

A coprecipitation technique to prepare ZnNb_2O_6 powders

V V DESHPANDE, M M PATIL, S C NAVALE[†] and V RAVI*

Physical and Materials Chemistry Division, [†]Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411 008, India

MS received 16 November 2004; revised 9 February 2005

Abstract. A simple coprecipitation technique was successfully applied for the preparation of pure ultrafine single phase, ZnNb_2O_6 (ZN). Ammonium hydroxide was used to precipitate Zn^{2+} and Nb^{5+} cations as hydroxides simultaneously. This precursor on heating at 750° , produced ZN powders. For comparison, ZN powders were also prepared by the traditional solid state method. The phase contents and lattice parameters were studied by the powder X-ray diffraction (XRD). Particle size and morphology were studied by transmission electron spectroscopy (TEM).

Keywords. Ceramics; electronic materials; electron microscopy; X-ray diffraction.

1. Introduction

Communication at microwave frequencies has lead to the proliferation of commercial wireless technologies such as cellular phones and global positioning systems. The requirement of ceramic dielectric resonators used at microwave frequencies are high dielectric constant, a high Q value (reciprocal of dielectric loss) and a low temperature coefficient of resonant frequency. Zinc niobate and its solid solution with zinc tantalate found applications as microwave dielectric materials due to their low dielectric loss and high dielectric constant (Lee *et al* 1997; Zhang *et al* 2003, 2004a,b). ZN with a coulombite structure is also used as a reference material for investigating the defects induced in LiNbO_3 substrates for waveguide fabrication. Traditionally ZN is prepared by ceramic method and that leads to inhomogeneity in composition and coarse particles. 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, it has been confirmed that they efficiently control morphology and chemical composition of the prepared powder. Among these wet chemical techniques, sol-gel using alkoxides, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and difficult to maintain reaction conditions. Coprecipitation is one of the more successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution (Dhage *et al* 2003; Gaikwad *et al* 2004, 2005). The purpose of this study was to prepare ultrafine ZnNb_2O_6 powder using coprecipitation 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. This method is not reported for the preparation of ZN powders in the literature.

2. Experimental

For preparing ZnNb_2O_6 , niobium (V) oxide, zinc nitrate and liquid ammonia were used as starting materials, and all were of AR grade (LOBA chemie). A stoichiometric amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water and Nb_2O_5 was dissolved in minimum amount of HF after heating in hot water bath for 20 h. Then, liquid ammonia was added with constant stirring to the above solution mixture until $\text{pH} > 10$ to ensure complete precipitation. After filtration, the precipitate was washed several times and dried in an oven at 100°C for 12 h. Then the precipitate was calcined at various temperatures ranging from 400 – 800°C for 6 h. For comparison, ZN 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 900°C for 12 h. Various techniques such as XRD (Rigaku miniflex 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 CuK_α . 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

*Author for correspondence (ravi@ems.ncl.res.in)

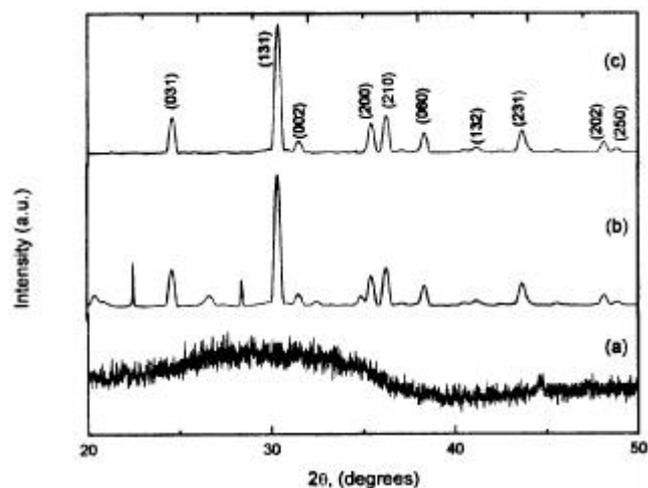


Figure 1. XRD of Zn powder calcined at (a) 100°C, (b) 500°C and (c) 750°C.

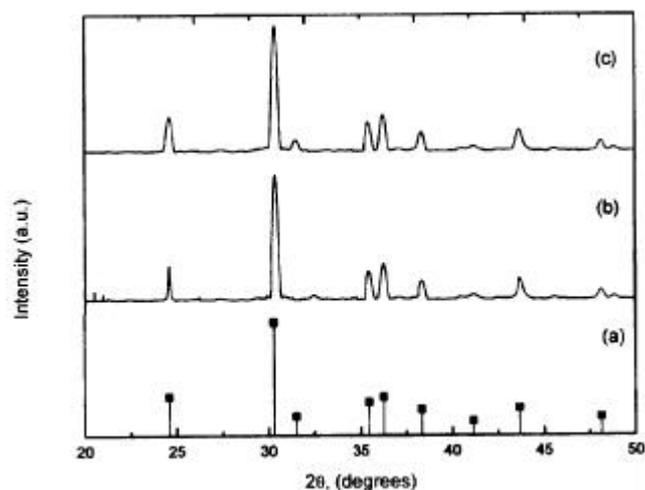


Figure 2. XRD of Zn (a) ideal, (b) ceramic method derived and (c) coprecipitation derived powders.

accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid.

3. Results and discussion

The hydroxides precursor obtained is calcined at various temperatures ranging from 300–800°C for 6 h. Figure 1 shows the XRD pattern of the calcined powder at three different temperatures. At 500°C, the *d*-line patterns show major phase as Zn with few extra lines corresponding to intermediate phases. Powders calcined at 750°C indicates the formation of phase pure Zn. The crystal structure of Zn is orthorhombic and all the *d*-line patterns match with

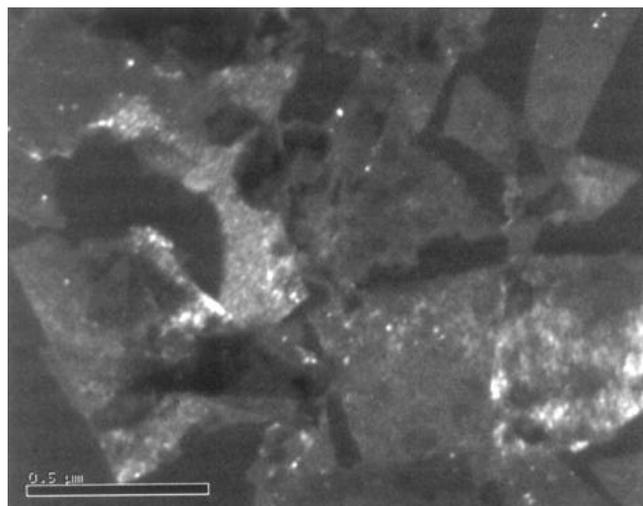


Figure 3. TEM of Zn powder (co-precipitation derived) calcined at 750°C.

reported values (JCPDS 25-1027). The calculated lattice parameters by least square fit are $a = 5.021 \text{ \AA}$, $b = 14.192 \text{ \AA}$ and $c = 5.728 \text{ \AA}$. Conventional solid state method also forms Zn phase at 900°C with comparatively larger particle size of $\sim 1 \mu\text{m}$. Figure 2 shows the *d*-line patterns for ideal case, powders prepared by the ceramic and coprecipitation methods. The particle size and morphology of the calcined powders were examined by transmission electron microscopy. Particle morphology of calcined powder (750°C for 6 h) prepared by the coprecipitation process was irregular in shape, with an average primary particle size of around 100 nm (figure 3). The average particle size calculated from Scherrer's formula

$$t = K \lambda / B \cos \theta_B, \quad (1)$$

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 the angle of diffraction, is 120 nm. The average particle size of Zn powders prepared by conventional ceramic method was in the range of 1–2 μm (not shown).

4. Conclusions

A simple coprecipitation method was used to prepare ultrafine particles of Zn. The Zn phase was found to be formed at 750°C with an average particle size of 100 nm.

Acknowledgement

One of the authors (VR) acknowledges DST, New Delhi (grant no. SP/S1/H-19/2000), for financial assistance.

References

- Dhage S R, Ravi V and Date S K 2003 *Bull. Mater. Sci.* **26** 215
- Lee H J, Hong K S, Kim S J and Kim I T 1997 *Mater. Res. Bull.* **32** 847
- Gaikwad S P, Dhesphande S B, Kholam Y, Samuel V and Ravi V 2004 *Mater. Lett.* **58** 3474
- Gaikwad S P, Potdar H S, Samuel V and Ravi V 2005 *Ceram. Int.* **31** 379
- Zhang Y C, Yue Z X, Gui Z and Li L T 2003 *Mater. Lett.* **57** 4531
- Zhang Y C, Yue Z X, Qi X, Li B, Gui Z L and Li L T 2004a *Mater. Lett.* **58** 1392
- Zhang Y C, Wang J, Yue Z X, Gui Z L and Li L T 2004b *Ceramic. Int.* **30** 87