J Mater Sci (2007) 42:3754–3760
DOI 10.1007/s10853-006-0404-1

Influence of calcination conditions on phase formation and particle size of indium niobate powders synthesized by the solid-state reaction

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Received: 4 November 2005 / Accepted: 2 May 2006 / Published online: 10 February 2007

Abstract A wolframite-type phase of indium niobate, $InNbO_4$, has been synthesized by a solid-state reaction via a rapid vibro-milling technique. The formation of the $InNbO_4$ phase in the calcined powders 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. Single-phase $InNbO_4$ powders have been obtained successfully for calcination condition of 900 °C for 4 h or 950 °C for 2 h with heating/cooling rates of 30 °C/min. Higher temperatures and longer dwell times clearly favoured particle growth and the formation of large and hard agglomerates.

Introduction

Indium niobate ($InNbO_4$, IN) is one of the binary niobate compounds with a wolframite crystal structure [1]. Earlier works concerning the $InNbO_4$ have been directed towards determining low-temperature dielectric [2], luminescent [3] and photocatalytic [4] properties. Recently, this compound is also a potential material for the development of photocatalytic systems capable of splitting water into H_2 and O_2 under visible light irradiation [5–7]. Moreover, it is well established as a key precursor for the partially successful preparation of single-phase ferroelectric perovskite lead indium niobate $Pb(In_{1/2}Nb_{1/2})O_3$ (PIN)-based ceramics, which is becoming increasingly important for actuator, transducer and ultrasonic motor applications [8, 9].

There has been a great deal of interest in the preparation of single-phase PIN powders as well as in the phase transition, ordering behaviour and electrical properties of PIN-based ceramics [10–18]. In general, the constituents In_2O_3 and Nb_2O_5 are first mixed and reacted together to form indium niobate ($InNbO_4$), 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 $InNbO_4$ itself [13–16]. However, powders prepared by a mixed oxide route have spatial fluctuations in their compositions. The extent of the fluctuations depends on the characteristics of the starting powders as well as on the processing schedule. Generally, the mixed oxide method involves the heating of a mixture of indium oxide and niobium oxide above 1,000 °C for long times i.e. 4 h [10, 13], 12 h [6], 24 h [14–17] and 48 h [4, 7]. The optimization of calcination conditions used in the mixed oxide process, however, has not received detailed attention, and the effects of applied dwell time and heating/cooling rates have not yet been studied extensively.

Therefore, the main purpose of this work is to explore a simple mixed oxide synthetic route for the production of $InNbO_4$ powders via a rapid vibro-milling technique and to perform a systematic study of the reaction between the starting indium oxide and niobium oxide precursors. The phase formation and morphology of the powders calcined at various conditions will be studied and discussed. The rapid vibro-milling technique is

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employed to explore the potentiality in obtaining nanosized powders, which would in turn lead to lower required firing temperature.

Experimental procedure

The starting materials were commercially available indium oxide, In_2O_3 (JCPDS file number 71-2195) and niobium oxide, Nb_2O_5 (JCPDS file number 30-873) (Aldrich, 99.9% purity). The two oxide powders exhibited an average particle size in the range of 1.0–3.0 μm. $InNbO_4$ powders were synthesized by the solid-state reaction of thoroughly ground mixtures of In_2O_3 and Nb_2O_5 powders that were milled in the required stoichiometric ratio. Instead of employing a ball-milling procedure [10, 16], a McCrone vibro-milling technique was used [19, 20]. In this technique, a vibratory laboratory mill (McCrone Micronizing Mill) powered by a 1/30 HP motor was employed. The grinding vessel consists of a 125 mL capacity polypropylene jar fitted with a screw-capped, gasketless, polythene closure. The jar is packed with an ordered array of identical, cylindrical, grinding media of polycrystalline corundum. A total of 48 milling media with a powder weight of 20 g was kept constant in each batch. The milling operation was carried out in isopropanal inert to the polypropylene jar. In order to combine mixing capacity with a significant time saving, the milling operation was carried out for 0.5 h with corundum cylindrical media in isopropyl alcohol (IPA). After drying at 120 °C for 2 h, the reaction of the uncalcined powders taking place during heat treatment was investigated by themogravimetric 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. Based on the TG-DTA results, the mixture (~10 g for each batch) was calcined at various conditions, i.e. temperatures ranging from 700 °C to 1,200 °C, dwell times ranging from 0.5 h to 4 h and heating/cooling rates ranging from 3 °C/min to 30 °C/min, in closed alumina crucible [cylindrical shape with 25 mL capacity (3 cm in diameter and 3.5 cm in height)], in order to investigate the formation of indium niobate.

Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Siemens-D500 diffractometer), using Ni-filtered CuK_α radiation to identify the phases formed and optimum calcination conditions for the formation of $InNbO_4$ powders. Powder morphologies and particle sizes were directly imaged, using scanning electron microscopy (SEM; JEOL JSM-840A). The chemical compositions of the phase formed were elucidated by an energy-dispersive X-ray (EDX) analyzer 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 proportion of $InNbO_4$ is displayed in Fig. 1. The TG curve shows two distinct weight losses. In the temperature range from room temperature to ~150 °C, both 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 (i.e. polyethylene milling jar, rubber gloves, skin, etc.) from the milling process [19, 20]. Increasing the temperature up to ~1,000 °C, the solid-state reaction occurred between In_2O_3 and Nb_2O_5 [10, 16]. The broad exotherm in the DTA curve represents that reaction, which has a maximum at ~500 °C. This is supported by a large fall in sample weight over the same temperature range. The causes for these observations are not well documented, but could probably be related to (i) the partial formation of InO_6 and NbO_6 octahedra prior to $InNbO_4$ formation [6, 7] and (ii) the possible formation of $InNbO_4$ in a very small container containing only 0.5 g of powder in TG-DTA apparatus. It should be noted, however, that in the calcination process, a much larger crucible containing ~10 g of powder was used, hence, higher calicination temperature than that observed from TG-DTA is expected. Although the DTA curve shows that there are other small peaks at ~750, 850 and 900 °C, however, it is to be noted that there is no obvious interpretation of these peaks. These data were used to

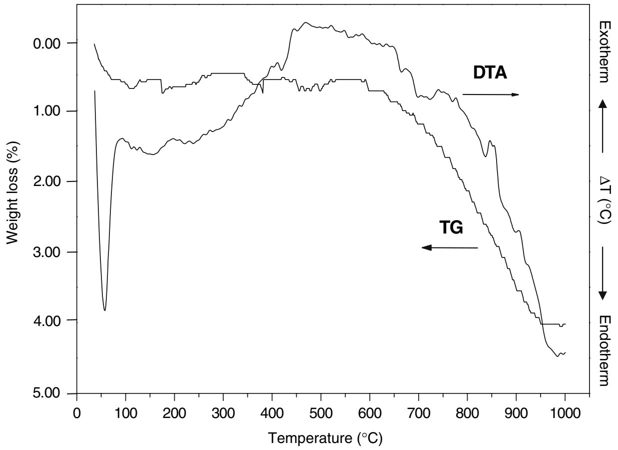

Fig. 1 TG-DTA curves for the mixture of In_2O_3–Nb_2O_5 powder

define the range of calcination temperatures for XRD investigation to between 700 °C and 1,200 °C.

To further study the phase development with increasing calcination temperature in the powders, they were calcined for 2 h in air at various temperatures, up to 1,200 °C, followed by phase analysis using XRD. As shown in Fig. 2, for the uncalcined powders and the powders calcined at 700 °C, only X-ray peaks of precursors In_2O_3 (•) and Nb_2O_5 (○), which could be matched with JCPDS file numbers 71-2195 [21] and 30-873 [22], respectively, are present, indicating that no reaction had yet been triggered during the milling or low firing processes. It is seen that fine $InNbO_4$ crystallites (∇) were developed in the powders at a calcination temperature as low as 750 °C, accompanying with In_2O_3 and Nb_2O_5 as separated phases. This observation agrees well with those derived from the TG-DTA results. As the temperature increased to 900 °C, the intensity of the wolframite-like $InNbO_4$ peaks was further enhanced and became the predominant phase. Upon calcination at 950 °C, an essentially monophasic of $InNbO_4$ phase is obtained. This $InNbO_4$ phase was indexable according to a monoclinic wolframite-type structure with lattice parameters $a = 514.40$ pm, $b = 577.09$ pm, $c = 483.55$ pm and $\beta = 91.13°$, space group $P2/a$ (no. 13), in consistent with JCPDS file numbers 83-1780 [23] and literature [3, 6]. This study also shows that monoclinic $InNbO_4$ is the only detectable phase in the powders, after calcination in the range of 950–1,200 °C. The variation of the intensity ratio between the two major peaks $(11\bar{1})$ and (111) at 2θ~29–31° could be attributed mainly to the expansion of the NbO_6 volume similar with those observed in other ABO_4 systems [3, 6]. In the structure of $InNbO_4$, there are two kinds of octahedron, InO_6 and NbO_6. The InO_6 octahedron connects to each other to form zigzag chain by sharing edges. These chains are connected through NbO_6 octahedron to form the three-dimensional network [6, 7, 24]. It is believed that the InO_6 chains are highly distorted because they must accommodate the strain of the defect, which probably leads to lattice rotation [11].

In earlier works [4, 6, 10, 14], long heat treatments at ~1,000–1,200 °C for 4, 12, 24 and 48 h were proposed for the formation of $InNbO_4$ by a conventional mixed oxide synthetic route, although no details on phase formation were provided. However, in the present study, it was found that, except the fluctuation of the intensity ratio between the $(11\bar{1})$ and (111) peaks, there are no significant differences between the powders calcined at 950 °C to 1,200 °C with dwell time of only 2 h, as shown in Fig. 2. This observation would clearly suggest the advantages of a rapid vibro-milling technique used in the present study.

Apart from the calcination temperature, the effect of dwell time was also found to be quite significant. From Fig. 3, it can be seen that the single phase of $InNbO_4$ (yield of 100% within the limitations of the XRD technique) was found to be possible in powders calcined at 950 °C with dwell time of 2 h or more. The appearance of In_2O_3 and Nb_2O_5 phases indicated that full crystallization has not occurred at relatively short calcination times. However, in the work reported here, it is to be noted that single phase of $InNbO_4$ powders was also successfully obtained for a calcination temperature of 900 °C with dwell time of at least 4 h

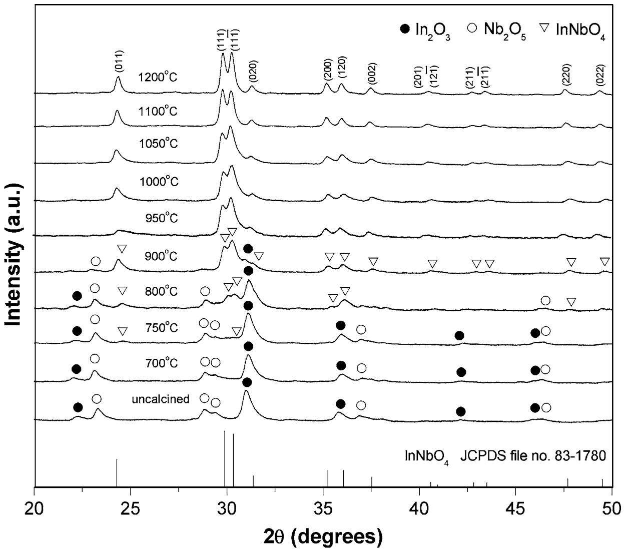

Fig. 2 XRD patterns of IN powders calcined at various temperatures for 2 h with heating/cooling rates of 10 °C/min

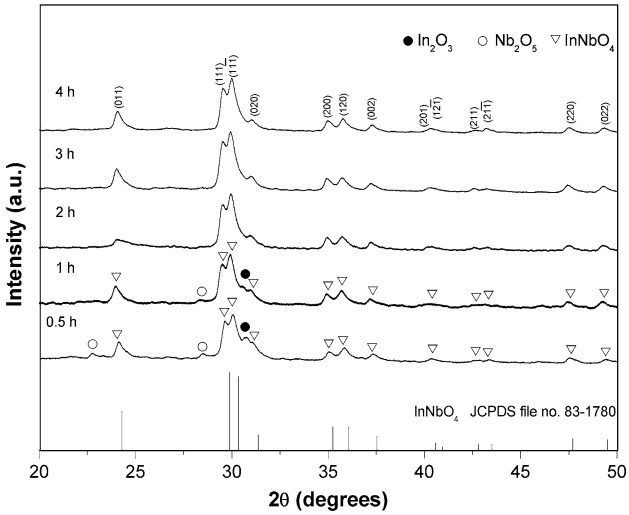

Fig. 3 XRD patterns of IN powders calcined at 950 °C with heating/cooling rates of 10 °C/min for various dwell times

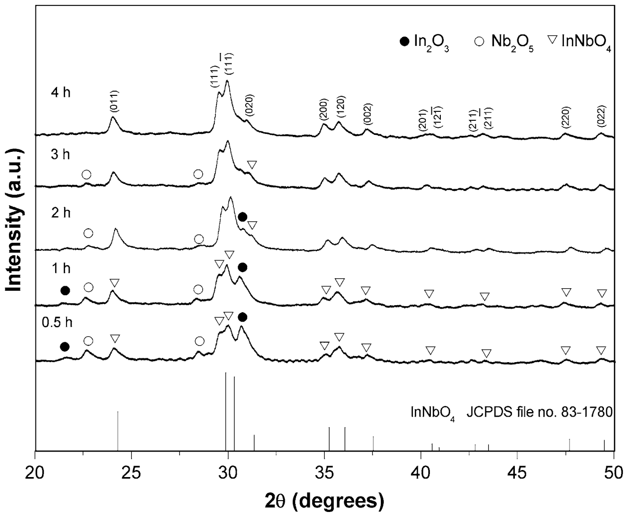

Fig. 4 XRD patterns of IN powders calcined at 900 °C with heating/cooling rates of 10 °C/min for various dwell times

applied (Fig. 4). This was apparently a consequence of the enhancement in crystallinity of the $InNbO_4$ phase with increasing dwell time. The observation that the dwell time effect may also play an important role in obtaining a single-phase wolframite product is also consistent with other similar systems [19, 25, 26]. It is also very interesting to see that the on-set firing time is approximately 2–22 h shorter than those reported earlier with a conventional ball-milling method [10–17]. The difference could be attributed to the effectiveness of vibro-milling and a carefully optimized reaction. Most importantly, this study suggests that a rapid vibro-milling method can significantly lower the optimum calcination temperature and dwell time for formation of single-phase $InNbO_4$ powders.

In the present study, an attempt was also made to calcine $InNbO_4$ powders under various heating/cooling rates. In this connection, it is shown that for the powders calcined at 950 °C for 2 h, the yield of $InNbO_4$ phase did not vary significantly with different heating/cooling rates, ranging from 3 °C/min to 30 °C/min (Fig. 5). However, for the powders calcined at 900 °C for 4 h, different result was observed. It is seen that single-phase $InNbO_4$ can be detected only in the powders where heating/cooling rates of 10 °C/min or faster were applied (Fig. 6). These results indicated that faster heating/cooling rates can probably lead to better crystallization of $InNbO_4$ phase without time for the indium vaporization (due to the volatilization of In_2O_3). The observation that faster heating/cooling rates are required for the mixtures containing *volatile* oxide constituent (In_2O_3), is in good agreement with early results reported in other similar systems [27, 28].

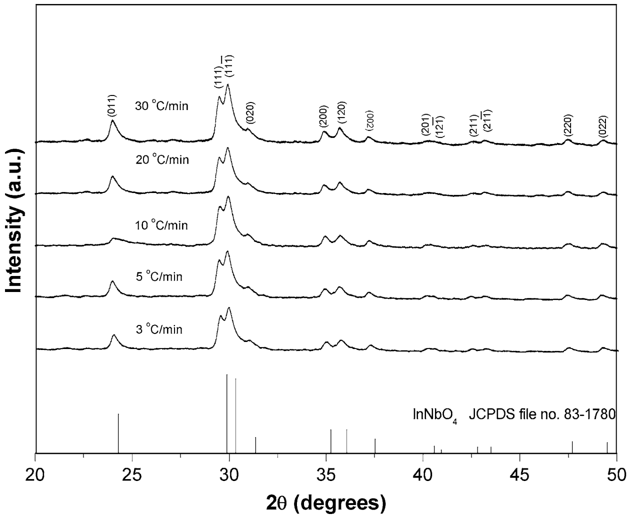

Fig. 5 XRD patterns of IN powders calcined at 950 °C for 2 h with various heating/cooling rates

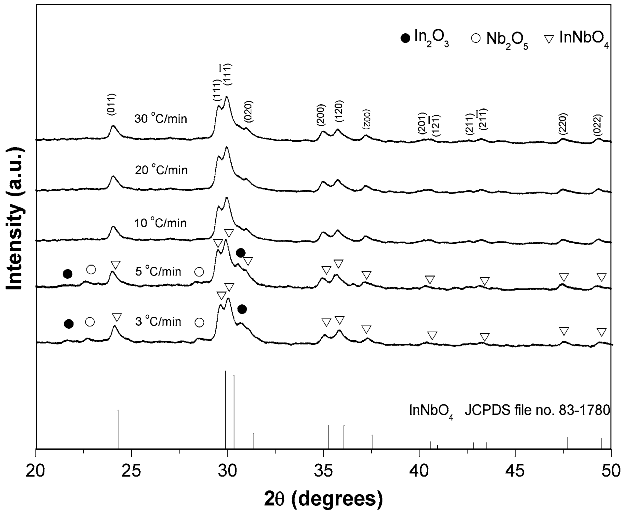

Fig. 6 XRD patterns of IN powders calcined at 900 °C for 4 h with various heating/cooling rates

Based on the TG-DTA and XRD data, it may be concluded that, over a wide range of calcination conditions, single-phase $InNbO_4$ cannot be straightforwardly formed via a solid-state mixed oxide synthetic route, unless a careful design of calcination condition is performed. It is well documented that powders prepared by a conventional mixed oxide method have spatial fluctuations in their compositions. The extent of the fluctuation depends on the characteristics of the starting powders as well as the processing schedules [20, 26]. It is rather surprising that no evidence of the monoclinic *P*2/*c* (13) of $InNbO_4$ [29, 30] was found in this study, nor was there any indication of the one with *P*2/*a* (13) reported by Brixner and Chen [3, 31] being present. The experimental work carried out here suggests that the optimal calcination conditions for single-phase $InNbO_4$ (with impurities undetected by XRD technique) is 950 °C for 2 h or 900 °C for 4 h, with heating/cooling rates as fast as 30 °C/min. Moreover, the formation temperature and dwell time for the production of $InNbO_4$ powders observed in this work are also lower than those reported earlier [13–17]. This clearly emphasizes the advantages of a combination between a rapid vibro-milling technique and a carefully optimized reaction.

The morphological evolution during calcination was investigated by scanning electron microscopy (SEM). Micrographs of $InNbO_4$ powders calcined at various temperatures, dwell times and heating/cooling rates are illustrated in Figs. 7 and 8. The influence of calcination conditions on particle size is also given in Table 1. After calcinations at 950–1,200 °C, the powders have similar morphology (Fig. 7). In general, the particles are agglomerated and irregular in shape, with a substantial variation in particle size, particularly in samples calcined at high temperature (Fig. 7d). The results indicate that averaged particle size tends to increase with calcination temperatures and dwell times but seems to decrease with faster heating/cooling rates (Table 1). After calcinations above 950 °C (Fig. 7b–d), the powders seem to display a significant level of necking and bonding as if they were in the initial stages of sintering.

The effects of dwell time and heating/cooling rates on the morphology of the calcined powders were also found to be quite significant. As expected, it is seen that longer heat treatment leads to larger particle sizes and hard agglomeration (Figs. 7a, 8a, b). As shown in Figs. 7a, 8c, d, and also Table 1, by increasing the heating/cooling rates, averaged particle size tends to decrease whilst the degree of agglomeration tends to increase. This observation could be attributed to the mechanism of surface energy reduction of the ultrafine powders, i.e. the smaller the powder the higher the specific surface area [32]. This finding is also similar to that in $Mg_4Nb_2O_9$ powders synthesized by Ananta [33]. To the author's knowledge, the present data are the first results for the morphology–calcination relationship of $InNbO_4$ powders prepared by the solid-state reaction. It is also of interest to point out that mass production of single-phase $InNbO_4$ nanopowders with the smallest particle size ~100 nm (estimated from SEM micrographs) can be achieved by employing a simple solid-state reaction combined with a rapid vibro-milling technique. In addition, EDX analysis using a 20 nm probe on a large number of particles of the calcined powders confirms that the chemical composition is $InNbO_4$ powders, in good agreement with XRD results. For example, a chemical composition of $In_{0.95}Nb_{1.03}O_4$ can be approximated through a chemical analysis of EDX spectra in Fig. 9, which were obtained from one measurement point.

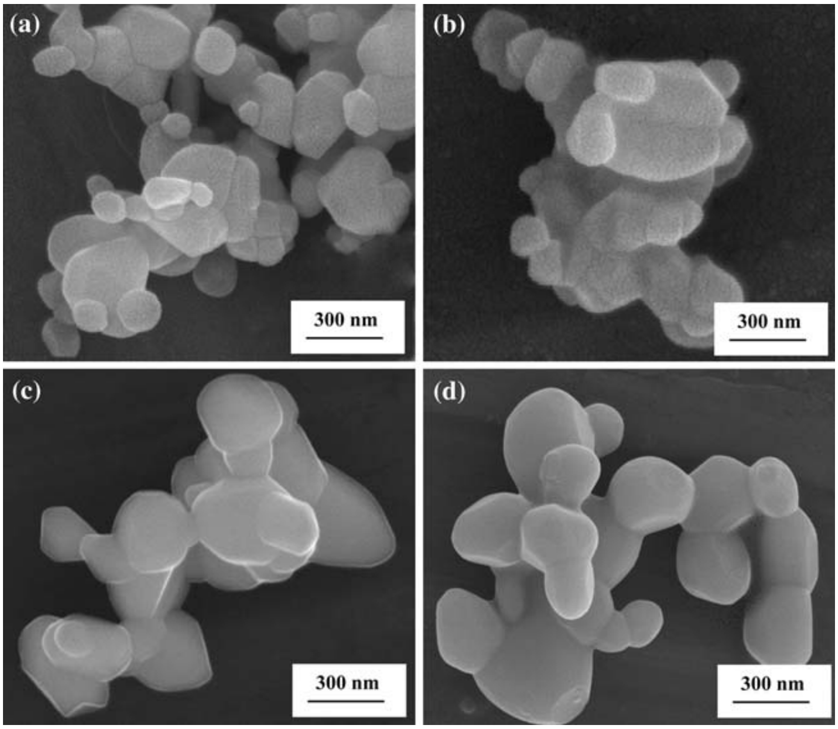

Fig. 7 SEM micrographs of the IN powders calcined for 2 h with heating/cooling rates of 10 °C/min at (**a**) 950, (**b**) 1,000, (**c**) 1,100 and (**d**) 1,200 °C

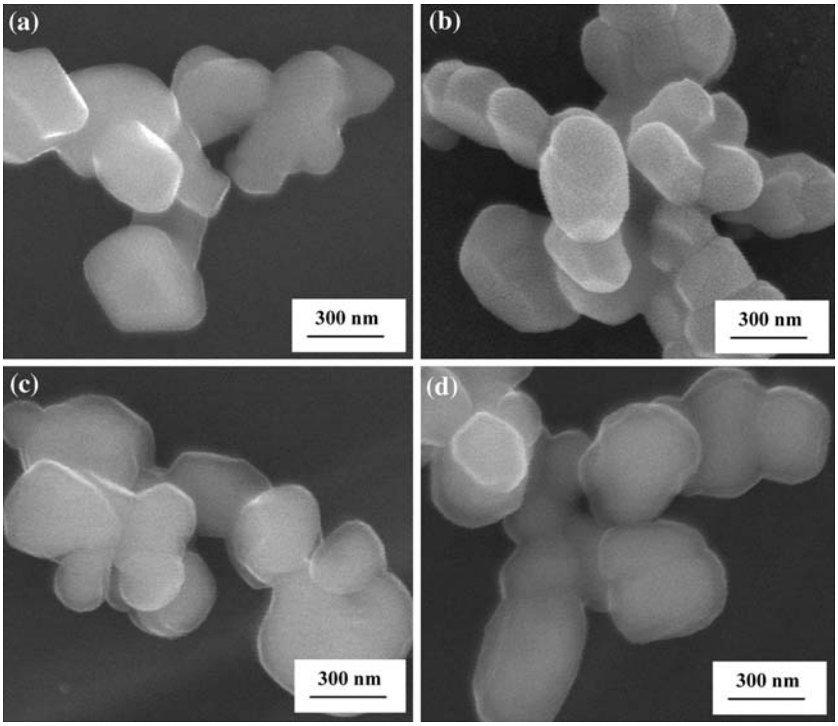

Fig. 8 SEM micrographs of the IN powders calcined at 950 °C with heating/cooling rates of 10 °C/min for (**a**) 3 h, (**b**) 4 h, and at 950 °C for 2 h with heating/cooling rates of (**c**) 3 and (**d**) 30 °C/min

Table 1 Particle size range of $InNbO_4$ powders calcined at various conditions

Calcination conditions			Estimated particle size range (±10 nm)
Temperature (°C)	Dwell time (h)	Rates (°C/min)	
900	4	10	250–600
900	4	30	200–450
950	2	3	150–550
950	2	10	150–350
950	2	30	100–350
950	3	10	300–450
950	4	10	300–700
1000	2	10	200–500
1100	2	10	250–600
1200	2	10	350–700

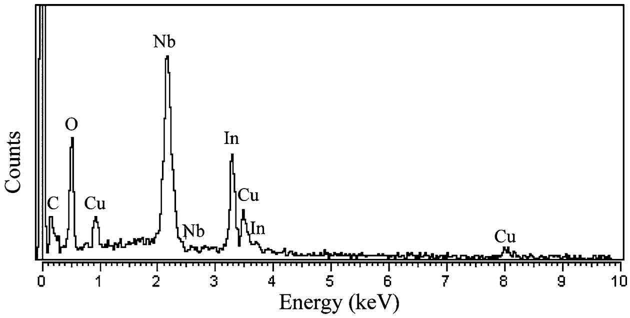

Fig. 9 EDX analysis of IN powders calcined at 950 °C for 2 h with heating/cooling rates of 30 °C/min (some spectra indexed as C and Cu come from coated electrode and sample stub, respectively)

The results obtained in this study clearly suggest that a systematic study of the effect of milling parameters such as milling times and milling speed on the phase and morphology evolutions of the $InNbO_4$ powders is required for better understanding and verifying the attractiveness of the vibro-milling technique. Further investigation of this relationship is underway and will be reported in the future.

Conclusions

The solid-state mixed oxide method via a rapid vibro-milling technique is explored in the preparation of single-phase $InNbO_4$ nanopowders. The calcination temperature, dwell time and heating/cooling rates have been found to show a pronounced effect on phase formation and particle size of the calcined $InNbO_4$ powders. This work demonstrated that single phase of indium niobate powders with particle size ranging from 100 nm to 450 nm can be produced via this technique by using a calcination temperature of 900 °C for 4 h or 950 °C for 2 h, with heating/cooling rates of 30 °C/min. The resulting $InNbO_4$ powders exhibit similar morphology and variety of agglomerated particle sizes, depending on calcination conditions.

Acknowledgements We thank the Thailand Research Fund (TRF) and the Commission on Higher Education (CHE), Graduate School and Faculty of Science, Chiang Mai University for all supports.

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