

Synthesis, formation and characterization of lead zinc niobate–lead zirconate titanate powders via a rapid vibro-milling method

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Abstract In this study, an approach to synthesizing pyrochlore-free lead zinc niobate – lead zirconate titanate powders with a formula $x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-(1-x)\text{Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (when $x=0.1-0.5$) by a mixed oxide synthetic route via a rapid vibro-milling has been developed. The formation of perovskite phase in calcined PZN-PZT powders has been investigated as a function of calcination temperature by TG-DTA and XRD techniques. Powder morphology and chemical composition have been determined with SEM and EDX techniques. The potential of a vibro-milling technique as a significant time-saving method to obtain single-phase PZN-PZT powders at low calcination temperature is also discussed. The results indicate that at calcination condition of 900 °C for 2 h, with heating/cooling rates of 20 °C/min single-phase PZN-PZT powders can be obtained for every composition ratio between $x=0.1-0.5$.

Keywords Phase formation · Calcination · Vibro-milling · Lead zinc niobate · Lead zirconate titanate

1 Introduction

Lead zirconate titanate, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ or PZT, is a well known piezoelectric that has been widely employed in a large number of sensing and actuating devices. PZT ceramics have very high Curie temperature (~390 °C).

They have excellent dielectric, piezoelectric and elastic properties suitable for wide range of practical applications [1–3]. Lead zinc niobate, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ or PZN, which exhibits a perovskite structure and a Curie temperature ~140 °C, is one of the most important relaxor ferroelectric materials with high dielectric constant and large electrostrictive coefficient [4, 5]. These characteristics make PZN a promising candidate for high performance electromechanical actuator and transducer applications. However, it has been recognized and widely accepted that inhomogeneous mixing in the conventional solid state reaction process leads to formation of pyrochlore phase and subsequent deterioration of electrical properties in PZN ceramics [6, 7]. The addition of other perovskite materials, such as barium titanate (BaTiO_3) [8], lead titanate (PbTiO_3) [9], or PZT [10], has been found to be effective in stabilizing PZN in the perovskite structure. However, recent work by Fan and Kim [11] has shown promise in producing only pure perovskite phase for PZN-PZT ceramics with the conventional mixed-oxide method.

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

2 Experimental procedure

In this study, reagent grade oxides of lead oxide, PbO (Fluka Chemical, 99.9% purity), zirconium dioxide, ZrO_2 (RdH laborchemikalin, 99.9% purity), zinc oxide, ZnO

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(Fluka Chemical, 99.9% purity), niobium pentoxide, Nb_2O_5 (Aldrich, 99.9% purity), and titanium dioxide, TiO_2 (RdH laborchemikalin, 99.9% purity), were used as the starting materials. PZN-PZT 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 $x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-(1-x)\text{Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3$ where $x=0.1, 0.2, 0.3, 0.4,$ and 0.5 . 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 isopropanol. High purity corundum cylindrical media were used as the milling media. After vibro-milling for 30 min and drying at 120°C , the reaction of the uncalcined powders taking place during heat treatment was investigated by thermogravimetric and differential thermal analysis (TG-DTA, Shimadzu) in air from room temperature up to 1350°C . Based on the TG-DTA results, the mixture was calcined at temperatures between 750 to 950°C for 2 h in alumina crucible to examine the phase formation behavior of PZN-PZT powders. A heating/cooling rate of $20^\circ\text{C}/\text{min}$ was selected for all of the compositions in this system because it was shown to be effective in reducing the total amount of pyrochlore phase [12].

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 for the PZN-PZT powders. The relative amounts of perovskite and pyrochlore phases were approximated by calculating the ratio of the major XRD peak intensities of the perovskite and pyrochlore phases via the following equation:

$$\text{Perovskite \%} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{pyro}}} \right) \times 100$$

where I_{perov} and I_{pyro} , refer to the intensity of the (110) perovskite peak and (222) pyrochlore peak, respectively.

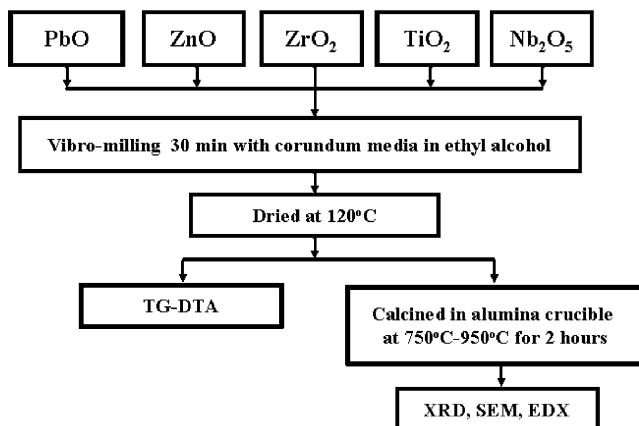


Fig. 1 Diagram of experimental procedure

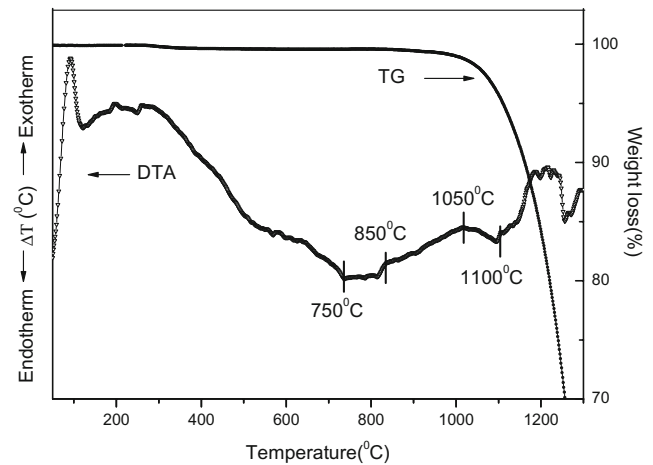


Fig. 2 TG-DTA curves for the mixture of PZN-PZT powder after vibro-milling

Powder morphologies and particle sizes were directly imaged using scanning electron microscopy (SEM; JEOL JSM-840A). EDX spectra were quantified with the virtual standards peaks supplied with the Oxford Instruments eXL software. Diagram of experimental procedure is shown in Fig. 1.

3 Results and discussion

3.1 Thermogravimetric and differential thermal analysis (TG/DTA)

TG-DTA curves obtained for powders mixed in the stoichiometric proportions of PZN and PZT powders are displayed in Fig. 2. In the temperature range 50 – 300°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 temperatures, 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 differently bounded species in the network [13]. In the temperature range 750 – 1050°C , both exothermic and endothermic peaks are observed in the DTA curve. The enlarge zone of this DTA curve shows that the endothermic peak centered at $\sim 800^\circ\text{C}$ may result from perovskite phase crystallization, and the last exothermic peak centered at $\sim 850^\circ\text{C}$ may be caused by the decomposition of lead oxide [14, 15]. Above 1000°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 ranges of calcination temperatures (750 to 950°C) used in subsequent powder processing steps.

3.2 X-ray diffraction analysis (XRD)

Powder XRD patterns of the calcined $0.5\text{PZN}-0.5\text{PZT}$ powders at different calcination temperatures are shown in Fig. 3. The XRD results show that the pyrochlore phase $\text{Pb}_{1.88}(\text{Zn}_{0.3}\text{Nb}_{1.25})\text{O}_{5.305}$ (JCPDS No.25-0446) is dominant at the calcination temperature below 850°C for the powders. The precursor phases of PbO , ZnO , Nb_2O_5 , ZrO_2 , TiO_2 are also detected in the powders by XRD when calcined below 800°C . Other compositions also show a similar trend. The pyrochlore-free $x\text{PZN}-(1-x)\text{PZT}$ powders with $x=0.1-0.4$ can be obtained at calcination temperatures above 850°C . Earlier study by Vittayakorn et al. [16] showed similar observation. However, in that study which used a conventional ball-milling method with excess PbO 2wt.% the calcination temperature was above 900°C . This clearly indicates that a rapid vibro-milling method can lower the calcination temperature for PZN-PZT powders.

As listed in Table 1, all the compositions in the present work exhibit pyrochlore-free XRD scans at calcination temperature of 900°C . It can be noticed that in most compositions the perovskite phase is formed in a sudden nature, which is significantly different from previous research [16] in which more perovskite phase was found with increasing calcination temperature. The difference could be attributed to the nano-sized mixed powders (50–300 nm) obtained from a rapid vibro-milling technique. The perovskite phase formation behavior for $x\text{PZN}-(1-x)\text{PZT}$ powders at the calcination temperature of 900°C is shown in Fig. 4. The percentage of perovskite phase in PZN-PZT powders is summarized in Table 1 as a function of calcination temperature. These experimental results indicate that when the concentration of the PZN phase increases the calcination temperature must be increased to obtain single

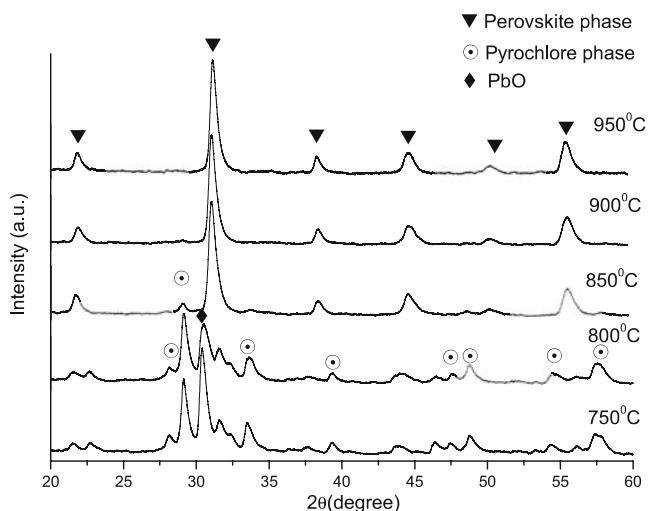


Fig. 3 XRD patterns of $0.5\text{PZN}-0.5\text{PZT}$ powder calcined at various temperatures for 2 h. with heating/cooling rates of $20^\circ\text{C}/\text{min}$

Table 1 Percentage of perovskite phase of $(1-x)\text{PZT}-x\text{PZN}$; $x=0.1-0.5$.

Calcination temperature ($^\circ\text{C}$)	Percentage of perovskite phase				
	$x=0.1$	$x=0.2$	$x=0.3$	$x=0.4$	$x=0.5$
750	–	–	–	–	–
800	100	78.2	–	–	–
850	100	100	100	100	87.7
900	100	100	100	100	100
950	100	100	100	100	100

perovskite phase of PZN-PZT powders. Even though pyrochlore-free PZN-PZT powders can be obtained at calcination temperature of 900°C for all compositions ($x=0.1-0.5$), it should be noted that the on-set calcination temperature for pyrochlore-free powders starts at 800°C for composition with $x=0.1$. It is also very interesting to see that the on-set temperature in every composition is approximately 50°C lower than those reported earlier with the conventional ball-milling method [16]. More importantly, this study suggests that the conventional mixed oxide method helps to stabilize the perovskite phase and the calcination temperature can be lowered by a vibro-milling technique.

3.3 SEM and EDX analysis

The morphological changes in the PZN-PZT powders formed by a mixed oxide method are illustrated in Fig. 5. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size, particularly in samples with more PZN contents. Generally, particle size of all compositions can be estimated from SEM micrographs to be in range of $0.2-2\ \mu\text{m}$. It should be noted that the morphology of the calcined

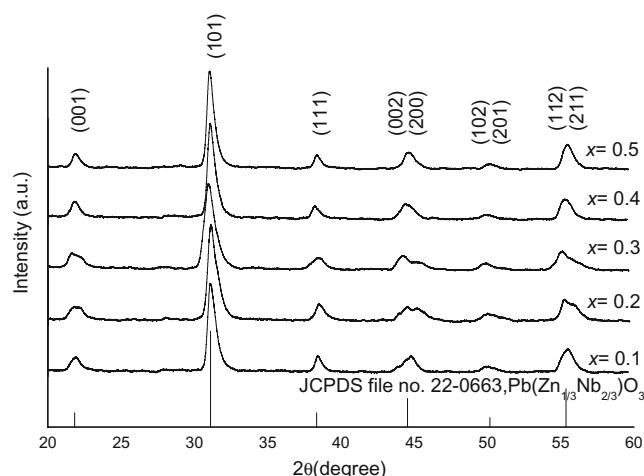
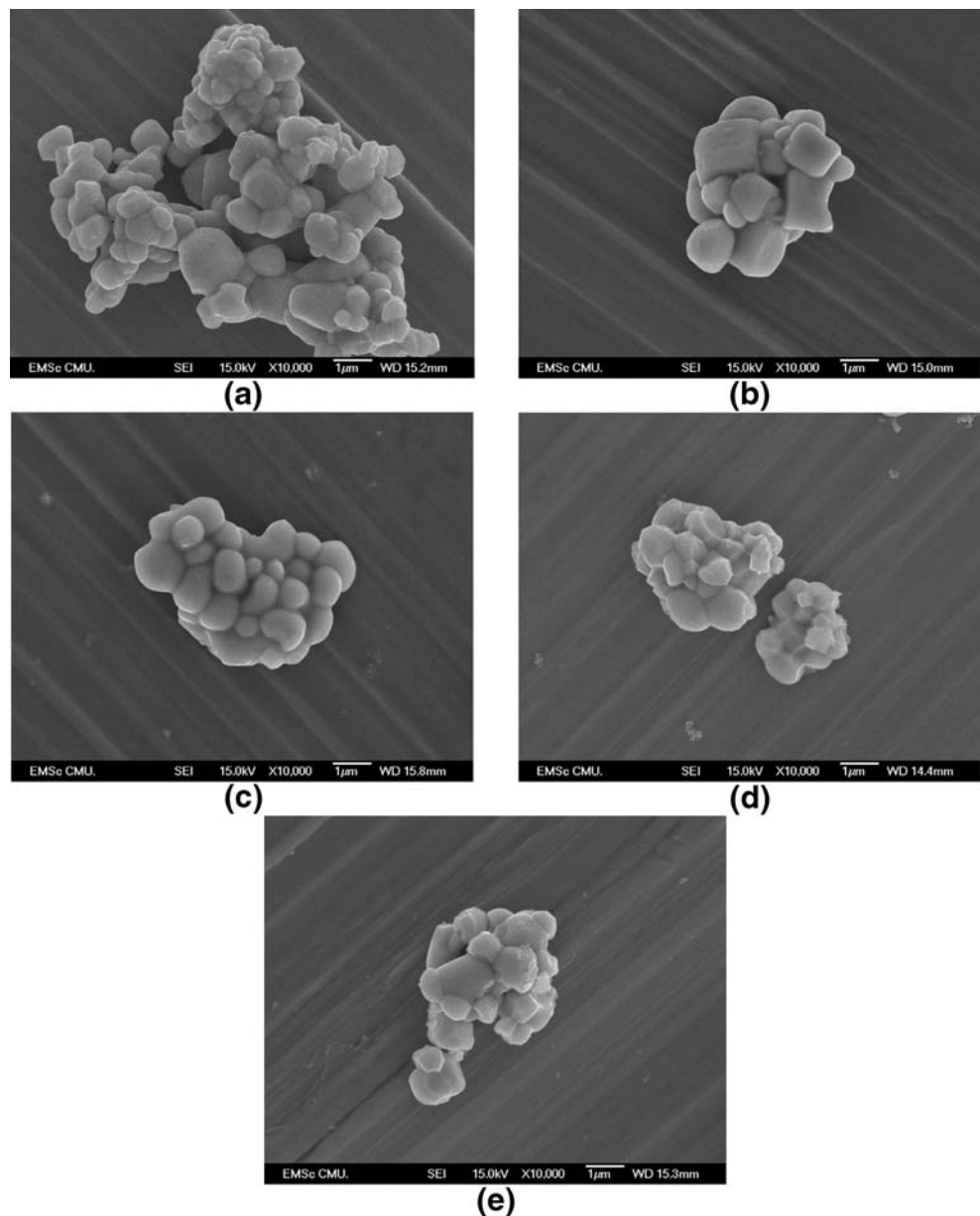


Fig. 4 XRD patterns of the $x\text{PZN}-(1-x)\text{PZT}$ powders (when $x=0.1, 0.2, 0.3, 0.4,$ and 0.5) calcined at 900°C with heating/cooling rates of $20^\circ\text{C}/\text{min}$ and soaking time of 2 h

Fig. 5 SEM micrographs of the x PZN–(1– x)PZT powders calcined at 900 °C with heating/cooling rates of 20 °C/min and soaking time of 2 h for (a) $x=0.1$, (b) $x=0.2$, (c) $x=0.3$, (d) $x=0.4$ and (e) $x=0.5$



0.1PZN–0.9PZT and 0.3PZN–0.7PZT powders is almost similar in size and shape, while for the other compositions the size and shape of the powders are significantly different.

Finally, EDX analysis using a 20 nm probe on a large number of particles of the calcined powders confirms that the parent composition is PZN–PZT powders, in good agreement with XRD results.

4 Conclusions

The solid-state mixed oxide method via a vibro-milling technique is explored in the preparation of pyrochlore-free solid solution of x PZN–(1– x)PZT powders (when $x=0.1–0.5$).

The optimum calcination condition for the formation of perovskite phase PZN–PZT powders is found to be 900 °C for 2 h with heating/cooling rates of 20 °C/min. Clearly, XRD study indicates that phase pure perovskite PZN–PZT powders have been obtained in this study. The potential of a vibro-milling technique as a significant time-saving method to obtain single-phase PZN–PZT powders at lower calcination temperature has also been demonstrated.

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