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Preparation of nanocrystalline ferroelectric $CaBi_4Ti_4O_{15}$ by citrate gel method

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Abstract

A gel was formed when an aqueous solution of $CaCl_2$, $BiNO_3$, $TiOCl_2$ and citric acid in stoichiometric ratio is heated on a water bath. This gel on decomposition at 700 °C produced nano crystallites of the ternary oxide, $CaBi_4Ti_4O_{15}$ (CBT). The phase contents and lattice parameters were studied by the powder X-ray diffraction (XRD). Particle size and morphology was studied by transmission electron spectroscopy (TEM). The room temperature dielectric constant at 1 kHz is 390. The ferroelectric hysteresis loop parameters of these samples were also studied by a home-built Sawyer-tower circuit.

Keywords: B. Electron microscopy; B. X-ray methods; Ceramics; Chemical synthesis; Oxides

1. Introduction

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 nonvolatile ferroelectric random access memories (FRAM) [1,2]. Large remnant polarization, low coercive field and high Curie temperature are required for better performance and reliable operation of the FRAM devices. This Aurivillius family of compounds [3–5] 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, Ti, etc. is in six-fold coordination and $n > 1$. Typical examples for first four members of this series is Bi_2MoO_6 ($n = 1$), $SrBi_2Nb_2O_9$ ($n = 2$), $Bi_4Ti_3O_{12}$ ($n = 3$) and $CaBi_4Ti_4O_{15}$ ($n = 4$). The lattice structure of this kind of compound is composed of n number of $(A_{n-1}B_nO_{3n+1})^{2-}$ unit cells sandwiched between $(Bi_2O_2)^{2+}$ slabs along the pseudo tetragonal c-axis, while the A-site cation occupies the cubo-octahedral sites in the perovskite layers. The aim of the present work is to prepare single phase $CaBi_4Ti_4O_{15}$ powders by a simple citrate gel method from simple inorganic salts. There have been reports [6–9] about the solid state preparation and properties of $CaBi_4Ti_4O_{15}$. Recently, both $CaBi_4Ti_4O_{15}$ and $SrBi_4Ti_4O_{15}$ are also reported to be prepared by mechanochemical activation [9,10].

The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. 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 reaction conditions. The citrate process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. This process involves complexation of metal ions by poly functional carboxyl acids such as citric acid or tartaric acid having one hydroxyl group. On heating this mixture, the solvent (water)

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evaporates resulting in increased viscosity. On complete removal of water, the dried product is a polymeric glass and its constituents mixed at atomic level. This resin on heating at higher temperature produces the respective oxides. The citrate gel process offers a number of advantages for the preparation of fine powders of many complex oxides as quoted in the literature [11–14].

2. Experimental

For preparing $CaBi_4Ti_4O_{15}$, titanium(IV) chloride, bismuth(III) nitrate, calcium chloride and citric acid were used as starting materials, which were of AR grade (LOBA cheme). $TiCl_4$ was diluted with ice-cold distilled water to prepare a known concentration of $TiOCl_2$ solution. To this solution, required quantity of citric acid, a stoichiometric amount of $CaCl_2{\cdot}6H_2O$ dissolved in distilled water and $Bi(NO_3)_3{\cdot}5H_2O$ dissolved in HNO_3 were added (the ratio of Ca: Bi: Ti: citric acid is 1:4:4:9, ratio of the total metal cations to citric acid is one). Since there was no precipitation during mixing of citric acid and these metal salts, the pH of the solution was not varied. On heating on a water bath at 100 °C, a gel was formed after evaporation of water. Subsequently, the gel is decomposed at various temperatures ranging from 400 to 800 °C. The gel 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.

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 800 °C for 12 h. The calcined powders were mixed with few drops of 1 wt.% solution of polyvinyl alcohol and pelletized at 1–2 t. The green pellets were sintered at 1000 °C for 2 h. The densities of the sintered sampled are 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. A LCR meter was used to measure the room temperature dielectric constant of the samples at 1 kHz. Various techniques such as XRD (Philips PW 1710 Diffractometer) and TEM were employed to characterize these powders. The powder X-ray pattern were recorded for all the 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 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.

3. Result and discussion

The citric acid added acts as a complexing agent. The mixture of citric acid and aqueous metal salts forms a gel on heating on a water bath which decomposes at higher temperatures >300 °C. During calcinations process, a black fluffy mass (foam-like) is formed which occupies large volumes of the furnace. As the temperature increases, the black mass turns to white in colour with the removal of carbon. Samples calcined at 500 °C for 30 min shows less than 1% of carbon. At higher temperatures of calcinations, no carbon was found to present. Fig. 1 shows the XRD pattern of CBT powder calcined at 700 °C indicating formation of phase pure powder. The crystal structure of CBT is orthorhombic and all the d-lines pattern match with reported values [6]. The calculated lattice parameters by least square fit are $a = 5.461$ Å, $b = 5.423$ Å and $c = 40.550$ Å. Conventional solid state method also forms CBT phase after heating at 800 °C (12 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 (700 °C for 6 h) prepared by citrate process was nearly spherical in shape, with an average primary particle size around 80 nm (Fig. 2). The particle size obtained 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 maximum of the diffracted peak and θ_B is the angle of diffraction is 90 nm. The ferroelectric hysteresis loop parameters measurements of the pellet (derived from citrate process) sintered at 1000 °C showed the values of remnant polarization, $P_r = 2.6$ μC/cm^2; spontaneous polarization, $P_s = 3.7$ μC/cm^2; and coercive field, $E_C = 70$ kV/cm at an applied voltage of 100 kV/cm without occurring an electric breakdown of the sample. The samples obtained by ceramic method have $P_r = 1.4$ μC/cm^2, $P_s = 2.2$ μC/cm^2 and coercive field, $E_C = 90$ kV/cm at an applied voltage of 150 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 room temperature relative dielectric constant (no units) measured at 1 kHz is 390 for the citrate process derived CBT samples.

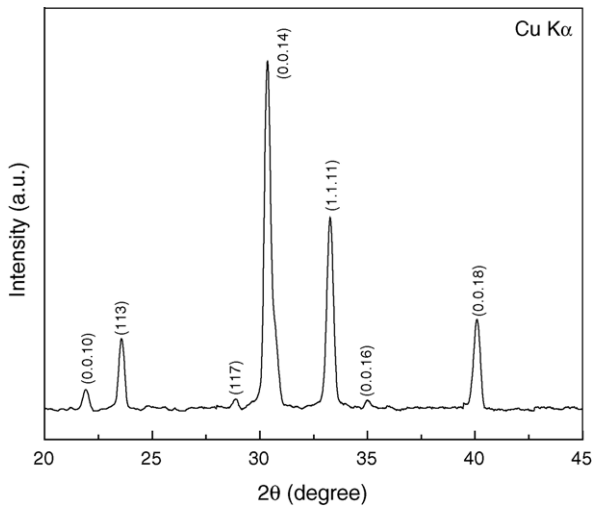

Fig. 1. XRD of CBT precursor powder calcined at 700 °C.

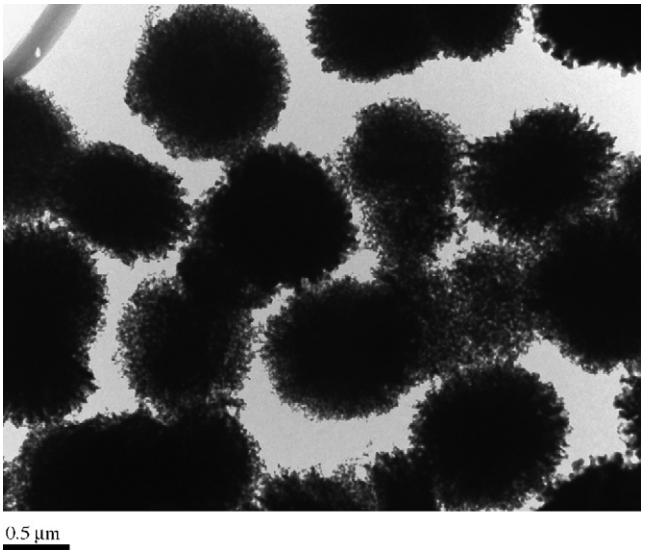

Fig. 2. TEM of CBT precursor powder calcined at 700 °C.

4. Conclusions

A simple citrate gel method was used to prepare ultrafine particles of CBT. The CBT phase was found to be formed at 700 °C with average particle size of 80 nm. The dielectric and ferroelectric properties of these samples were also reported.

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