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Co-precipitation method for the preparation of fine ferroelectric $BaBi_2Nb_2O_9$

S.P. Gaikwad[a], H.S. Potdar[a], Violet Samuel[b], V. Ravi[a,*]

[a]*Physical and Materials Chemistry Division, National Chemical Laboratory, Pune 411008, India*
[b]*Catalysis Division, National Chemical Laboratory, Pune 411008, India*

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Abstract

A simple co-precipitation technique had been successfully applied for the preparation of pure fine powders of single phase $BaBi_2Nb_2O_9$. Ammonium hydroxide and ammonium oxalate were used to precipitate Ba^{2+}, Bi^{3+} and Nb^{5+} cations simultaneously. No pyrochlore phase was formed while heating powder at 800 °C and pure $BaBi_2Nb_2O_9$ phase was found to be formed by X-ray diffraction (XRD). Particle size and morphology was studied by transmission electron spectroscopy (TEM). The room temperature dielectric constant at 1 kHz is 100. The ferroelectric hysteresis loop parameters of these samples were also studied.

Keywords: A. Powders chemical preparation; B. Electron microscopy; C. Dielectric properties; C. Ferroelectric properties

1. Introduction

Recently, bismuth-based compounds with Aurivillus type structure have attracted much attention because of their low operating voltage, fast switching speed, negligible fatigue up to 10^{12} switching cycles, excellent retention characteristics and low leakage current density on Pt electrodes for integrated device applications in non-volatile ferroelectric random access memories (FRAM) [1]. For FRAM device applications, large remnant polarization, low coercive field and high Curie temperature are required for better performance and reliable operation. This Aurivillus family of compounds [2–6] 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 or 1/2 integer. The lattice structure of this kind of compounds compose of n number of $(A_{n-1}B_nO_{3n+1})^{2-}$ unit cells sandwiched between $(Bi_2O_2)^{2+}$ slabs along pseudo tetragonal c-axis, while A-site cation occupies the cubo-octahedral sites in perovskite layers. $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) are most intensively studied members of this in comparison to $BaBi_2Ta_2O_9$ (BBT), $BaBi_2Nb_2O_9$ (BBN), $CaBi_2Ta_2O_9$ (CBT), $CaBi_2Nb_2O_9$ (CBN), etc. [2–7]. In this communication, we present a simple co-precipitation technique to produce ultrafine phase pure BBN powders. However, bulk BBN ceramic powder synthesis has very limited reports using non-conventional techniques other than conventional solid-state method [7]. The Bulk BBN powders can be used as a target for dc sputtering and laser ablation methods for the preparation of corresponding thin films.

The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Using chemical methods, e.g. co-precipitation, sol–gel, hydrothermal and colloid emulsion technique 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

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* Corresponding author. Tel.: +91 20 5893300; fax: +91 20 5893044.
E-mail address: ravi@ems.ncl.res.in (V. Ravi).

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reaction conditions. Co-precipitation is one of the more successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution [6,8]. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. This co-precipitation method is not reported for the preparation of BBN powders in the literature.

2. Experimental

For preparing $BaBi_2Nb_2O_9$, niobium(V) oxide, bismuth(III) nitrate and barium chloride were used as starting materials, which were of AR grade (LOBA cheme). A stoichiometric amount of $BaCl_2{\cdot}6H_2O$ (2.44 g) was dissolved in distilled water (100 ml), $Bi(NO_3)_3{\cdot}5H_2O$ (4.64 g) was dissolved in minimum amount of dilute HNO_3 to avoid precipitation of Bi ions and Nb_2O_5 (2.65 g) was dissolved in minimum amount of HF after heating at hot water bath for 20 h. An excess quantity of concentrated HCl is added to the above solution to dissolve the barium fluoride formed by the mixing of NbF_5 and $BaCl_2{\cdot}6H_2O$. Ammonia and ammonium oxalate mixed aqueous solution is added with constant stirring to the above solution mixture at room temperature until $pH > 10$ to ensure complete precipitation. After filtration, the precipitate was washed several times and dried in an oven at 100 °C for 12 h. The oven-dried precursor was calcined at various temperatures to get phase pure samples. For comparison, BBN samples are also prepared by ceramic method. The corresponding oxides or carbonates are taken in stoichiometric ratio and mixed, ground several times and heated at 1000 °C for 72 h. The calcined powders were mixed with few drops of 1 wt.% solution of poly vinyl alcohol and pelletized at 1–2 tonnes. The green pellets were sintered at 1000 °C for 2 h. 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. A LCR meter was used to measure the room temperature dielectric constant of the samples at 1 kHz.

The oven dried precursor of barium oxalate and bismuth niobium hydroxide was characterized by various physico-chemical techniques. The powder X-ray pattern were recorded for oven dried and samples sintered at various temperatures by using Philips PW-1710 model X-ray diffractometer using Cu Kα. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10°–80° for a 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 transmission electron spectroscopy (TEM) picture 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.

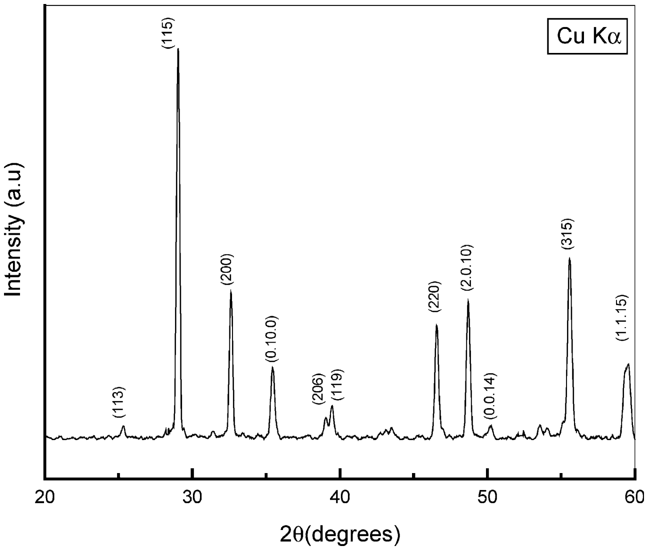

Fig. 1. XRD of BBN precursor powder calcined at 800 °C.

3. Result and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of BBN powder calcined at 800 °C indicating formation of phase pure BBN. The crystal structure of BBN is tetragonal and all the d-lines pattern match with reported values [7]. The calculated lattice parameters by least square fit are a = 3.929 Å and c = 25.598 Å. Conventional solid-state method also forms BBN phase at 1000 °C [7] after prolonged heating (72 h) with comparatively larger particle size of ~1 μm. The particle size and morphology of the calcined powders were examined by transmission electron microscopy. Particle morphology of calcined powder (800 °C for 6 h) prepared by co-precipitation was irregular in shape, with an average primary particle size around 100 nm (Fig. 2). The particle size calculated from Scherrer's formula ($t = K\lambda/B\cos\theta_B$) where t is the average size of the particles, assuming particles are spherical, K = 0.9, λ, wavelength of X-ray radiation; B, full width at half maximum of the diffracted peak and θ_B is the angle of diffraction is 200 nm. The average particle size of BBN powders prepared by conventional ceramic method was in the range of 1–2 μm (not shown). The density of all the sintered samples (both ceramic and co-precipitated) are above 93% of the single crystal values.

Fig. 3 shows the curve 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 = 1.5 μC/cm^2 and coercive field, E_C = 9.2 kV/cm at an applied voltage of 60 kV/cm without occurring an electric breakdown of the sample. It is well-known that the ferroelectric properties obtained depends on sinter-density and defects present in the sample. The samples prepared by the ceramic technique have remnant polarization P_r = 0.3 μC/cm^2 and coercive field, E_C ~ 10 kV/cm at an applied field of 50 kV/cm

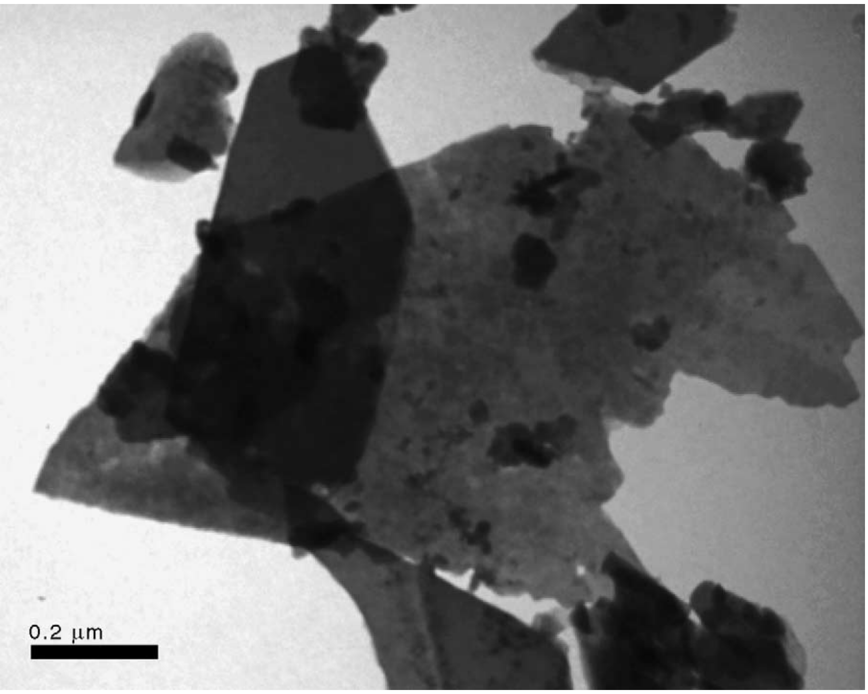

Fig. 2. TEM of BBN precursor powder calcined at 800 °C.

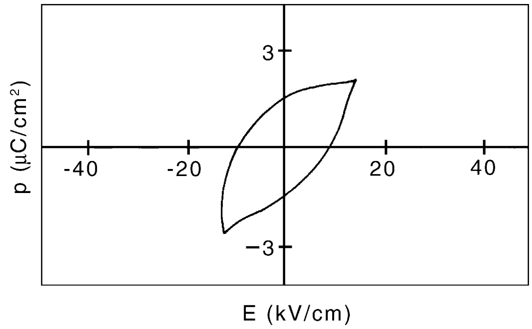

Fig. 3. P–E loop for the sintered BBN pellet derived from co-precipitation.

without occurring an electric breakdown. The room temperature dielectric constant measured at 1 kHz is 100 for the co-precipitation derived BBN samples.

4. Conclusions

A simple co-precipitation technique is described for the preparation of fine powders of $BaBi_2Nb_2O_9$. The BBN phase was found to be formed on calcining the precipitate at 800 °C with average particle size of 100 nm. The dielectric and ferroelectric properties of BBN prepared by this process are also reported.

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References

[1] C.A. De Araujo Paz, J.D. Cuchiaro, L.D. Mcmillan, M.C. Scott, J.F. Scott, Fatigue-free ferroelectric capacitors with platinum electrodes, Nature 374 (1995) 627–629.

[2] B. Aurivillius, Mixed bismuth oxides with layer lattices, Ark. Kemi. 1 (1949) 463–470.

[3] E.C. Subarrao, A family of ferroelectric bismuth compounds, J. Phys. Chem. Solids 23 (1962) 665–676.

[4] R.E. Newnham, R.W. Wolfe, J.F. Dorrian, Structural basis of ferroelectricity in bismuth titanate family, Mater. Res. Bull. 6 (1971) 1029–1040.

[5] Y. Shimakawa, Y. Kubo, Y. Tauchi, T. Kamiyama, H. Asanoa, F. Izumi, Structural distortion and ferroelectric properties of $SrBi_2(Ta_{1-x}Nb_x)_2O_9$, Appl. Phys. Lett. 77 (2000).

[6] S.R. Dhage, Y. Khollam, S.B. Dhespande, V. Ravi, Coprecipitation technique for the preparation of nanocrystalline ferroelectric $SrBi_2Ta_2O_9$, Mater. Res. Bull. 38 (2003) 1601–1605.

[7] Isamunandar, B.J. Kennedy, Effect of temperature on cation disorder in $ABi_2Nb_2O_9$ (A = Sr, Ba), J. Mater. Chem. 9 (1999) 541–544.

[8] S.R. Dhage, V. Ravi, S.K. Date, Preparation of microwave dielectric $Sn_{0.20}Zr_{0.80}TiO_4$, Bull. Mater. Sci. 26 (2003) 215–216.