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Short communication

A co-precipitation method for preparation of Bi_3TiNbO_9 powders

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Abstract

A simple co-precipitation technique has been successfully used for the preparation of pure, ultrafine, single phase Bi_3TiNbO_9 (BTN). An aqueous ammonium hydroxide solution was used to simultaneously precipitate Bi^{3+}, Ti^{4+} and Nb^{5+} cations as hydroxides under basic conditions (pH ~9). No pyrochlore phase was found while heating powder at 500 °C and pure BTN phase was found to be formed by X-ray diffraction (XRD). For comparison, BTN samples were also synthesized by the traditional solid state method. The sequence of phase formation in both cases were investigated by XRD studies.

Keywords: Ceramics; Electronic material; Oxides; Chemical synthesis; XRD

1. Introduction

Aurivillius family of compounds [1–3] 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. in 12-fold coordination, B = Ta, Nb, etc. in six-fold coordination and n is any integer or 1/2 integer. Typical examples for first four members of this Series are 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 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 the 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]. Recently, these compounds 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) [1–3]. For FRAM device applications, large remnant polarization, low coercive field and high Curie temperature are required for better performance and reliable operation.

However, there are not much reports [4–9] on Bi_3TiNbO_9 compound ($n = 2$). The purpose of this study was to prepare ultrafine Bi_3TiNbO_9 powder using co-precipitation technique from simple water soluble inorganic salts. Co-precipitation is one of the more successful wet-chemical techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution [1–3]. This process can avoid complex steps such as refluxing of alkoxides and make use of relatively inexpensive simple inorganic salts. This co-precipitation method is not reported for the preparation of BTN powders in the literature.

2. Experimental

For preparing Bi_3TiNbO_9, niobium(V) oxide, bismuth(III) nitrate and titanium(IV) chloride were used as starting materials, which were of AR grade (Loba cheme). $TiCl_4$ was diluted with ice-cold distilled water to form $TiOCl_2$ solution (0.2 M). A stoichiometric amount of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in minimum amount of dilute HNO_3 to avoid precipitation of Bi ions (0.6 M) and Nb_2O_5 was dissolved in HF by heating it at hot water bath for 10 h (0.1 M). All these three solutions in required quantity are mixed well and standard

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ammonia solution was added dropwise with constant stirring to the above solution mixture until pH ~9 to ensure complete precipitation of all the cations as hydroxides. The precipitate was filtered, washed several times with double distilled distilled water and dried in an oven at 100 °C for 12 h. The oven-dried precursor was calcined at various temperatures ranging from 200 to 800 °C for 6 h. For comparison, BTN samples are also prepared by the solid state method. The corresponding oxides (bismuth trioxide, niobium pentoxide and titanium dioxide) are taken in stoichiometric ratio and mixed, ground several times and heated at 800 °C for 72 h. The powder X-ray patterns were recorded for 2θ at 4°/min for oven dried and samples calcined 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 the period of 5 s in the step scan mode. Silicon was used as an internal standard. A Least squares method was employed to determine the lattice parameters.

3. Result and discussion

Fig. 1 shows the XRD pattern of the precursor powder calcined at different temperature ranging from 200 to 800 °C. For the temperatures ~300 °C, the sample was in amorphous state as XRD does not show any distinct peaks. However, the BTN phase forms at temperatures as low as 500 °C as illustrated in Fig. 1. This is the lowest temperature reported for the formation of BTN phase. No changes in XRD observed even after heating at 700 °C for 6 h. The crystal structure of BTN is orthorhombic and all the d-lines pattern match with the reported values (JCPDS; 7–192, space group *Fmmm*). The calculated lattice parameters by least squares fit are $a = 5.401$ Å, $b = 5.443$ Å and $c = 25.11$ Å. The conventional solid state method also forms Bi_3TiNbO_9 phase at 800 °C after prolonged heating (72 h) as depicted in Figs. 2 and 3. The XRD results show that in the case of solid state method, the formation of BTN phase begins only after calcinations at ~700 °C. This shows the advantage of the co-precipitation method over solid state method. It should be noted that no pyrochlore phase was found to be formed during the heat treatment. The average particle size for the samples prepared by co-precipitation was calculated from Scherrer's formula:

$$t = \frac{K\lambda}{B\cos\theta_B}$$

where t is the average size of the particles, assuming particles are spherical, $K = 0.9$, λ the wavelength of X-ray radiation, B the full width at half maximum of the diffracted peak and θ_B is the angle of diffraction, ~60 nm.

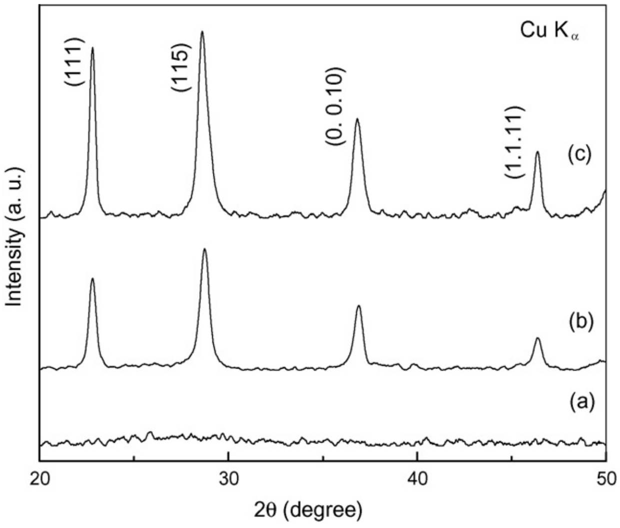

Fig. 1. XRD of BTN precursor powder calcined at: (a) 300 °C, (b) 500 °C and (c) 700 °C.

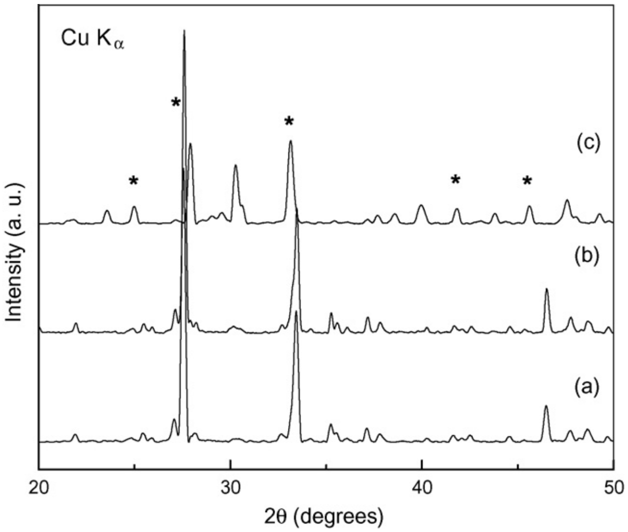

Fig. 2. XRD of BTN powder (prepared by solid state method) calcined at: (a) 300 °C, (b) 500 °C and (c) 700 °C. The '*' marked peaks correspond to Nb_2O_5.

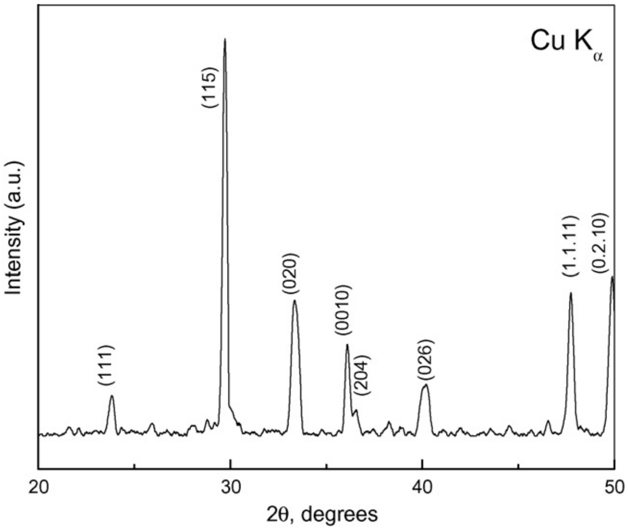

Fig. 3. XRD of BTN powder (prepared by solid state method) calcined at 800 °C.

4. Conclusions

A simple co-precipitation technique was described for the preparation ultrafine powders of Bi_3TiNbO_9. The BTN phase was found to be formed on calcining the precipitate at 500 °C with average particle size of 60 nm. The advantages of the present method over traditional solid state method is illustrated using XRD studies.

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