

Preparation and Characterization of Nickel Niobate (NiNb_2O_6) Nanopowders

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ABSTRACT

Single-phase columbite powders of nickel niobate (NiNb_2O_6 , NN) were prepared by the solid-state reaction via a vibro-milling technique, being well known as a significant time-saving method to obtain single-phase nanopowders at low temperature. The powders were characterized by thermogravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The calcination temperature was found to have a pronounced effect on the phase formation of the calcined nickel niobate powders. It was also found that minor phases of unreacted NiO and Nb_2O_5 precursor tended to form together with the columbite NiNb_2O_6 phase, depending on calcination conditions. Furthermore, it was observed that the pure columbite phase of NiNb_2O_6 nanopowders were successfully obtained from a calcination condition of 800°C for 4 h with heating/cooling rates of $20^\circ\text{C}/\text{min}$.

Key words: Nickel niobate (NiNb_2O_6), Nanopowders, Phase formation, Calcination

INTRODUCTION

Lead nickel niobate ($\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ or PNN) is one of the relaxor ferroelectrics which exhibits high dielectric permittivity (~ 4000) over a wide range of the transition temperature ($\sim -120^\circ\text{C}$ at 1kHz) (Alberta and Bhalla, 2002). PNN is becoming increasingly important for multilayer ceramic capacitor, electrostrictor and actuator applications (Moulson and Herbert, 2003). However, it is very difficult to synthesize the high-purity PNN compound via a conventional solid-state reaction process which normally uses oxide-substance as starting materials, due mainly to the poor reactivity of nickel oxide (NiO) (Xiang et al., 2005). As a result, it is required to use another technique to obtain single-phase PNN at a high purity level. One of the promising techniques is to use a columbite precursor method which is known to provide the minimal level of impurity. Consequently, within this columbite precursor method, it is required to prepare the high-purity columbite-structure material for this precursor method, i.e., nickel niobate (NiNb_2O_6 , NN) for the PNN. It is known that the nickel niobate (NiNb_2O_6) is a good precursor for the successful preparation of single-phase perovskite lead nickel niobate, $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Lu and Hwang, 1996). However, as being aware in literatures (Lu and Hwang, 1996; Bove et al., 2001; Alberta and Bhalla, 2002), high-purity NiNb_2O_6 powders, especially at an ultrafine level (NiNb_2O_6 nanopowders) which is an important condition to obtain highly-efficient material processing, is far from being available in bulk quantities and is also very expensive. Thus, in this study, an approach to synthesize single-phase NiNb_2O_6 nanopowders with a mixed oxide synthetic route is developed via a columbite method assisted.

MATERIALS AND METHODS

The starting materials were commercially-available nickel oxide, NiO (Aldrich, 99% purity) and niobium oxide, Nb₂O₅ (Aldrich, 99.9% purity). The two oxide powders exhibited an average particle size in the range of 3.0 to 5.0 μm. NiNb₂O₆ powders were synthesised by the solid-state reaction of thoroughly-ground mixtures of NiO and Nb₂O₅ powders that were milled in the required stoichiometric ratio. The two oxide powders were milled via a rapid vibro-milling technique (McCrone micronising mill) for 25 h with Al₂O₃ media in ethanol. After drying at 120°C, various calcination temperatures ranging from 750 to 1,000°C for 4 h using heating/cooling rates of 20°C/min, were applied in order to investigate the formation of NiNb₂O₆. The reactions of the uncalcined NiNb₂O₆ powders taking place during heat treatment were investigated by thermogravimetric and differential thermal analysis (TG-DTA, Shimadzu), using a heating rate of 10°C/min in air from room temperature up to 1,000°C. Calcined powders were subsequently examined by X-ray diffraction (XRD; Siemen-D500 diffractometer) using Ni-filtered CuK_α radiation to identify the phases formed and optimum calcination conditions for the manufacture of NiNb₂O₆ powders. The powder morphology was directly imaged using scanning electron microscopy (SEM; JEOL JSM-840A). The chemical compositions of the phases formed were elucidated by an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. EDX spectra were quantified with the virtual standard peaks supplied with the Oxford Instruments eXL software.

RESULTS AND DISCUSSION

The TG-DTA simultaneous analysis of a powder mixed in the stoichiometric proportions of NiNb₂O₆ is shown in Figure 1. The TG curve shows two distinct weight losses. In the temperature range from room temperature to ~ 150°C, both small exothermic and endothermic peaks are observed in the DTA curve in consistent with the first weight loss. These observations can be attributed to the decomposition of the organic species from the milling process. Increasing the temperature up to ~ 1,000°C, the solid-state reaction occurs between NiO and Nb₂O₅. The broad exothermic peak in the DTA curve represents that reaction which has a maximum at ~ 550°C. This is supported by a second fall in sample weight over the same temperature range. However, the DTA curve shows that there are other small peaks at ~ 600 and 800°C. It is to be noted that there is no obvious interpretation of these peaks, although it is likely to correspond to a phase transition reported earlier (Lu and Hwang, 1996). These data were used to define the range of temperatures for XRD investigation to between 600 and 1,000°C.

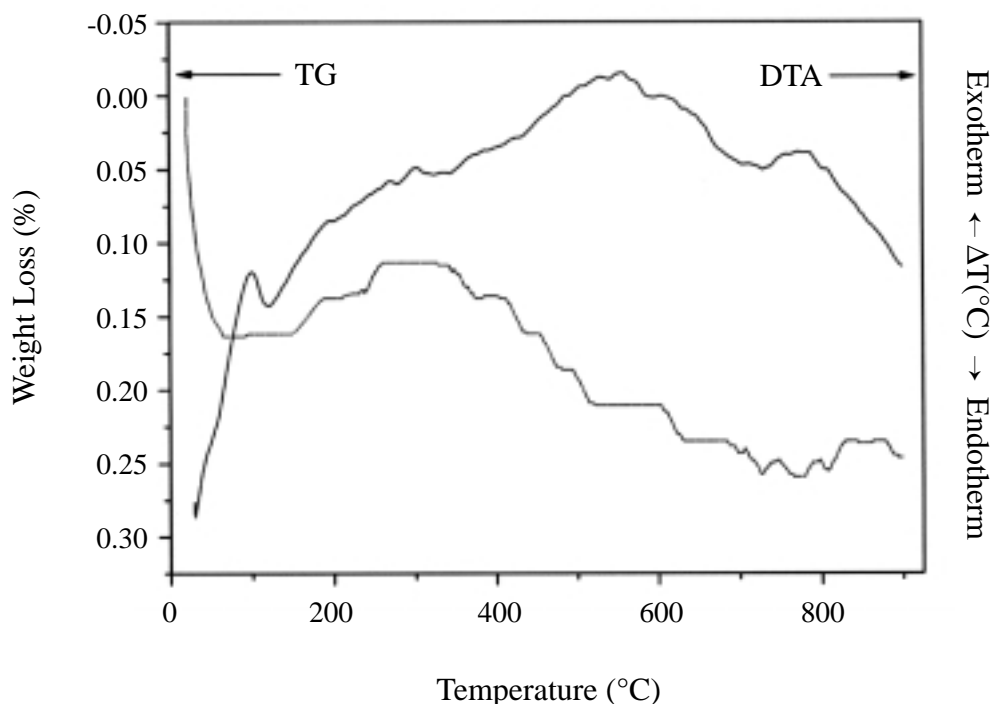


Figure 1. TG-DTA curves for the mixture of NiO-Nb₂O₅ powders.

To further study the phase development with increasing calcination temperature in the powders, they were calcined for 4 h in air at various temperatures, up to 1,000°C, followed by phase analysis using XRD. As shown in Figure 2, after calcination at 750°C, major crystalline phase of NiNb₂O₆ (•) was developed, accompanying with NiO (+) and Nb₂O₅ (◊) as separated phases. X-ray peaks of precursors NiO and Nb₂O₅ can be matched with JCPDS file numbers 73–1519 and 30–873, respectively (Powder diffraction file ICDD, 2000). As the temperature increased to 800°C, a single phase of the NiNb₂O₆ had already been obtained. The XRD pattern of this NiNb₂O₆ phase was indexable according to an orthorhombic columbite-type structure with lattice parameters $a = 1403$ pm, $b = 568.7$ pm and $c = 503.3$ pm, space group $Pbcn$ (no. 60), in consistent with JCPDS file numbers 76–2354 (Powder diffraction file ICDD, 2000) and literature (Cruz et al., 1999). It should be noted that in the present study, there were no significant differences between the powders calcined at 800°C to 1,000°C, as shown in Figure 2. This observation agrees well with those derived from the TG-DTA results (Figure 1).

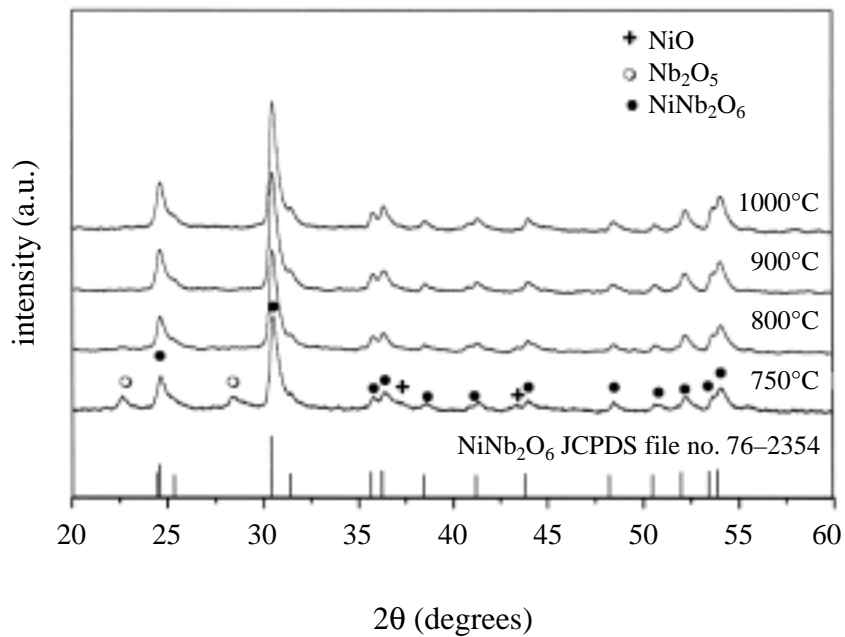


Figure 2. XRD patterns of NiNb₂O₆ powders calcined at various temperatures for 4 h with heating/cooling rates of 20°C/min.

SEM micrograph of the calcined NiNb₂O₆ powders (800°C for 4 h with heating/cooling rates of 20°C/min) is given in Figure 3. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size and morphology. These agglomerates consisted of ~ 50–100 nm NiNb₂O₆ particles. In general, EDX analysis from a large number of particles of the calcined powders confirmed the parent composition to be NiNb₂O₆, in agreement with XRD results.

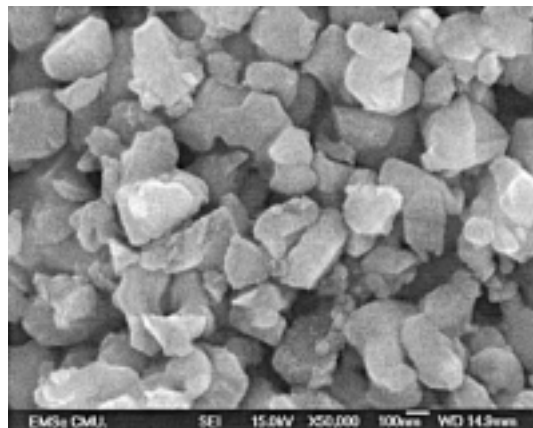


Figure 3. SEM micrograph of the NiNb₂O₆ powders calcined at 800°C for 4 h with heating/cooling rates of 20°C/min.

CONCLUSION

The columbite-type compound of NiNb₂O₆ nanopowders were successfully prepared by a simple mixed oxide synthetic route. The preparative method involved the use of inexpensive and widely-available oxide precursors, moderate calcination conditions (800°C for 4 h with heating/cooling rates of 20°C/min) and rapid vibro-milling technique.

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REFERENCES

- Alberta, E.F., and A.S. Bhalla. 2002. Low-temperature properties of lead nickel-niobate ceramics. *Mater. Lett.* 54: 47–54.
- Bove, T., W. Wolny, E. Ringgaard, and A. Pedersen. 2001. New piezoceramic PZT-PNN material for medical diagnostics applications. *J. Eur. Ceram. Soc.* 21: 1469–1472.
- Cruz, A.M., N.L. Alcaraz, A.F. Fuentes, and L.M. Torres-Martínez. 1999. Electrochemical lithium insertion in some niobates $M\text{Nb}_2\text{O}_6$ (M=Mn, Co, Ni, Cu, Zn and Cd). *J. Power Sources.* 81–82: 255–258.
- Lu, C.H., and W.J. Hwang. 1996. Phase and microstructural developments of $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ prepared by the columbite precursor process. *Ceram. Int.* 22: 373–379.
- Moulson, A.J., and J.M. Herbert. 2003. *Electroceramic*. 2nd ed, Wiley, Chichester.
- Powder Diffraction File no. 30–873. International Centre for Diffraction Data, Newton Square, PA, 2000.
- Powder Diffraction File no. 73–1519. International Centre for Diffraction Data, Newton Square, PA, 2000.
- Powder Diffraction File no. 76–2354. International Centre for Diffraction Data, Newton Square, PA, 2000.
- Xiang, P.H., N. Zhong, X.L. Dong, C.D. Feng, and Y.L. Wang. 2005. Single-calcination synthesis mechanism of pure-perovskite $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ using a coating method. *J. Am. Ceram. Soc.* 88: 239–242.