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Short communication

A co-precipitation technique to prepare $BiNbO_4$ powders

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Abstract

A simple co-precipitation technique was successfully used for the preparation of pure ultrafine single phase $BiNbO_4$. A standard ammonium hydroxide solution was used to precipitate Bi^{3+} and Ta^{5+} cations as hydroxides simultaneously under basic conditions. For comparison, BN powders were also prepared by the traditional solid-state method. It is observed that the co-precipitation technique produces $BiNbO_4$ on heating at 600 °C, whereas complete phase formation occurs only at 800 °C in the solid-state method. The phase contents and lattice parameters were studied by powder X-ray diffraction (XRD).

Keywords: B. Electron microscopy; Ceramics; Oxides; Chemical synthesis; X-ray diffraction; $BiNbO_4$

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1. Introduction

Communication at microwave frequencies has lead to the proliferation of commercial wireless technologies such as cellular phones and global positioning systems. The requirements of ceramic dielectric resonators used at microwave frequencies are a high dielectric constant, a high Q value (reciprocal of dielectric loss) and a low temperature coefficient of resonant frequency [1–5]. Most of the known commercial microwave dielectrics such as $Sn_xZr_{1-x}TiO_4$ and Ba(Mg, Ta)O_3 can be sintered only at very high temperatures (>1400 °C). The so-called passive integration for miniaturization is performed using multiplayer ceramic technology where green ceramic tapes of different materials corresponding to different passive functions are laminated and co-fired at low temperatures. Therefore it is necessary to develop microwave dielectric materials that can be sintered at temperatures lower than the melting point of internal metal conductor such as Cu or Ag. Recently, $BiNbO_4$ was reported to be promising microwave dielectric material with relatively lower melting point [1–5]. The reported values for $BiNbO_4$ are the temperature coefficient of resonant frequency ~50 ppm/°C, the dielectric constant ~45, and $Q = 14,000$ [1–5].

Generally, the traditional solid-state method is used for the preparation of oxides and its drawbacks are well documented in the literature. The wet-chemical techniques such as combustion, alkoxide sol–gel and co-precipitation were found to produce these oxides with several advantages, namely, nanosized particles (hence high surface area), high reactivity and very good homogeneity in composition. Sometimes metastable phases also formed by these methods. Recently citrate gel method was reported to prepare nanocrystalline $BiNbO_4$ powders [1]. Co-precipitation is one of the more successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution [6–13]. The purpose of this study was to prepare ultrafine $BiNbO_4$ powders using co-precipitation technique from simple water-soluble inorganic salts. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The only drawback of this method is that all the cations should have similar solubility product.

2. Experimental

For preparing $BiNbO_4$ compound, niobium(V) oxide, bismuth(III) nitrate, bismuth oxide and ammonium hydroxide were used as starting materials and they were of AR grade (Loba cheme). For the preparation of $BiNbO_4$ by co-precipitation, stoichiometric amount of $Bi(NO_3)_3{\cdot}5H_2O$ was

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dissolved in minimum amount of dilute HNO_3 to avoid precipitation of Bi ions and required quantity of Nb_2O_5 was dissolved in minimum amount of HF after heating at hot water bath for 5 h and both are mixed together. An excess of ammonium hydroxide is added by dropwise with constant stirring to the above solution mixture to precipitate both bismuth and niobium as hydroxides and addition of ammonium hydroxide was continued until pH ~ 9 at room temperature to ensure complete precipitation. After precipitation, it is filtered and washed several times with distilled water to remove the anions 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 12 h to get phase pure samples. For comparison, the samples are also prepared by the conventional ceramic method. Bismuth oxide (Bi_2O_3) and niobium oxide (Nb_2O_5) are taken in stoichiometric ratio and mixed, ground several times and heated at 800 °C for 12 h. To ensure completion of reaction, the powders were reground after first cycle of calcination and heated few times at this temperature. The XRD (Rigaku miniflex X-ray Diffractometer) was employed to characterize these powders. The powder X-ray pattern were recorded for all the samples calcined at various temperatures by 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. The standard least squares method was used to determine the lattice parameters.

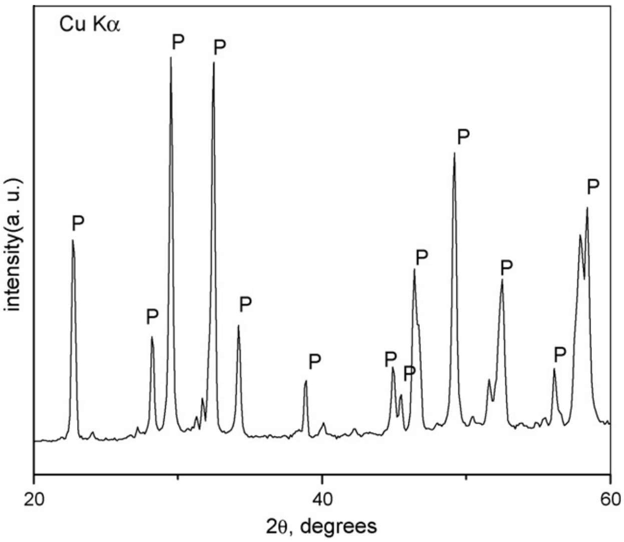

Fig. 2. XRD of $BiNbO_4$ powder calcined at 600 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the co-precipitated powders calcined at different temperatures ranging from 200 to 400 °C for 6 h. At 200 °C, the peaks corresponding to bismuth oxide (45–1344) and niobium oxide (43–1042) were seen in XRD. It can be observed that the incipient product phase begins to form at temperatures as low as at 400 °C. The complete phase formation occurs at 600 °C as observed from Fig. 2. It is the lowest temperature reported for the formation of $BiNbO_4$ phase. These powders are highly crystalline as compared to that prepared by ceramic method and this was supported by the strong intense XRD peaks. The crystal structure is orthorhombic and all the d-lines pattern match with reported values (JCPDS- 16–295). The calculated lattice parameters by least squares fit are $a = 4.981$ Å, $b = 11.713$ Å and $c = 5.673$ Å. Fig. 3 illustrates the XRD for samples prepared by the solid-state method and calcined at different temperatures. At lower temperatures, the XRD peaks corresponding to individual oxides are observed and the product phase begins to form only at 600 °C. The XRD shows the reaction is incomplete as the individual oxides also present along with the product. However, all the peaks corresponding to the phase formation is complete

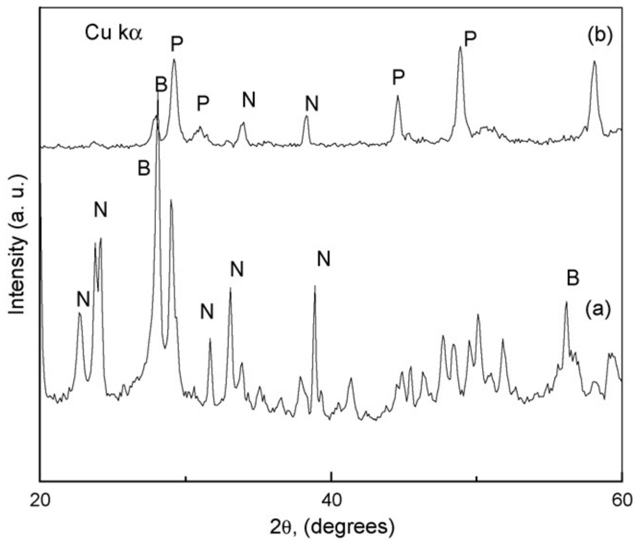

Fig. 1. XRD of $BiNbO_4$ precursor powder calcined at (a) 200 °C and (b) 400 °C. The alphabet 'B' correspond to Bi_2O_3, 'N' to Nb_2O_5 and 'P' to product phases.

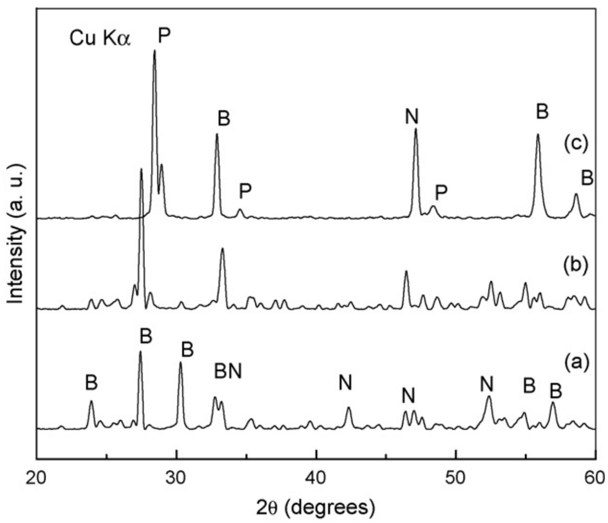

Fig. 3. XRD of $BiNbO_4$ powder (prepared by the solid-state method) calcined at (a) 200 °C, (b) 400 °C and (c) 600 °C. The alphabet 'B' correspond to Bi_2O_3 and 'N' to Nb_2O_5 and 'P' to product phases.

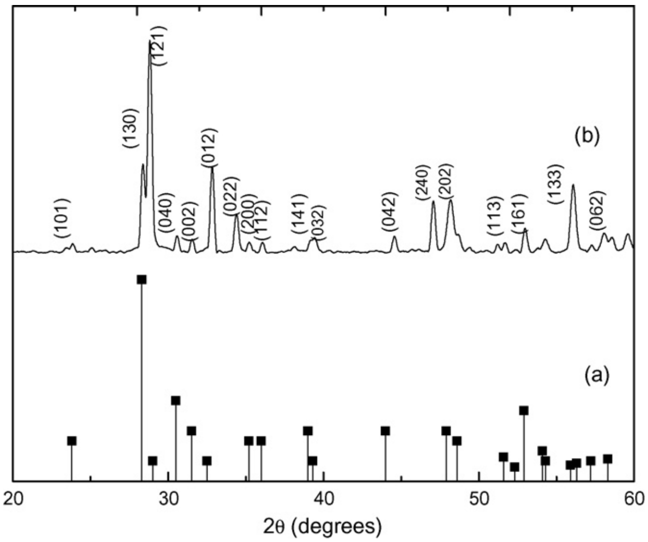

Fig. 4. XRD of $BiNbO_4$ powder (a) ideal case and (b) calcined at 800 °C prepared by the solid-state method.

only at 800 °C (Fig. 4). For compassion, ideal XRD pattern of $BiNbO_4$ was also shown in that figure. The average particle size for the co-precipitated powders (calcined at 600 °C for 6 h) 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 maximum of the diffracted peak and θ_B is the angle of diffraction were ranging from 50 nm.

4. Conclusions

A simple co-precipitation method was used to prepare ultrafine particles of $BiNbO_4$. This method has advantage of forming this phase at much lower temperature as compared to samples prepared by the traditional solid-state method.

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