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Preparation of nanocrystalline ferroelectric $CaBi_2Ta_2O_9$ by the urea method

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Abstract

A precipitate was formed when a aqueous solution of $CaCl_2$, $BiCl_3$, TaF_5 and urea in stoichiometric ratio (total metal cations to urea ratio is 5) is heated on a water bath. This precipitate on decomposition at 600 °C yielded the nanocrystallites of ternary oxide $CaBi_2Ta_2O_9$ (CBT) as confirmed by X-ray diffraction (XRD). Particle size and morphology was studied by transmission electron spectroscopy (TEM). Ferroelectric hysteresis loop parameters such as remnant polarization (P_r) and coercive field (E_C) were also determined. TEM investigations revealed that the average particle size of the polycrystalline powder is 70 nm. The room temperature dielectric constant was found to be 110.

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

1. Introduction

Recently, $SrBi_2Ta_2O_9$ (SBT) become important candidate for application in nonvolatile ferroelectric random access memories (FRAM) due to its low coercive field and low leakage current densities on Pt electrodes [1–3]. It has potential application as a new generation material for use as FRAM due to its excellent fatigue endurance even after 10^{12} cycles of operation. Most of the early developments of FRAM were carried out using lead zirconate titanate (PZT) perovskite ferroelectric due to its large remanent 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 are not yet commercially available. A layered ferroelectric oxide based on the Aurivillus family such as $SrBi_2Ta_2O_9$ was reported as a potential alternative to PZT for the FRAM applications. The 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., B = Ta, Nb, etc. and n is any integer or 1/2 integer. $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ (SBN) are most intensively studied members of this series in comparison to $BaBi_2Ta_2O_9$ (BBT), $BaBi_2Nb_2O_9$ (BBN), $CaBi_2Ta_2O_9$ (CBT), $CaBi_2Nb_2O_9$ (CBN), etc. [1–3,6]. Neutron diffraction studies by Shimakawa et al. (references citated in [7]) showed that replacement of A-site cation in SBT by Ca increases the structural distortion between AO and TaO_2 planes which can enhance the spontaneous polarization. Synthesis of CBT thin films is also known by pulse laser deposition [7]. However, bulk CBT ceramic powder synthesis has very limited reports using non-conventional techniques other than conventional solid state method [8].

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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reaction conditions. The purpose of this study was to prepare ultrafine $CaBi_2Ta_2O_9$ powder using urea 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. Urea is used as a fuel, precipitating agent and as a resin former with formaldehyde. When urea is used along with nitrate salt of a cation and heated at 673 K, the exothermic reaction between nitrate (oxidant reactant) and urea (fuel) leads to formation of corresponding nanocrystalline oxides. The main advantage is that necessary heat for synthesis is obtained directly from the reaction [9,10]. In the case of homogeneous precipitation, urea acts as a precipitant. Since urea decomposed around 373 K to produce carbon dioxide and ammonia thereby increasing the pH of the solution at which metal cation precipitation takes place [11]. In yet another method [12] urea forms polymeric resin with formaldehyde along with reactants and on the decomposition of the resin at higher temperatures, the final product is formed.

2. Experimental

For preparing $CaBi_2Ta_2O_9$, tantalum (V) fluoride, bismuth (III) nitrate, calcium chloride and urea were used as starting materials, which were of AR grade (LOBA cheme). A stoichiometric amount of $CaCl_2{\cdot}6H_2O$ 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 Ta_2O_5 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 calcium fluoride formed by the mixing of TaF_5 and $CaCl_2{\cdot}6H_2O$. The above mixture is mixed with required quantity of urea. The ratio of the total metal cations to urea is five. Since there was no precipitation during mixing, the pH of the solution was not varied. On heating on a water bath at 373 K a light yellowish precipitate was formed after evaporation of water. Subsequently, the precipitate is decomposed at various temperatures ranging from 423 to 1173 K. The precipitate initially started to swell and filled the beaker producing a foamy precursor. This foam consists of very light and homogeneous flakes of very small particle size. Various techniques such as XRD (Philips PW 1710 Diffractometer) and TEM were employed to characterize these powders. 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 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.

For comparison, CBT 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 polyvinyl alcohol and pelletized at 1–2 tons (pellet dia 12 mm, thickness 2 mm) i.e., at the pressure of 200 MPa. The green pellets were sintered at 1050 °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. The room temperature dielectric constant was measured using a LCR bridge at 1 kHZ.

3. Results and discussion

The mixture of urea and aqueous metal cations forms a precipitate on heating on a water bath, which on decomposition at 873 K yields nanoparticles of corresponding Aurivillus phase. During calcinations process, a yellowish fluffy mass (foam-like) is formed which occupies large volumes of the furnace. The urea decomposes into ammonia and carbon dioxide. Fig. 1 shows the XRD pattern of CBT powder calcined at 873 K for 12 h. The indexed *d*-values match the reported values for CBT phase. The crystal structure of CBT is orthorhombic [8]. The calculated lattice parameters by least square fit are $a = 5.487$ Å, $b = 5.4997$ Å and $c = 24.985$ Å. The particle size of calcined powders was found to be 70 nm by TEM studies (Fig. 2). Conventional solid state method forms CBT phase at 1000 °C after prolonged heating (72 h) with comparatively larger particle size of 0.8 μm. 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 is the wavelength of X-ray radiation, B is the full width at half

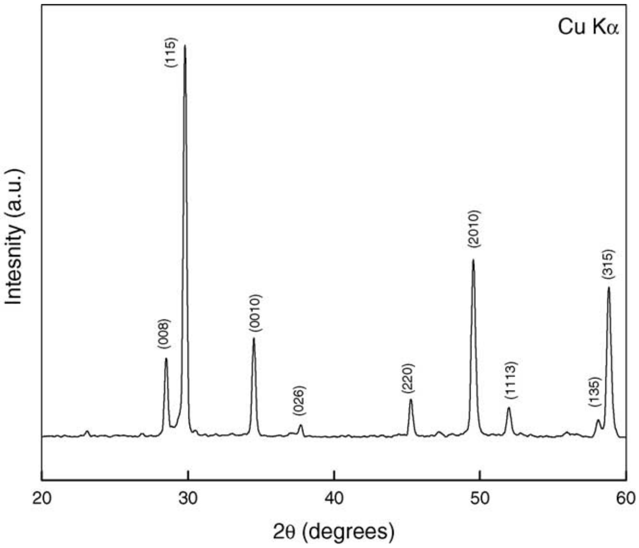

Fig. 1. XRD of CBT powder calcined at 873 K.

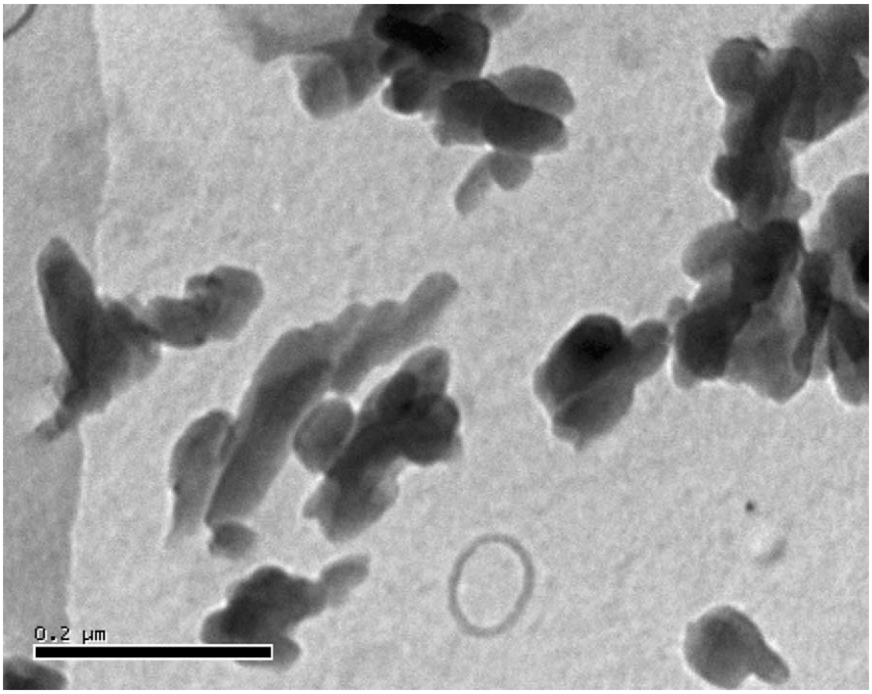

Fig. 2. TEM of CBT powder calcined at 873 K.

maximum of the diffracted peak and θ_B is the angle of diffraction) is 100 nm. The room temperature dielectric constant was found to be 110. The ferroelectric hysteresis loop parameters measurements of the pellet sintered at 1050 °C showed the values of spontaneous polarization, $P_s = 1.8$ μC/cm^2, remnant polarization $P_r = 0.8$ μC/cm^2 and coercive field, $E_C = 16$ kV/cm at an applied voltage of 40 kV/cm without occurring an electric breakdown of the sample. The reported values of these parameters varies as $E_C \sim 22$–40 kV/cm and $P_r \sim 1$–3 μC/cm^2 depending on preparative conditions [10]. The samples prepared by the ceramic technique have $P_s = 0.7$ μC/cm^2, remnant polarization $P_r = 0.5$ μC/cm^2 and coercive field, $E_C \sim 13$ kV/cm at an applied field of 40 kV/cm without occurring an electric breakdown.

4. Conclusions

A simple urea method was used to prepare ultrafine particles of $CaBi_2Ta_2O_9$. The CBT phase was found to be formed at 600 °C with average particle size of 70 nm. The dielectric and ferroelectric properties of urea derived CBT powders are reported.

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