Synthesis and Characterisation of Zinc Niobate Nanopowders via a Rapid Vibro-Milling Method

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ABSTRACT

In this study, an approach to synthesize single-phase ZN nanopowders with a mixed oxide synthetic route via a rapid vibro-milling technique has been developed. The formation of columbite $ZnNb_2O_6$ phase in the calcined powder has been investigated as a function of calcination conditions by TG-DTA and XRD techniques. Morphology, particle size and chemical composition have been determined via a combination of SEM and EDX techniques. The potentiality of a vibro-milling technique as a significant time-saving method to obtain single-phase ZN nanopowders at low temperature was demonstrated. It is seen that single-phase ZN powders were successfully obtained from a calcination condition of 600°C for 0.5h with heating/cooling rates of 30°C/min. In addition, by employing an appropriate choice of the milling time, an average particle size in the range of 50–300 nm could be achieved.

Key words: Phase formation , Calcination ,Vibro-milling , Zinc niobate , Columbite

INTRODUCTION

Zinc niobate ($ZnNb_2O_6$, ZN) material has been shown to be a good candidate for microwave dielectric applications (Maeda et al., 1987; Lee et al., 1996; Kim et al., 2001). The columbite-structured $ZnNb_2O_6$ is also an attractive B-site precursor for the preparation of lead zinc niobate ($Pb(Zn_{1/3}Nb_{2/3})O_3$ or PZN)-based ferroelectric ceramics, used for high performance in electromechanical actuators and transducers and piezoelectric ultrasonic motors (Jaffe et al., 1971; Xu, 1991; Park and Shrout, 1997). This is significant because it is very difficult to synthesize those compounds via the conventional solid-state reaction process using oxides as starting materials (Gururaja et al., 1987; Sekar et al., 1996). $ZnNb_2O_6$ powders were usually prepared by a solid-state reaction process (Lee et al., 1997). Recent work by Vittayakorn et al., (2003) has shown promise in producing phase-pure columbite ZN powders with the conventional mixed-oxide ball-milling method, while Kong et al., (2002) has successfully synthesized ZN powders via high-energy ball-milling or mechanochemical processing.

The present work is aimed at synthesizing single-phase zinc niobate nanopowders. The conventional mixed oxide synthetic route via a rapid vibro-milling technique has been developed with one-step reaction of all starting materials. The rapid vibro-milling technique is employed for the first time in this work as a significant time-saving method to obtain single-phase ZN nano-sized powders at low temperature.

MATERIALS AND METHODS

In this study, reagent-grade oxides of zinc oxide, ZnO (Fluka Chemical, 99.9% purity), and niobium pentaoxide, Nb_2O_5 (Aldrich, 99.9% purity) were used as starting materials. $ZnNb_2O_6$ powders were synthesized by the solid-state reaction of these raw materials. Ground mixtures of the powders were required with stoichiometric ratios for the general composition of ZnO and Nb_2O_5 powders. A McCrone vibro-milling technique was employed in order to combine mixing capacity with a significant time saving. The milling operation was carried out in isopropanal. High-purity corundum cylindrical media were used as the milling media. After vibro-milling for 30 minutes and drying at 120°C, the reaction of the uncalcined powders taking place during heat treatment was investigated by themogravimetric and differential thermal analysis (TG-DTA, Shimadzu) in air from room temperature up to 1,350°C. Based on the TG-DTA results, the mixture was calcined at various conditions, i.e., temperatures ranging from 500 to 900°C, dwell times ranging from 0.5 to 2 hours and heating/cooling rates ranging from 5 to 30°C/min , in alumina crucible to investigate the phase formation behavior of ZN powders.

Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Siemens-D500 diffractrometer), using Ni-filtered CuK(radiation to identify the phases formed for the ZN powders. Powder morphologies and particle sizes were directly imaged, using scanning electron microscopy (SEM; JEOL JSM-840A). EDX spectra were quantified with the virtual standard peaks supplied with the Oxford Instruments eXL software.

RESULTS AND DISCUSSION

Themogravimetric and Differential Thermal Analysis (TG/DTA)

TG-DTA curves obtained for powders mixed in the stoichiometric proportions of ZnO and Nb_2O_5 powders are displayed in Figure. 1. In the temperature range of 50–200°C, the sample shows several large exothermic peaks in the DTA curve. These DTA peaks can be attributed to the decomposition of the organic species from the milling process. The different temperature, intensities and shapes of the thermal peaks are probably related to the different natures of the organic species and, consequently, caused by the removal of species differently bounded in the network (Ananta et al., 2000).

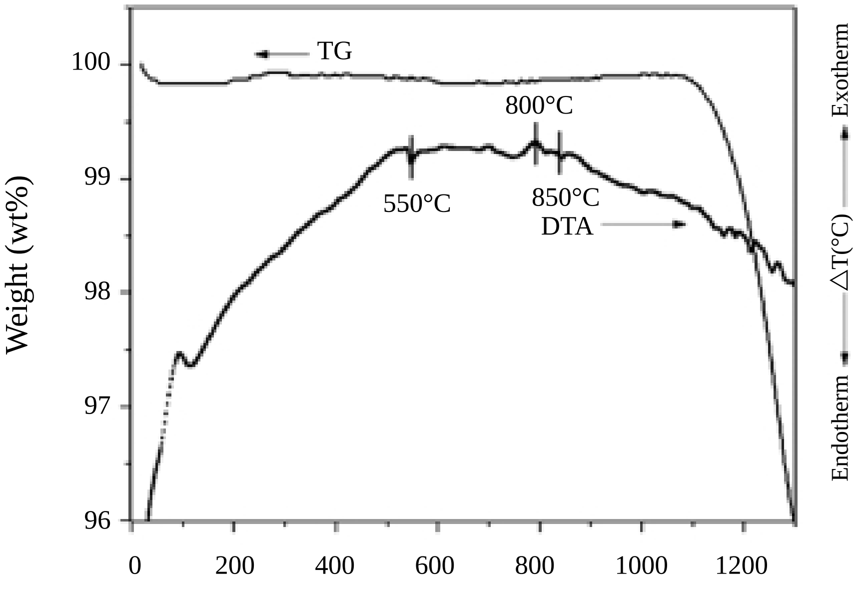

Figure 1. TG-DTA curves for the mixture of ZnO-Nb_2O_5 powder.

In the temperature range of 550–850°C, both exothermic and endothermic peaks are observed in the DTA curve. The enlarged zone of this DTA curve shows that the endothermic peak centered at ~ 800°C which may have been resulted from columbite phase crystallization. Above 1,000°C, TG curve indicates that higher weight loss of substance occurs. This TG result implies the upper limit of the calcination temperature for the mixed powders. Therefore, these temperatures are used to define the range of calcination temperatures (500 to 900°C) used in subsequent powder processing steps.

X-Ray Diffraction Analysis (XRD)

Powder XRD patterns of the calcined ZN powders at different calcination temperatures are shown in Figure. 2. As shown in Figure 2, for the uncalcined powder, only X-ray peaks of precursors ZnO and Nb_2O_5, which could be matched with JCPDS file numbers 89–1397and 30–0873 (Powder diffraction file ICDD, 2000), respectively, are present, indicating that no reaction had yet been triggered during the milling process. Above 600°C, the ZN powders (matched with JCPDS file numbers 76–1827)has been found to form. However, the precursor phases ZnO and Nb_2O_5 are also detected in the powders by XRD when calcined below 600°C. From Figure 3, it was also found that there were no significant differences between the powders calcined at 600°C with dwell time ranging from 0.5 to 2 h. An attempt was also made to calcine ZN powders under various heating/cooling rates as shown in Figure 4. In this connection, it indicated that the yield of $ZnNb_2O_6$ phase did not vary significantly with different heating/cooling rates ranging from 5 to 30°C /min.

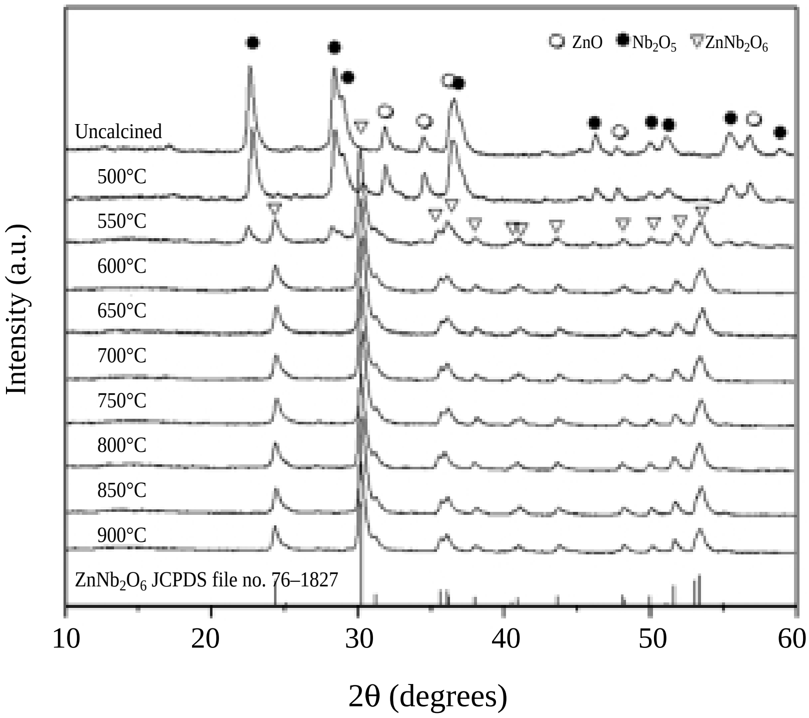

Figure 2. XRD patterns of ZN powder calcined at various temperature for 2 h. with heating/ cooling rates of 10°C / min.

It should also be noticed from Figure 2, which shows XRD scans at calcination temperatures above 600°C, that in most compositions the columbite phase is formed in a sudden nature, which is significantly different from previous research by Vittayakorn et al., (2003) in which a convention at ball-milling method was used and the calcination temperature was above 900°C. It is also very interesting to see that these on-set temperatures in every composition are approximately 300°C lower that those reported earlier with a conventional ball-milling method (Vittayakorn et al., 2003). The difference could be attributed to nano-sized mixed powders obtained from a rapid vibro-milling technique. More importantly, this study suggests that a rapid vibro-milling method can significantly lower the calcination temperature for ZN powders.

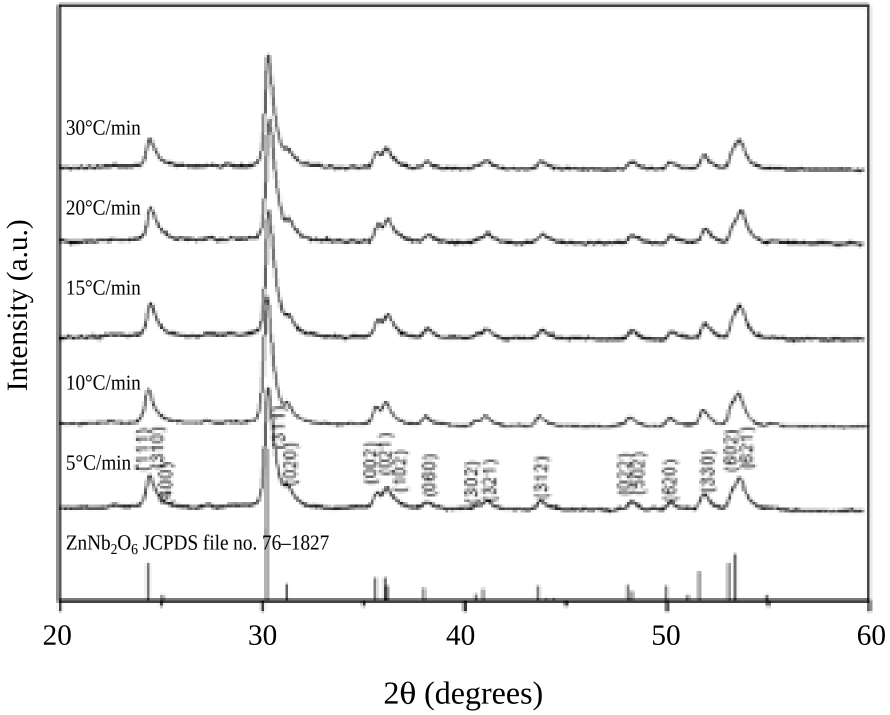

Figure 3. XRD patterns of ZN powder calcined at 600°C for various dwell times with heating/cooling rates of 10°C/min.

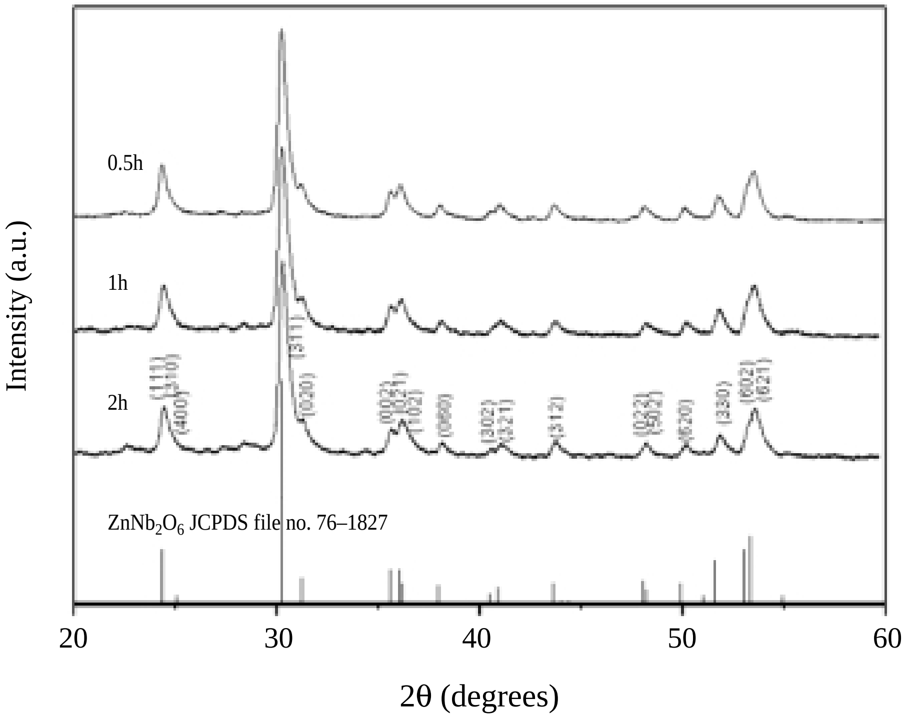

Figure 4. XRD patterns of ZN powder calcined at 600°C for 2 h., various heating/cooling rates.

Based on XRD data, it may be concluded that over a wide range of calcination conditions, single-phase $ZnNb_2O_6$ can be straightforwardly formed via a solid-state mixed oxide synthetic route. This work carried out here suggests that the optimal calcination condition for single-phase $ZnNb_2O_6$ (with impurities undetectable by XRD technique) is 600°C for 0.5 h, with heating/cooling rates as fast as 30°C/min.

SEM and EDX Analysis

The morphological changes in the ZN powders (600°C for 0.5 h, with heating/cooling rates of 30°C/min.) formed by a mixed oxide method are illustrated in Figure 5. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size. Generally, particle size can be estimated from SEM micrographs to be in the range of 50–300 nm.

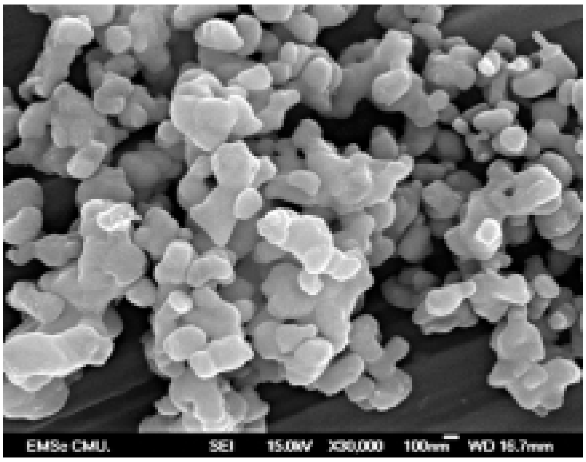

Figure 5. SEM micrographs of the ZN powders calcined at 600°C for 0.5 h, with heating/cooling rates of 30°C /min.

Finally, EDX analysis using a 20 nm probe on a large number of particles of the calcined powders confirms that the parent composition is ZN powders, in good agreement with XRD results as shown in Figure 6.

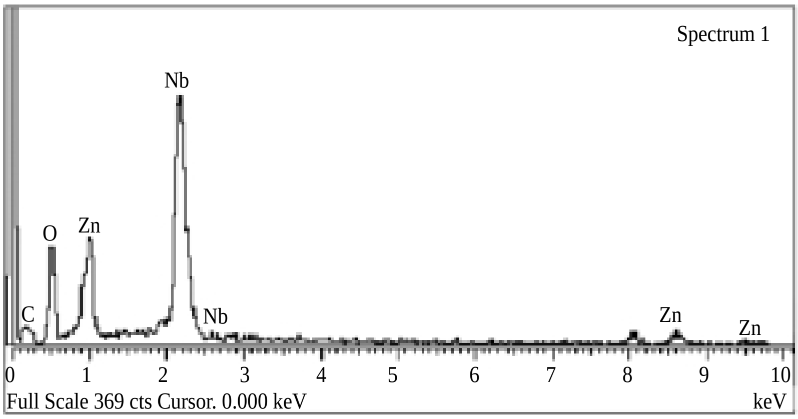

Figure 6. EDX analysis of the ZN powders calcined at the optimised condition.

CONCLUSION

The solid-state mixed oxide method via a rapid vibro-milling technique was explored in the preparation of single-phase ZN nanopowders. The effects of calcination conditions (temperature, dwell time, and heating/cooling rates) on the phase formation behaviour of ZN powders were investigated. It was found that the minimum calcination temperature was at 600°C. There were also no significant differences between the powders calcined at 600°C at dwell time ranging from 0.5 to 2 hours and heating/cooling rates ranging from 5 to 30°C/min. The optimum calcination condition for the formation of single-phase ZN powder was found to be 600°C for 0.5 hour with heating/cooling rates of 30°C / min. The potentiality of a vibro-milling technique as a significant time-saving method to obtain single-phase ZN nano-sized powders at lower calcination temperature had also been demonstrated.

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