

A coprecipitation technique to prepare NaNbO₃ and NaTaO₃

V SAMUEL^{††}, A B GAIKWAD[†] and V RAVI*

Physical and Materials Chemistry Division, [†]Centre for Materials Characterization, ^{††}Catalysis Division, National Chemical Laboratory, Pune 411 008, India

MS received 18 October 2005; revised 8 December 2005

Abstract. A simple coprecipitation technique has been used successfully for the preparation of pure, ultrafine, single phases of NaNbO₃ (NN) and NaTaO₃ (NT). An alcoholic solution of ammonium carbonate and ammonium hydroxide was used to precipitate Na⁺ and Nb⁵⁺ (or Ta⁵⁺) cations under basic conditions as carbonate and hydroxide, respectively. On heating at 700°C, these precursors produce respective products. For comparison, both NN and NT powders were also prepared by the traditional solid state method. The phase purity and lattice parameters were studied by powder X-ray diffraction (XRD). The particle size and morphology were studied by scanning electron microscopy (SEM).

Keywords. Ceramics; oxides; chemical synthesis; X-ray methods; electronic materials; electron microscopy.

1. Introduction

Alkali metal niobates and tantalates (LiNbO₃ and LiTaO₃) have excellent electro-optical and photorefractive properties and find extensive applications as optical wave guides and modulators and surface acoustic wave devices, e.g. NaNbO₃ is reported (Raveski and Prosandeev 2002; Aydi *et al* 2004; Castro *et al* 2004) to be a promising anti-ferroelectric material for lead free piezoelectric applications. NaTaO₃ has also been investigated (Istomin *et al* 2002; Kato and Kudo 2003) for possible application as a photocatalyst for splitting of water into H₂ and O₂. Traditionally these materials were prepared by solid state reaction which leads to inhomogeneity in composition and coarse particles. Chemical methods, e.g. co-precipitation, sol-gel, hydrothermal and colloid emulsion techniques, allow to efficiently control the morphology and chemical composition of the prepared powders. Sol-gel using alkoxides, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and difficult to maintain reaction conditions. Co-precipitation is one of the more successful wet-chemical techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution (Dhage *et al* 2003; Gaikwad *et al* 2004, 2005a, b). The purpose of this study was to prepare ultrafine NaNbO₃ and NaTaO₃ powders using the 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 limitation of the co-

precipitation process is that cations should have similar solubility product.

2. Experimental

For preparing NaNbO₃ and NaTaO₃, niobium(V) oxide, tantalum(V) oxide, sodium hydroxide, ethyl alcohol, ammonium carbonate and standard ammonia solution were used and all the starting materials were of AR grade (Loba chemie). A stoichiometric amount of NaOH was dissolved in distilled water (100 ml) and required quantity of Nb₂O₅ or Ta₂O₅ was dissolved in HF after heating in a hot water bath for 10 h. Then an equal amount of ethyl alcohol was added to the above solution mixture containing both sodium hydroxide and niobium (or tantalum) fluoride. Then, aqueous solution of ammonium carbonate and ammonium hydroxide was added with constant stirring to the above solution mixture to reach pH ~9 to ensure complete precipitation of sodium carbonate and niobium (or tantalum) hydroxide. The precipitate was filtered, washed several times with distilled water to remove anions and dried in an oven at 100°C for 12 h. The oven dried powders were calcined at various temperatures ranging from 200–800°C for 12 h. For comparison, both NN and NT samples were also prepared by the ceramic powder processing method from stoichiometric mixtures of oxides or carbonates which were mixed, ground several times and heated at 900°C for 12 h. The powder X-ray pattern was recorded for all the samples by using a Philips PW-1710 model X-ray diffractometer and CuK_α radiation. 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 inter-

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

nal standard. Least squares method was used to determine the lattice parameters. SEM observations were made using a Leica Cambridge 440 microscope. All powders were dispersed in amyl acetate.

3. Results and discussion

The precursor obtained has been calcined at 700°C for 6 h. Figures 1 and 2 show the XRD pattern of the calcined powders indicating formation of pure NaNbO_3 and NaTaO_3 . The observed d -lines pattern (crystal structure is orthorhombic) for NaNbO_3 is similar to that reported in the literature (JCPDS 14-603). The calculated lattice parameters by least squares fit are $a = 5.511 \text{ \AA}$, $b = 5.557 \text{ \AA}$ and $c = 15.540 \text{ \AA}$. The compound, NaTaO_3 , has cubic structure (JCPDS 2-873). The calculated lattice parameter

by least squares fit is $a = 3.88 \text{ \AA}$. The conventional solid state method also produces NN and NT phases at 900°C with a comparatively larger particle size of $\sim 1 \mu\text{m}$. The particle size and morphology of the calcined powders were examined by scanning electron microscopy. Particle morphology of calcined powder (700°C for 6 h) prepared by the coprecipitation process was irregular in shape, with an average primary particle size of around 200 nm (figures 3 and 4). The average particle size of 150 nm was calculated from Scherrer's formula

$$t = K\lambda/B\cos\theta_B,$$

where t is the average size of the particles assuming particles to be spherical, $K = 0.9$, λ is the wavelength of X-ray radiation, B the full width at half maximum of the di-

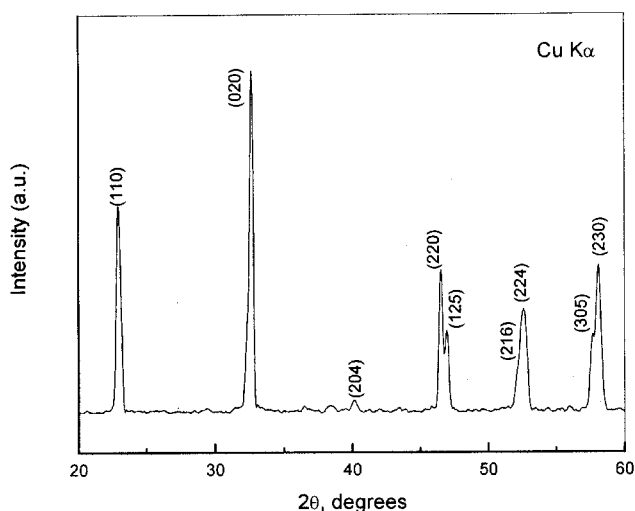


Figure 1. XRD of NN powder calcined at 700°C.

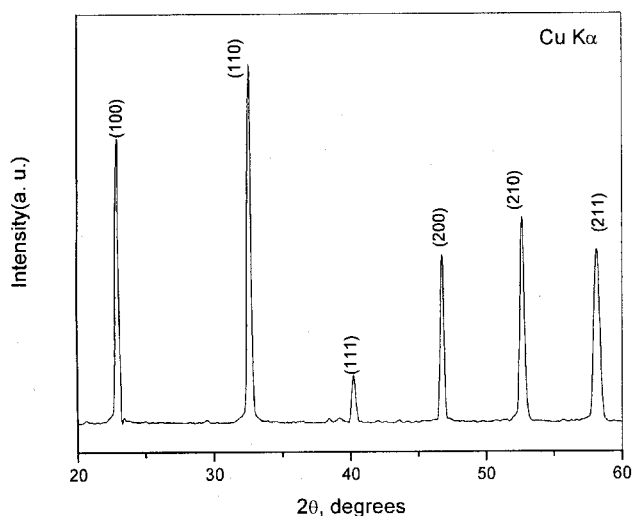


Figure 2. XRD of NT powder calcined at 700°C.

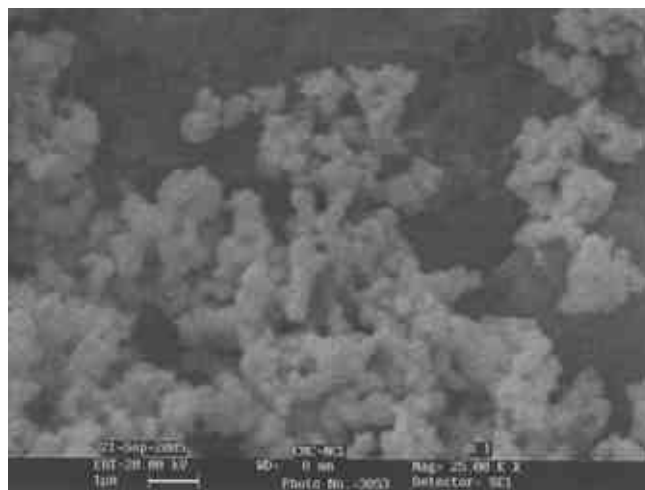


Figure 3. SEM of NN powder calcined at 700°C.



Figure 4. SEM of NT powder calcined at 700°C.

ffracted peak (after correcting for instrumental broadening) and θ_B the angle of diffraction.

4. Conclusions

A simple coprecipitation method was used to prepare ultrafine particles of NaNbO_3 and NaTaO_3 . Both NN and NT phases were crystallized at 700°C with average particle size of 200 nm.

Acknowledgement

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

References

- Aydi A, Khemakhem H, Boudaya C, Muhl R V and Simon A 2004 *Solid State Sci.* **6** 333
- Castro A, Jimenez B, Hungria T, Moure A and Pardo L 2004 *J. Euro. Ceram. Soc.* **24** 941
- Dhage S R, Ravi V and Date S K 2003 *Bull. Mater. Sci.* **26** 215
- 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 2005a *Ceram. Int.* **31** 379
- Gaikwad S P, Dhage S R and Ravi V 2005b *J. Mater. Sci. Mater. Electron.* **16** 229
- Istomin S Y, Svensson G and Kohler J 2002 *Solid State Sci.* **4** 191
- Kato H and Kudo A 2003 *Catalysis Today* **78** 561
- Raveski I P and Prosandeev S A 2002 *J. Phys. & Chem. Solids* **63** 1939