness of the pellet, $\varepsilon_o$ is the vacuum permittivity and $\varepsilon_r$ is the relative dielectric constant of the sample. The room temperature relative dielectric constant measured at 1 kHz is in the range of 95–100 and Curie temperature is found to be 428°C for coprecipitation derived SBN samples.

## 4.  Conclusions

A simple co-precipitation technique is described for the preparation ultrafine powders of SrBi₂Nb₂O₉. The SBN phase was found to be formed on calcining the precipitate at 850°C with average particle size of 30 nm. The dielectric and ferroelectric properties of SBN prepared by this process are also reported.

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