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Effect of vibro-milling time and calcination condition on phase formation and particle size of nickel niobate nanopowders

O. Khamman *, Y. Laosiritaworn, R. Yimnirun, S. Ananta

Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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Abstract

The effect of milling time on the phase formation and particle size of nickel niobate, $NiNb_2O_6$, powder synthesized by a solid-state reaction via a vibro-milling technique was investigated. Powder samples were characterized using DTA, XRD, SEM and laser diffraction techniques. It was found that the smallest particle size of 32 nm was achieved at 25 h of vibro-milling after which a higher degree of particle agglomeration was observed on continuation of milling to 35 h. In addition, by employing an appropriate choice of the milling time, a narrow particle size distribution curve was also observed.

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1. Introduction

There has been a great deal of interest in the preparation of single-phase PNN powders as well as in the sintering and electrical properties of PNN-based ceramics [1–3]. In general, the constituents NiO and Nb_2O_5 are first mixed and reacted together to form nickel niobate ($NiNb_2O_6$), prior to mixing and reacting with PbO in the second step of calcination at elevated temperature. Interestingly, this mixed oxide route has been employed with minor modifications in the synthesis of $NiNb_2O_6$ itself [2,3]. Although some research has been done in the preparation of $NiNb_2O_6$ powders via a vibro-milling technique [2,4], to our knowledge a systematic study regarding the influence of milling time on the preparation of $NiNb_2O_6$ powders has not yet been reported. Thus, in the present study, the effect of milling time on phase formation and particle size of nickel niobate powders was investigated in this connection.

2. Experimental procedure

The starting materials were commercially available nickel oxide, NiO (JCPDS file number 73-1519) and niobium oxide, Nb_2O_5 (JCPDS file number 30-0873) (Aldrich, 99.9% purity). The two oxide powders exhibited an average particle size in the range of 3.0–5.0 μm. $NiNb_2O_6$ powders were synthesized by the solid-state reaction of these raw materials. Powder-processing was carried out in a manner similar to that employed in our previous works [4–6]. A vibratory laboratory mill (McCrone Micronizing Mill) was employed for preparing the stoichiometric $NiNb_2O_6$ powders. The milling operation was carried out in isopropanal inert to the polypropylene jar. Various milling times ranging from 0.5 to 35 h were selected in order to investigate the phase formation characteristic of nickel niobate and the smallest particle size. After drying at 120 °C for 2 h, the reaction of the uncalcined powders taking place during heat treatment was investigated by differential thermal analysis technique (DTA, Shimadzu) at a heating rate of 10 °C/min in air from room temperature up to 900 °C. Based on the DTA result and literature [2,4], the mixture was calcined at 900 °C (in closed alumina crucible) for 4 h with heating/cooling rates of 30 °C/min.

All powders were subsequently examined by room temperature X-ray diffraction (XRD; Siemens-D500 diffractometer), using Ni-filtered Cu Kα radiation to identify the phases formed and optimum milling time for the production of $NiNb_2O_6$ powders having the smallest particle size. The relative amount of columbite and secondary phases was determined from XRD patterns of the samples by measuring the major

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* Corresponding author.
E-mail address: Orawan2006@yahoo.com (O. Khamman).

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Table 1
Effect of milling time on the phase formation and particle size of $NiNb_2O_6$ powders measured by different techniques

Milling time (h)	Columbite phase (wt%)	XRD			SEM			Laser scattering	
		A (nm)	*a* (Å)	*b* (Å)	*c* (Å)	*D* (nm)	*P* (nm)	*D* (nm)	*P* (nm)
0.5	87	173.40	15.72	4.96	4.98	900	560–1400	3200	400–5000
1	92	93.69	15.50	5.00	5.02	820	500–1300	2500	320–5000
5	100	73.12	15.01	5.24	5.02	708	467–1160	1500	250–3000
15	100	59.44	14.71	5.32	5.00	545	167–949	450	250–750
25	100	34.54	15.64	4.99	4.99	120	32–164	240	40–750
35	100	20.57	15.52	5.05	5.00	250	63–570	690	45–6000

A = crystallite size, *a*, *b*, *c* = lattice parameters, *D* = average particle sizem and *P* = particle size range or distribution.

characteristic peak intensities for the columbite (3 1 1) or I_P and secondary (o) phases or I_S. The following qualitative equation was used [5].

$$\text{columbite phase (wt\%)} = \frac{I_P}{I_P + I_S} \times 100 \qquad (1)$$

The crystalline lattice constants, lattice strain and average particle size were also estimated from XRD patterns [7]. The particle size distributions of the powders were determined by laser diffraction technique (DIAS 1640 laser diffraction spectrometer) with the particle sizes and morphologies of the powders observed by scanning electron microscopy (JEOL JSM-840A SEM). The particle sizes of $NiNb_2O_6$ powders milled at different times obtained from different measuring techniques are provided in Table 1.

3. Results and discussion

The DTA results for the powders milled at different times are compared and displayed in Fig. 1. In general, similar thermal characteristics are observed in all cases. In the temperature range from room temperature to ~150 °C, all samples show both exothermic and endothermic peaks in the DTA curves. These observations can be attributed to the decomposition of the organic species originating from the milling process [4-6]. Increasing the temperature up to ~900 °C, the solid-state reaction occurred between NiO and Nb_2O_5 [4,8]. The broad exotherm with several peaks in the DTA curves represents that reaction, which has a maximum at ~550 and 750 °C. The slightly different temperature, intensities and shapes of the thermal peaks for the powders are probably related to the different sizes of the powders subjected to different milling times [3,5].

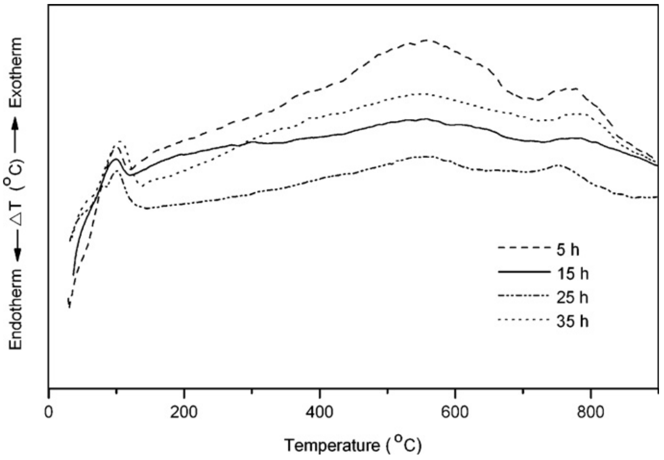

Fig. 1. DTA analysis for the mixture of NiO and Nb_2O_5 powders milled at different times.

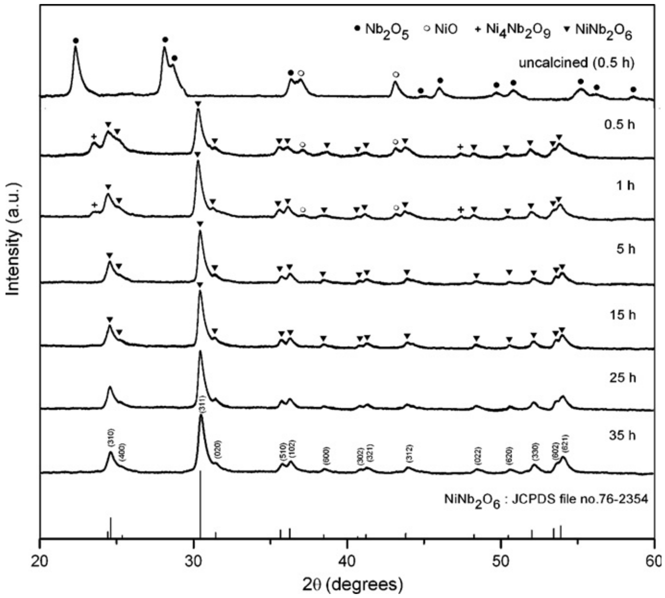

Fig. 2. XRD patterns of $NiNb_2O_6$ powders milled at different times (calcined at 900 °C for 4 h with heating/cooling rates of 30 °C/min).

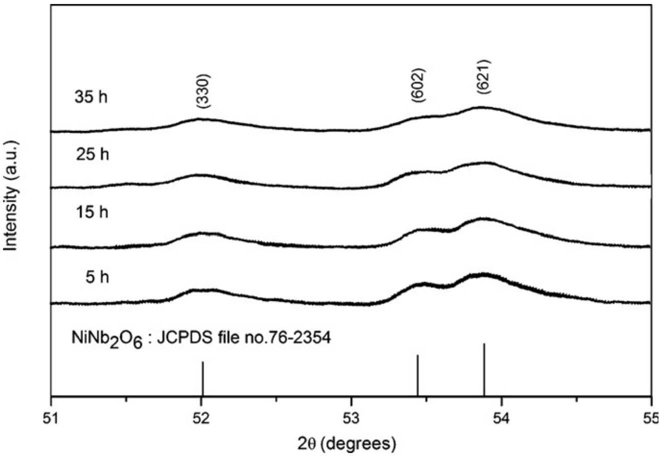

Fig. 3. Enlarged zone of XRD patterns showing (6 0 2) and (6 2 1) peaks broadening as a function of milling times.

To further study the effect of milling time on phase formation, each of the powders milled for different times was calcined at 900 °C for 4 h in air, followed by phase analysis using XRD. For the purpose of estimating the concentrations of the phase present, Eq. (1) has been applied to the powder XRD patterns obtained, as given in Table 1. As shown in Fig. 2, for the uncalcined powder subjected to 0.5 h of vibro-milling, only X-ray peaks of precursors NiO (○) and Nb_2O_5 (●) are present, indicating that no reaction had been initiated during the milling process. However, after calcination, it is seen that the columbite-type $NiNb_2O_6$ becomes the predominant phase in the powder milled for 0.5 h, indicating that the reaction has occurred to a considerable extent. It is seen that traces of unreacted NiO and Nb_2O_5 precursors and corundum-type $Ni_4Nb_2O_9$ earlier reported by Khamman et al. [8] have been found along with the $NiNb_2O_6$ parent phase at a milling time of 1 h or less. This observation could be attributed mainly to the poor mixing capability under short milling time, similar with

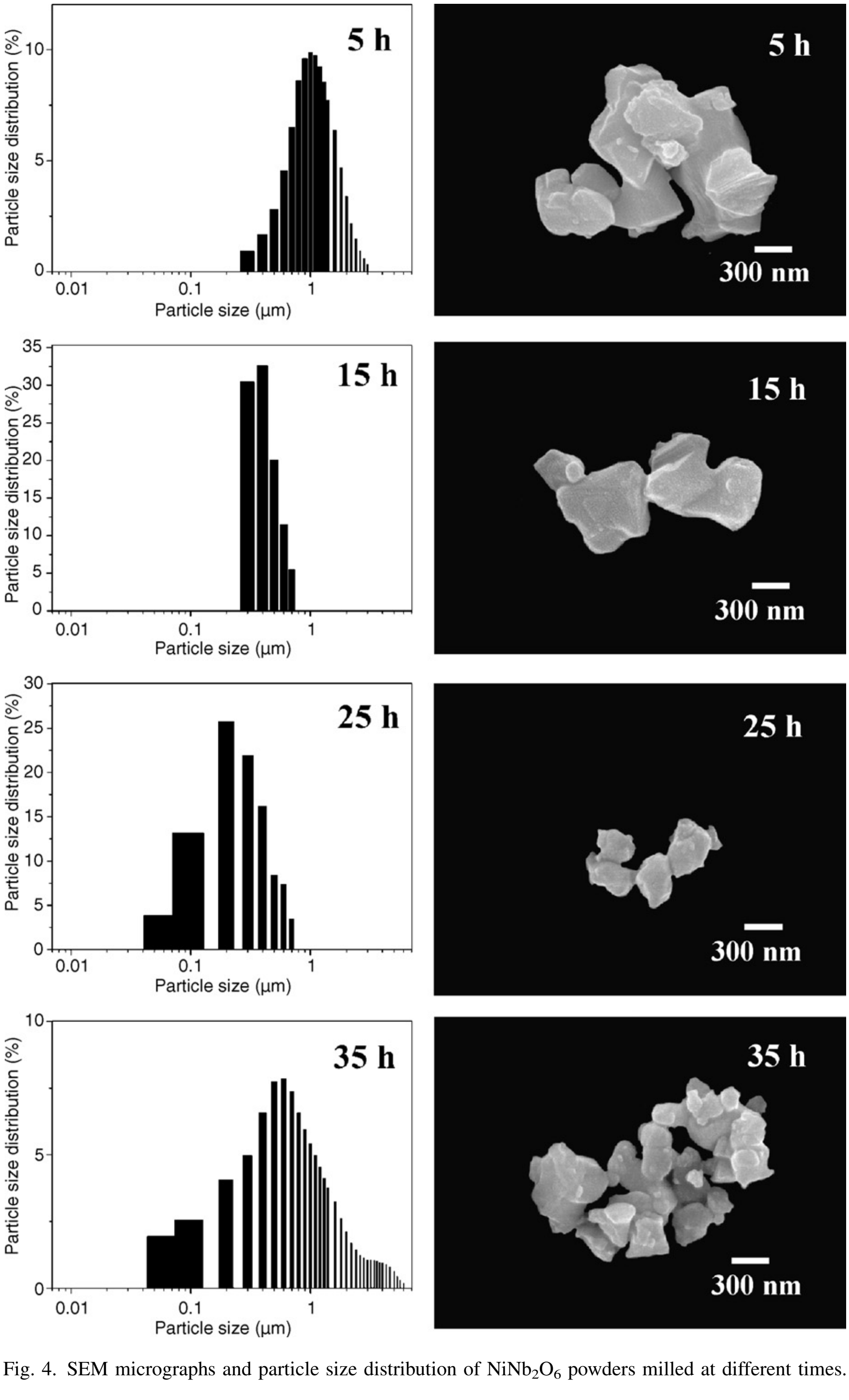

Fig. 4. SEM micrographs and particle size distribution of $NiNb_2O_6$ powders milled at different times.

other work [4–6]. With milling time of 5 h or more, it is apparent that a single-phase columbite $NiNb_2O_6$ was found to be possible after the same calcination process was applied.

In general, the strongest reflections found in the majority of these XRD patterns indicate the formation of the nickel niobate, $NiNb_2O_6$ (JCPDS file number 76-2354) [9]. Moreover, it has been observed that with increasing milling time, all diffraction lines broaden, e.g. (6 0 2) and (6 2 1) peaks at $2\theta \sim 53–54^\circ$ (Fig. 3), an indication of a continuous decrease in particle size and of the introduction of lattice strain. These observations indicate that the prolonged milling treatment affects the particle size and evolution of crystallinity of the phase formed (Table 1), in good agreement with other similar system [10,11]. For $NiNb_2O_6$ powders, the longer is the milling time, the finer is the particle size, down to a certain level. The results suggest that the steady state of the vibro-milling is attained at ~25 h of milling. Moreover, it is worthy to note that, in this condition, the mean crystalline size is close to ~35 nm.

Scanning electron microcopy was also employed for particle size measurement (Table 1). The morphological evolution of the powders and their corresponding particle size distributions as a function of milling time were also revealed, as illustrated in Fig. 4. At first sight, the morphological characteristic of $NiNb_2O_6$ powders with various milling times is similar for all cases. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle sizes. The powders consist of primary particles nanometers in size. Increasing the milling time over the range 5–35 h, the average size of the $NiNb_2O_6$ particles decreases significantly, until at 25 h, the smallest particle size (estimated from SEM micrographs to be ~32 nm) is obtained. However, it is also of interest to point out that larger particle size was obtained for a milling time longer than 25 h. This may be attributed to the occurrence of hard agglomeration with strong inter-particle bonds within each aggregate resulting from dissipated heat energy of prolong milling [5,12].

As shown in Fig. 4, after milling times of 5, 15 and 25 h, the powders exhibit a single peak covering the size ranging from 40 to 3000 nm. With milling time of 25 h, a uniform particle size distribution with a much lower degree of particle agglomeration (<1 μm) is found. However, upon further increase of milling time up to 35 h, a bimodal distribution curve with peak broadening between 45 and 6000 nm is observed. First is a monomodal distribution corresponding to the primary size of the $NiNb_2O_6$ particles. The second group (peak) is believed to arise mainly from particle agglomeration. Table 1 compares the results obtained for $NiNb_2O_6$ powders milled for different times via different techniques. Variations in these data may be attributed mainly to the formation of hard and large agglomerations, as observed in the SEM results.

4. Conclusions

The results infer that the milling time influences not only the development of the solid-state reaction of nickel niobate phase but also the particle size and morphology. The resulting $NiNb_2O_6$ powders have a range of particle size, depending on milling times. Production of a single-phase nickel niobate nanopowder can be successfully achieved by employing a combination of 25 h milling time and calcination condition of 900 °C for 4 h, with heating/cooling rates of 30 °C/min.

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