

Synthesis, formation and characterization of lead indium niobate–lead titanate powders

S. Wongsanmai · O. Khamman · S. Ananta ·
R. Yimnirun

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Abstract In this study, powders of lead indium niobate–lead titanate $(1-x)\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ (PINT) binary system near the morphotropic phase boundary (MPB) composition with $x=38$ mol% PbTiO_3 are synthesized with the conventional mixed oxide and the wolframite methods via a rapid vibro-milling technique for the first time. The preparation method and calcination temperature have been found to show pronounced effects on the phase formation behavior of the PINT powders. The stabilized perovskite phase form of PINT can be synthesized by the wolframite method, while precursor phases are still found in powders prepared by the conventional method. Finally, this study shows that the rapid vibro-milling mixing technique is effective in preparing the phase pure perovskite of PINT powders.

Keywords PIN–PT · Conventional mixed oxide · Wolframite method · Vibro-milling technique

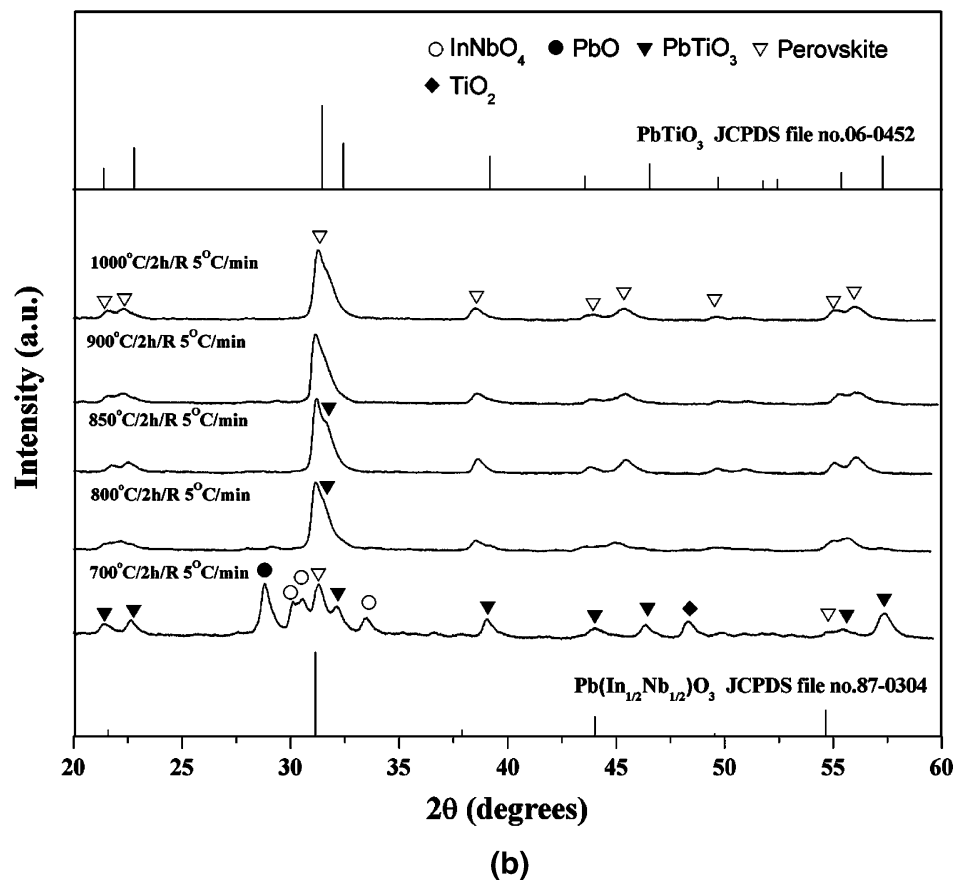
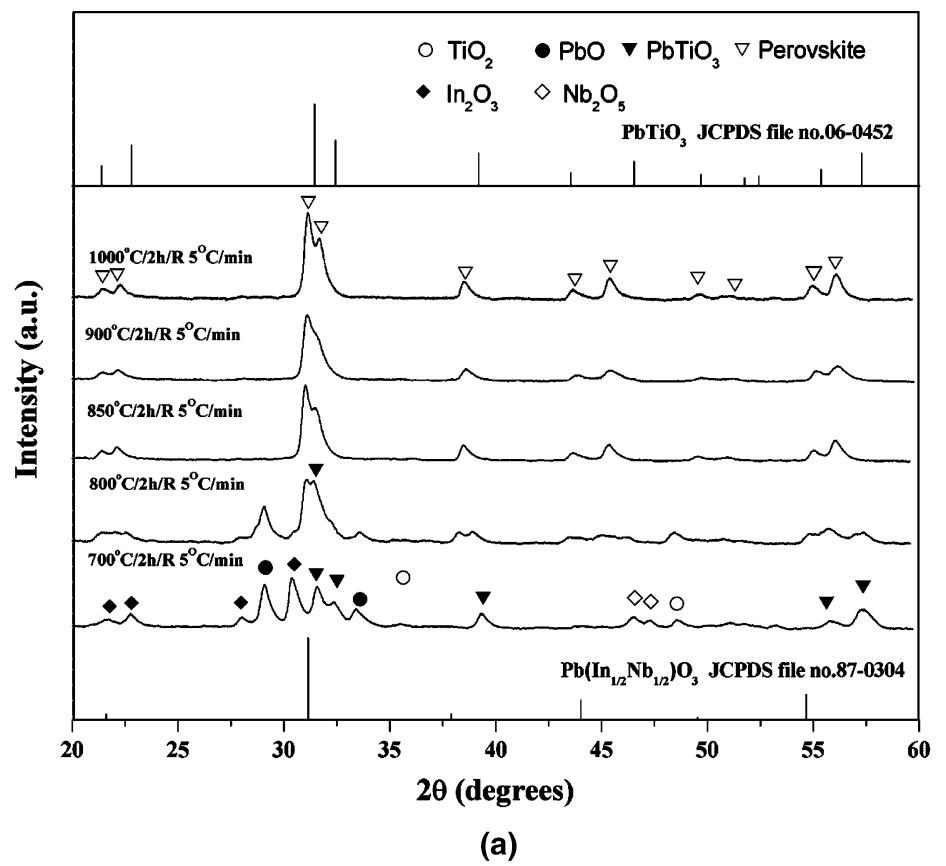
1 Introduction

Lead indium niobate $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PIN) compounds are interesting for studying the kinetics of compositional ordering [1]. It has been reported that the degrees of ordering on the B-site can be varied by thermal annealing and by forming solid solutions with perovskite compounds that exhibit normal dielectric behavior, such as $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN), PbZrO_3 (PZ) and PbTiO_3 (PT) [2]. With

different thermal treatments, the degrees of the In/Nb cation ordering on the B-site in a perovskite structure can be manipulated from a structurally disordered state into various degrees of ordering. The disorder PIN is a relaxor ferroelectric with a pseudo-cubic perovskite structure. It shows the relaxor behavior with a broad dielectric maximum near 66°C , when measured at 1 kHz [3, 4]. On the other hand, the ordered PIN has the antiferroelectric orthorhombic phase [5–9] with a sharp peak in the dielectric constant at 168°C [4, 10]. However, pure-phase perovskite PIN ceramics free of the pyrochlore phase are very difficult to prepare using a conventional mixed oxide method [7, 11]. This is because the tolerance and the electronegativity difference of PIN are very low compared with other perovskite compounds such as PMN [2, 12]. The wolframite method, as used by Groves [13] for the preparation of perovskite PIN ceramic, is not effective in suppressing pyrochlore phase formation. The addition of excess In_2O_3 was shown to yield higher amount of perovskite phase [13]. Recently, Alberta and Bhalla [7] were able to produce 100% phase-pure perovskite PIN ceramic with the addition of excess indium and/or lithium with wolframite method. Moreover, the solid solution with perovskite compounds such as PT, can stabilize the perovskite phase of PIN and chemical ordering may be suppressed. It has also been reported that a morphotropic phase boundary (MPB) of the solid solution system $(1-x)\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ (PINT) is located at a composition with $x=0.38$ [14, 15] and this binary system near MPB composition belongs to one of the relaxor-PT systems with T_c higher than 250°C [16, 17]. Previous studies have focused on the properties of solid solution PIN–PT single crystals, while the information on PIN–PT ceramics is still limited.

S. Wongsanmai (✉) · O. Khamman · S. Ananta · R. Yimnirun
Department of Physics, Faculty of Science,
Chiang Mai University,
Chiang Mai 50200, Thailand
e-mail: wongsanmai@yahoo.com

Fig. 1 XRD patterns as a function of the calcination temperature for (a) the conventional method and (b) the wolframite method



This study is intended to explore a synthetic route for the pure-phase perovskite bodies of PINT binary system near MPB composition. Both the conventional mixed-oxide and the wolframite methods have been employed. More importantly, a rapid vibro-milling mixing technique is utilized to obtain phase-pure perovskite powders. Finally, the phase formation and morphology of the powders calcined at various temperatures are studied.

2 Experimental

For the conventional method, the starting materials of lead oxide, PbO (Fluka, 99% purity), titanium oxide, TiO₂ (Riedel-de Haën, 99% purity), niobium oxide, Nb₂O₅ (Aldrich, 99.9% purity) and indium oxide, In₂O₃ (Aldrich, 99.99% purity) were mixed in the required stoichiometric ratio for the composition (1-x)Pb(In_{1/2}Nb_{1/2})O-(x)PbTiO₃ where x=0.38. The oxide powders were milled via a rapid vibro-milling technique for 30 min with corundum media in ethanol [18]. After drying at 120°C, the mixture was calcined at temperature between 700 to 1000°C with dwell time of 2 h and heating/cooling rate of 10°C/min in a double crucible [19]. On the other hand, in the wolframite method the wolframite precursor was first prepared from oxide powders of niobium oxide, (Nb₂O₅) and indium oxide, (In₂O₃). The intermediate precursor InNbO₄ was synthesized at an optimized calcination temperature of

1100°C for 2 h [20]. The wolframite precursor was then mixed with lead oxide (PbO) and titanium oxide (TiO₂) and re-milled. After drying, the mixture was calcined at temperature between 700 to 1000°C with dwell time of 2 h and heating/cooling rate of 10°C/min in a double crucible.

In order to study the reaction of the uncalcined PINT powders, a differential thermal analysis (DTA) and thermal-gravity analysis (TG) were performed on a DTA-TG apparatus (Perkin Elmer) using heating/cooling rate of 10°C/min in air from room temperature up to 1300°C. X-ray diffraction (XRD; Siemen-D500 diffractometer) was used to determine the phase formation behavior of the calcined powders. The microstructure was observed with a scanning electron microscope (SEM; Joel JSM-840A). The chemical compositions of the phase formed were elucidated by an energy-dispersive X-ray (EDX) analyzer with an ultra-thin window.

3 Results and discussion

Initially, the DTA-TG analysis was performed on uncalcined powders to obtain thermal behavior to define the range of calcination temperature for the XRD investigation. The results from DTA-TG studies indicate that the suitable range of the calcination temperature is between 700 and 1000°C.

Fig. 2 XRD patterns for PINT powders at optimum calcination temperature of both methods, with comparison to standard JCPDS files for PIN and PT compound

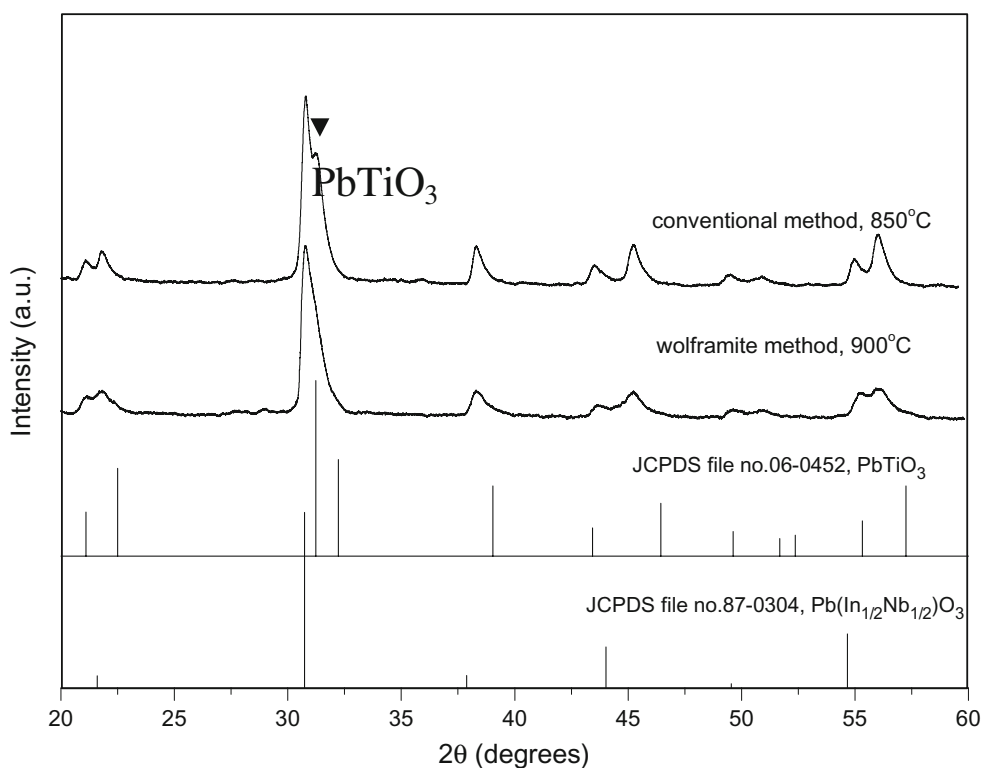
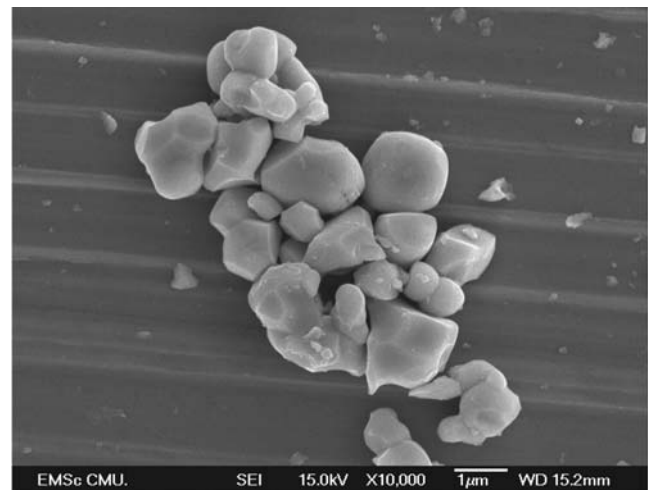


Table 1 Chemical compositions of calcined powders from SEM–EDX analysis.

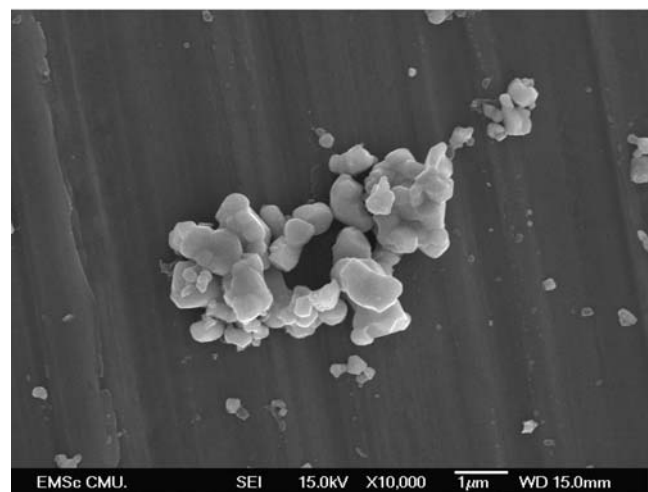
Method	Composition (at.%)				Possible phases
	Pb (M)	In (L)	Nb (L)	Ti (K)	
Conventional	43.9	11.3	14.4	30.4	$\text{PbIn}_{0.31}\text{Nb}_{0.31}\text{Ti}_{0.38}\text{O}_3$, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$, PbTiO_3 , TiO_2
Wolframite	46.6	11.9	21.0	20.5	$\text{PbIn}_{0.31}\text{Nb}_{0.31}\text{Ti}_{0.38}\text{O}_3$, Nb_2O_5

Figure 1 shows the XRD patterns of powders calcined for 2 h between 700 and 1000°C with heating/cooling rate of 10°C/min. The differences in XRD patterns for both methods are clearly apparent. The calcination temperature of 700°C does not yield the perovskite phase for both methods. At 850 and 800°C, respectively, the perovskite phase is found to form for the conventional and wolframite methods. The optimum calcination temperature for the formation of phase pure perovskite PINT is found to be about 900°C for the wolframite method, while the conventional method is found to be about 850°C with PT peak. The experiment indicates that the wolframite method helps to stabilize the perovskite phase in PINT system. More importantly, though the conventional method yields the perovskite phase at lower temperature than the wolframite method, the strong PT peak is still observed in the XRD patterns of powders calcined with the conventional method as high as 1000°C (as seen in Fig. 1a). Clearly, the significant difference between the XRD patterns is the presence of the strong PT peak at 31.5° for the powders calcined with the conventional method. As seen in Fig. 2, the diffraction peak does not match any peaks of PIN and PT compounds. Instead, the peaks closely match to those of a hypothetical solid solution formed between the two compounds. Furthermore, for the wolframite method the peaks are not a simple superposition corresponding to the two compounds, while the corresponding diffraction angle at 31.5° can be matched to maximum peak of PT for the conventional method [21]. This observation points to the formation of PT phase in the powders from the conventional method, which could be a result of better reaction of PbO and TiO₂ to form PT phase rather than PINT phase. As listed in Table 1, the quantitative analysis by EDX shows that, in addition to the PINT phase, the PIN, PT and TiO₂ phases are also present in the powders calcined by the conventional method, while only additional Nb₂O₅ phase (undetected by XRD) is possible in the powders obtained from the wolframite method. A combination of the XRD and EDX methods has indicated that the wolframite method yields XRD-phase pure PINT powders, while the conventional one results in a mixture of PINT, PIN PT, and TiO₂ (undetected by XRD) phases. This clearly emphasizes the importance of the synthetic route used to prepare the PINT

powders. Moreover, effects of soaking time and heating/cooling rates have also been studied in this work. For this study, it is found that the soaking time and heating/cooling rate do not significantly affect the phase formation behavior of PINT powders.



(a)



(b)

Fig. 3 SEM micrographs of PINT powders calcined at optimum temperature for (a) the conventional method and (b) the wolframite method

The morphological evolution of the calcined powders was investigated by SEM. Figure 3 shows the SEM micrographs of the powders synthesized by conventional and wolframite methods. In general, the particles are agglomerated and irregular in shape. As seen in Fig. 3(a), the particles synthesized by the conventional method show relatively large agglomerates ranging in diameter from about 0.5 to 2 μm . On the other hand, the particles synthesized by wolframite method, with diameter in the range ~ 0.1 to 1 μm (Fig. 3(b)), are lower in particle agglomeration than the conventional method.

4 Conclusions

The powders of a solid solution of PINT binary system with $x=0.38$ was successfully prepared by both the conventional mixed oxide and the wolframite methods. The results from DTA-TG technique were used to define the range of calcination temperature with 700 to 1000°C. The optimum calcination temperature for the formation of phase pure perovskite was determined to be 900 and 850°C for the wolframite, and the conventional methods, respectively, with soaking time of 2 h and heating/cooling rate of 10°C/min. Moreover, the perovskite phase was found to form at lower temperature with the conventional method than the wolframite method. However, the EDX studies showed that the stabilized perovskite phase form of PINT can be synthesized by the wolframite method, while precursor phases were still found in powders prepared by the conventional method. Moreover, the large agglomeration and particles size were observed in powder synthesized by the conventional method.

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References

1. A.A. Bokov, I.P. Rayevskii, V.G. Smotrakov, O.I. Prokopalo, *Phys. Status Solidi A Appl. Res.* **93**, 411–417 (1986)
2. T.R. Shrout, A. Halliyal, *Am. Ceram. Soc. Bull.* **66**(4), 704–711 (1987)
3. E.F. Alberta, A.S. Bhalla, *Mater. Lett.* **40**, 114–117 (1999)
4. E.F. Alberta, A.S. Bhalla, *J. Phys. Chem. Solids* **63**, 1759–1769 (2002)
5. C.A. Randall, D.J. Barber, P. Groves, R.W. Whatmore, *J. Mater. Sci.* **23**, 3678–3682 (1988)
6. N. Yasuda, T. Mizuno, *Appl. Phys. Lett.* **66**(5), 571–573 (1995)
7. E.F. Alberta, A.S. Bhalla, *Mater. Lett.* **29**, 127–129 (1996)
8. E.F. Alberta, A.S. Bhalla, *Ferroelectrics* **188**, 96–107 (1996)
9. N. Yasuda, H. Ohwa, T. Mizunao, M. Iwata, Y. Ishibashi, *Appl. Phys. Lett.* **68**(24), 3404–3406 (1996)
10. M. Iwata, S. Katagiri, H. Orihara, M. Maeda, I. Zusuki, H. Ohwa, N. Yasuda, Y. Ishibashi, *Ferroelectrics* **301**, 179–183 (2004)
11. Y. Yoshikawa, *J. Eur. Ceram. Soc.* **21**, 2041–2045 (2001)
12. Y. Guo, H. Luo, T. He, Z. Yin, *Solid State Commun.* **123**, 417–420 (2002)
13. P. Groves, *Ferroelectrics* **65**, 67–77 (1985)
14. E.F. Alberta, A.S. Bhalla, *J. Korean Phys. Soc.* **32**, S1265–S1267 (1998)
15. N. Yasuda, H. Ohwa, D. Hasegawa, H. Hosono, Y. Yamashita, M. Iwata, Y. Ishibashi, *Ferroelectrics* **270**, 247–252 (2002)
16. N. Yasuda, H. Ohwa, M. Kume, Y. Yamashita, *J. Appl. Phys.* **39** (2A), L66–L68 (2000)
17. N. Yasuda, H. Ohwa, M. Kume, K. Hayashi, Y. Hosono, Y. Yamashita, *J. Cryst. Growth* **229**, 299–304 (2001)
18. R. Tipakontitikul, S. Ananta, *Mater. Lett.* **58**(3), 449–454 (2004)
19. N. Vittayakorn, G. Rujijanagul, T. Tunkasiri, X. Tan, D.P. Cann, *Mater. Sci. Eng. B Solid-state Mater. Adv. Technol.* **108**, 258–265 (2004)
20. N. Yasuda, M. Fujie, *Jpn. J. Appl. Phys.* **31**, 3128–3131 (1992)
21. N. Yasuda, H. Ohwa, M. Kume, K. Hayashi, H. Hosono, Y. Yamashita, *J. Cryst. Growth* **229**, 299–304 (2001)