

Synthesis and characterization of nanocrystalline SrBi₂Nb₂O₉ ferroelectric ceramics using TEA as the polymeric matrix

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Abstract

The processing conditions, reaction mechanism, fine structure of the powders, microstructure, and dielectric properties of SrBi₂Nb₂O₉ (SBN) were systematically studied. A relative density of >80% was obtained using a two-step sintering process at moderate pressure. XRD showed that a single phase with the layered perovskite structure of SrBi₂Nb₂O₉ (SBN) was formed after calcining at 600 °C. No intermediate phase was found during heat treatment at and above 600 °C. The crystallite size (*D*) and the effective strain (*η*) were found to be 38.8 nm and 0.01475, respectively, while the particle size obtained from TEM was laid between 25 and 36 nm. SEM revealed that the average grain size after sintering at 900 °C for 4 h was 0.67 μm. Dielectric constant and corresponding tangent loss were measured in the frequency range from 1 kHz to 1 MHz from which the Curie temperature (*T_c*) was found to be at 450 °C.

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1. Introduction

Previous research has focused on Pb(Ti, Zr)O₃ (PZT), but one of the current problems with PZT is the fatigue resistance of the material. PZT thin films tend to degrade after 10⁶ to 10⁸ cycles of full polarization switching.¹ Bismuth layered perovskite materials have high fatigue resistance and are able to withstand 10¹² erase/rewrite operations² and therefore have attracted an increasing attention for NvRAM application.³ The crystal structure and chemical composition of these layered perovskites were systematically studied by Aurivillius⁴ in the 1950's with a general formula of (Bi₂O₂)²⁺(A_{*m*-1}B_{*m*}O_{3*m*+1})²⁻, consisting of *m*-perovskite units sandwiched between bismuth oxide layers called the family of bismuth layered structured ferroelectrics (BLSFs),⁵ where A and B are the two types of cations that enter the perovskite unit. A is Bi³⁺, Ba²⁺, Sr²⁺, Pb²⁺ or K¹⁺; B is Ti⁴⁺, Ta⁵⁺, Nb⁵⁺, Mo⁶⁺ or W⁶⁺ and *m* = 1–6.³ The crystal structure is built up of two perovskites-like layers, infinite in two dimensions, alternating with a layer of (Bi₂O₂)²⁺ along the *c*-axis. The

O–Nb–O chains of the perovskites along the same axis are interrupted to this class have been found to have wide spread applications in a variety of ferroelectric-based devices.^{2,3} However, the conventional way to synthesize SBT and SBN based on the solid-state reaction at high temperatures (typically >1200 °C)² is not suitable for ferroelectric applications, since they suffer from relatively high processing temperature, relatively low spontaneous polarization, and relatively high dielectric loss.^{6,7} Much research has been reported in the open literature aimed at improving the dielectric and ferroelectric properties of such materials.^{8,9}

The phase formation temperature, chemical homogeneity, phase purity and electrical properties of multicomponent electroceramic materials like SBN and SBT are highly dependent on the cation homogeneity in the oxide precursor.¹⁰ In this respect the sol–gel synthesis,^{9,11–14} and the Pechini-type polymerizable complex (PC)¹⁵ are extremely useful. Unfortunately, the non-aqueous based solution methods (i.e. the alkoxide based solution methods using organic solvents)¹⁶ experience hindrance in the synthesis of ceramics that contain niobium (V) ions because of the cost, and moisture sensitivity of the starting materials (such as niobium ethoxide and other alkoxides). On the other hand, the alternative aqueous based chemical processes get complicated due to scarcity of water-soluble salts of niobium and easy hydrolysis of the available ones (such as NbCl₅).

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In the present work, we report the use of water soluble, coordinated complex of niobium-tartrate as a starting material for the preparation of nanocrystalline $\text{SrBi}_2\text{Nb}_2\text{O}_9$ powders through an aqueous based chemical process. Niobium-tartrate is stable in aqueous medium and is appropriate for the preparation of multi-component oxide systems comprising Nb(V) ions. The route involves the complete dehydration of an aqueous precursor solution that have the constituent metal ions in solution through formation of coordinated complexes with readily available, inexpensive compounds, such as, tartaric acid, ethylenediamine tetraacetic acid (EDTA) and triethanolamine (TEA).

2. Experimental

Chemical required for this synthesis are $\text{Sr}(\text{NO}_3)_2$ (MERCK, India; 99.99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (MERCK, India; GR grade), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Aldrich; 99.999%), Nb_2O_5 (Aldrich; 99.99%), TEA (triethanolamine) (MERCK, India; GR grade), EDTA (ethylenediamine tetraacetic acid), HNO_3 (65%) (MERCK, India; GR grade), and NH_4OH (25%) (MERCK, India; GR grade).

2.1. Preparation of water-soluble Bi- and Sr-EDTA complex

Bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1 mol), and ethylenediamine tetraacetic acid, abbreviated as $\text{H}_4\text{-EDTA}$ (0.1 mol), were mixed with 300 ml of water with stirring to form a colloid of Bi-species hydrolyzed. The colloidal solution was treated with 70–80 ml of 28 wt.% ammonia solutions to form a water-soluble Bi-EDTA complex. The pH of the solution was adjusted to seven drop wise using 6 mol l^{-1} HNO_3 , followed by addition of water to prepare 0.2 mol l^{-1} Bi-EDTA stock solutions. The corresponding stock solution of Sr-EDTA was prepared starting from strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, in the way similar to that of the Bi-EDTA. The metal content was determined by ICP (inductive coupled plasma) analysis.

2.2. Preparation of water-soluble Nb-tartrate complex

Aqueous solutions of the niobium tartarate complex were prepared in the laboratory starting from its hydrous oxide. To begin with, the niobium oxide (Nb_2O_5) was dissolved in HF (>7 M) by warming the mixture over a water bath for 24 h to obtain a clear solution of the niobium-fluoride complex (i.e. NbF_5^{2-} complexes). The hydrous niobium oxide ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) was then precipitated out from the clear solution of the niobium-fluoride complex by the addition of aqueous solutions of dilute (25%) ammonia. The precipitate of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was filtered, washed with 5% ammonia solution to make it fluoride free and then assayed at 1000°C for 2 h to estimate niobium oxide. The required amount of hydrous niobium oxide was then taken and slowly dissolved in aqueous solution of tartaric acid (2 M per unit mol of niobium ion) with continuous stirring on a magnetic stirrer to obtain the stock of the clear, aqueous solution niobium tartarate. The entire process for obtaining the aqueous

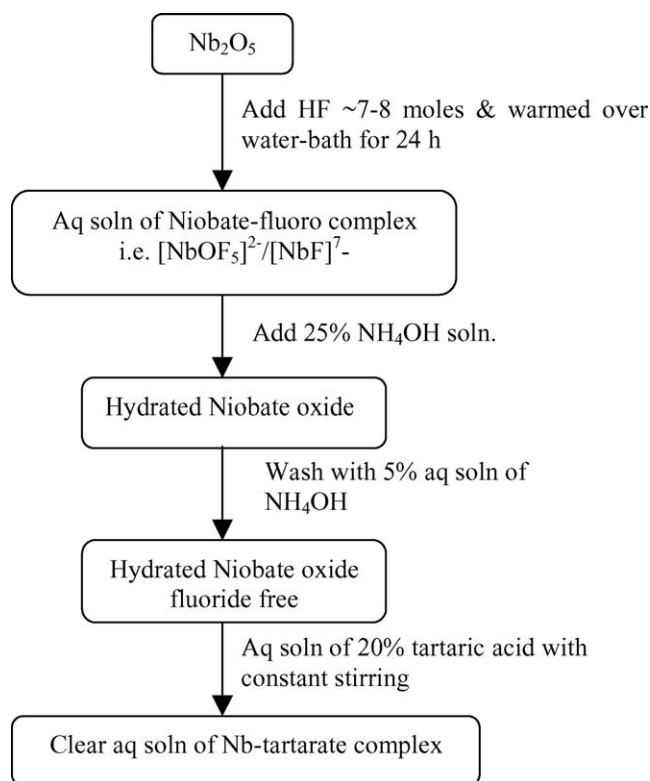


Fig. 1. Schematic representation of the preparation of niobate-tartrate complex.

of niobium tartarate has been depicted through a flow chart in Fig. 1.

2.3. Preparation of $\text{SrBiNb}_2\text{O}_9$ via an aqueous solution route

For the preparation of $\text{SrBiNb}_2\text{O}_9$ appropriate volumes of the Sr-EDTA, Bi-EDTA, and Nb-tartrate complexes were taken from their respective stock solutions, in accordance with the desired stoichiometries, and mixed together. As shown in Fig. 2, the precursor solution was subsequently obtained by adding TEA, which acts as a complexing agent,¹⁷ to the resultant mixture of the metal ion complexes. 4.5 wt.% of extra Bi-EDTA was taken to avoid any possible weight loss during heat treatment. To avoid any chances of precipitation of the metal ions from the precursor solution, the amount of TEA added was always kept in excess (i.e. 3 mol ratios with respect to per mol of the total metal ions) for the required stoichiometry and the pH of the solution mixture was maintained at 6. The entire precursor solution was then rapidly evaporated by heating at $\sim 200^\circ\text{C}$, complete dehydration of the precursor solution was accompanied by the decomposition of the metal complexes followed by the generation of a voluminous, carbonaceous mesoporous precursor mass, which was ground to fine powder and subsequently calcined at different temperatures ($500\text{--}800^\circ\text{C}$) for 2 h to result in the desired nano-sized SBN powders. The details of the mechanism of solution decomposition method using TEA has been discussed in a recent communication by our group.¹⁸

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