Co-Precipitation Method for the Preparation of Nanocrystalline Ferroelectric SrBi$_2$Nb$_2$O$_9$ Ceramics

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Abstract. A simple co-precipitation technique had been successfully applied for the preparation of pure ultrafine single phase SrBi$_2$Nb$_2$O$_9$. 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$^\circ$C and pure SrBi$_2$Nb$_2$O$_9$ (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$_2$Ta$_2$O$_9$ (SBT) and SrBi$_2$Nb$_2$O$_9$ (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 $(\text{Bi}_2\text{O}_3)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2+}$ 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 ($P_r \approx 40 \mu$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

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SrBi$_2$Nb$_2$O$_9$ 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$_2$Nb$_2$O$_9$ 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$_2$·6H$_2$O was dissolved in distilled water, Bi(NO$_3$)$_3$·5H$_2$O was dissolved in minimum amount of dilute HNO$_3$ to avoid precipitation of Bi ions and Nb$_2$O$_5$ 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$_2$·6H$_2$O. 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.

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