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Mechanical activation-induced B site order–disorder transition in perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Mg_{1/2}W_{1/2})O_3$

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Abstract

Mechanical activation-induced B site order–disorder transition was observed in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Mg_{1/2}W_{1/2})O_3$ of complex perovskite structure. The disorder triggered by mechanical activation can be steadily recovered by thermal annealing at elevated temperature, as shown by XRD diffraction results. The degree of ordering calculated from Raman spectra demonstrates similar behaviors as those of XRD, except in the low ordering states, i.e. when the ordering domain size in 0.4PMN–0.6PMW is out of the coherence range of XRD. The above order–disorder transition was explained by the competition between the activation-triggered refinement of ordering domains leading to disordering and the thermal activation, which builds up the ordering domains. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mechanical activation; Order–disorder transition; Relaxor ferroeletrics

1. Introduction

Mechanical alloying has long been employed for synthesis of alloying materials over the past decades [1,2]. Many interesting phenomena, i.e. a refinement of crystalline size, amorphization of crystals, phase transitions and chemical reactions, which may or may not be triggered by thermal activation were observed in association with mechanical activation [2–5]. Mechanical activation has recently been successfully applied in synthesis of lead-based relaxor ferroelectrics such as $Pb(Zn_{1/3}Nb_{2/3})O_3$ [6] and $Pb(Mg_{1/3}Nb_{2/3})O_3$ [7]. Several unique phenomena were observed during the mechanical activation of mixed oxides. There are some perovskites that can be formed by a single step of mechanical activation, while they could not be synthesized by solid-state reaction of mixed oxides [6]. Also, certain perovskites that can steadily formed by solid-state reaction cannot be formed by the mechanical activation [8]. Transitional phases, such as the pyrochlore phases, which are always involved in the conventional solid-state reaction, can be bypassed in mechanical activation [6–8].

The B site ordering in complex perovskites has attracted extensive investigations because of its strong effect on the dielectric properties of relaxor ferroelectrics [9–11]. Previously, order–disorder transition is usually obtained by thermal treatment [11]. It is reported that quenching from a high temperature can eliminate the B site ordering in $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST), and a long time annealing at a relatively low temperature can recover the B site ordering [11]. In our experiments, we observed order–disorder transitions in certain lead-based perovskite compounds such as $Pb(Sc_{1/2}Ta_{1/2})O_3$ and $Pb(Mg_{1/3}N_{2/3})O_3$–$Pb(Mg_{1/2}W_{1/2})O_3$ (PMN–PMW) can be triggered by mechanical activation. Inspired by this observation, we study the order–disorder transformation in PMN–PMW triggered by mechanical activation.

2. Experiments

Commercially available PbO (99% in purity, J.T. Baker), MgO (99.6% in purity, J.T. Baker), Nb_2O_5 (99% in purity, Aldrich, USA) and WO_3 (99.9% in purity, Aldrich, USA) were used as the starting materials. To prepare pyrochlore-free relaxor ferroelectrics, mechanical activation of Columbite precursor was employed as described in the previous studies [6]. $MgWO_4$ and $MgNb_2O_4$ Columbite phases were first synthesized by calcination of mixed oxides of MgO and WO_3 or MgO and Nb_2O_5 at 1000 °C for 6 h. Then the resulting Columbites and PbO were then mixed together using conventional ball mill in the weight ratios according to the designed stoichiometric composition of $(1-x)$PMN $-$ xPMW. The resulting powder mixtures were subjected to

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mechanical activation for 10 h and then calcined at 900 °C for 2 h, resulting in formation of $(1-x)$PMN $-\ x$PMW of perovskite structure, as confirmed by XRD diffraction. They were mechanically activated for various time periods ranging from 0 to 20 h, to investigate the order–disorder phase transition triggered by mechanical activation.

Phase characterization of mechanically activated compositions was carried out using X-ray diffractometer for phase identification (Cu Kα, X' per Diffractometer, Phillips). The degree of long-range ordering was measured by comparing the intensity of principle perovskite (2 0 0) peak with that of the supperlattice (1 1 1) peak. Crystallite size was determined using the Scherrer equation on the basis of broadening of (2 2 0) peak at 2θ of 31.7° [12], while the ordered domain size was calculated on the basis of (1 1 1) superlattice peaks at 2θ of 19.4°. Micro-Raman spectra were acquired at room temperature from single-grating Raman spectrometer. The relative degree of long-range ordering was also calculated on the basis of the intensity ratio of the band at around 384 cm^{-1} to that at 278 cm^{-1}.

3. Results and discussion

Fig. 1(a) shows XRD θ–2θ diffraction patterns of 0.4PMN–0.6PMW as a function of mechanical activation time. Strong B site ordering was observed in the initial unactivated state, as shown by the (1 1 1) diffractions at around 2θ of 19.4°. The superlattice peaks decrease steadily in intensity with increasing mechanical activation duration. A significant peak broadening occurs at the initial hour of mechanical activation, followed by the decrease in peak intensity with further increase in mechanical activation time. The superlattice diffraction peaks of (1 1 1) had completely disappeared from XRD trace upon 5 h of mechanical activation. As shown in Fig. 1(b), a steady recovery of ordering in 0.4PMN–0.6PMW is observed when the mechanically activated compositions were thermally annealed at an increasing temperature. The recovery of ordering started at around 700 °C and it was largely completed at 900 °C.

Fig. 2 shows the dependence on mechanical activation time in crystallite size and ordered domain size for 0.4PMN–0.6PMW, calculated using the Scherrer equation [12]. Both the domain size and crystallite size decrease dramatically during first hour of mechanical activation, followed by a fall in the decreasing rate when mechanical activation is extend to more than 2.0 h. This shows that the refinement in crystallite and ordered domain sizes took place simultaneously at the initial stage of mechanical activation, and the order–disorder transition occurs when the crystalline size was fine enough.

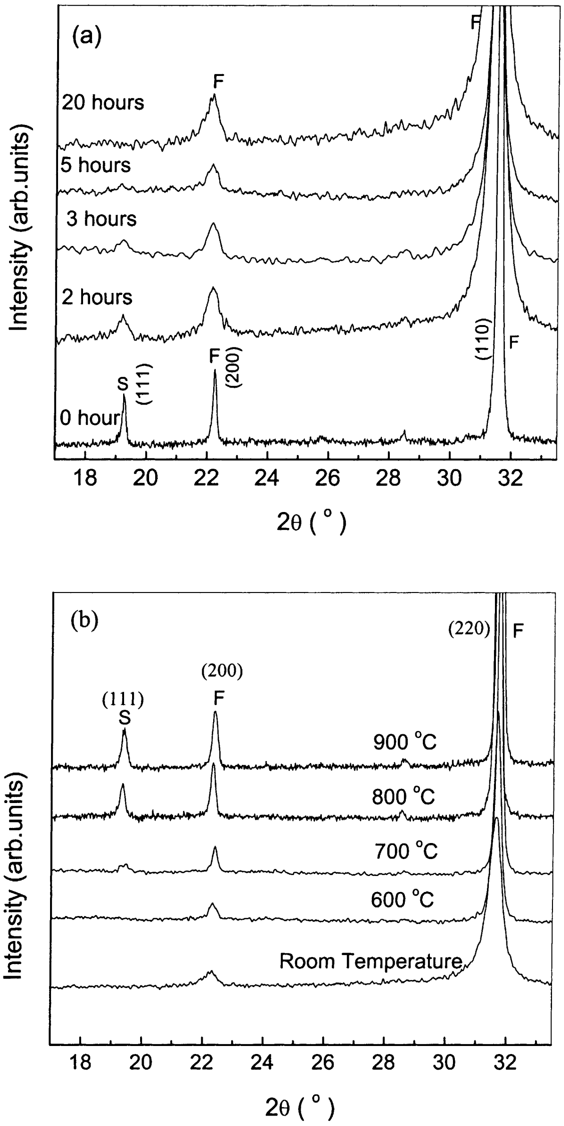

Fig. 1. XRD traces of 0.4PMN–0.6PMW (a) subjected to various periods of mechanical activation and (b) consequently calcined at various temperatures. S: the supperlattice diffraction peak indicating the B site ordering; F: the principle diffraction peak of perovskite structures.

To further investigate the ordering behaviors of PMN–PMW, Raman spectroscopic studies were employed. The Raman spectra of PMN–PMW were similar to those of PMN, PMW and PST [13–15]. Although the origins of Raman modes in these perovskites are still subjected to argument and confirmation, it is generally accepted that the Raman bands can be ascribed to the Fm3m group mode, where the high-frequency bands at 786 and 841 cm^{-1} can be assigned to A_{1g}. The band at around 278 and 496 cm^{-1} can be attributed to either E mode or second-order mode; while the band at 384 cm^{-1} can be ascribed to F_{2u}, which is due to the ordering of the B site cations and can be used as an indication for B site ordering [13–15]. The band at around 841 cm^{-1} also demonstrates a strong dependence on degree of ordering, which can also be used as an indication of B site ordering. The Raman spectra of 0.4PMN–0.6PMW subjected to various mechanical activation durations, are illustrated in Fig. 3, where the change in band intensity

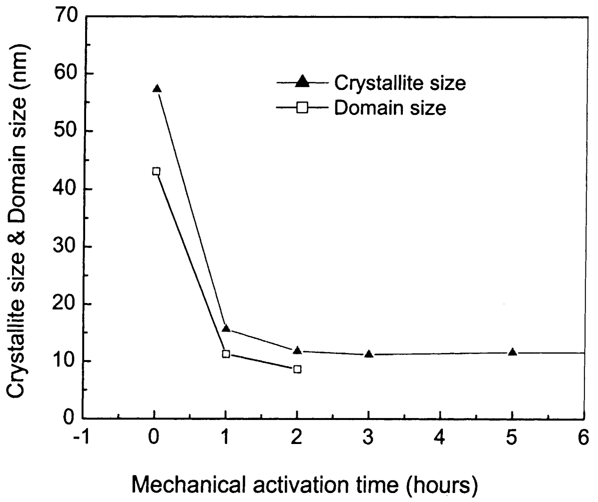

Fig. 2. The crystallite size and domain size for 0.4PMN–0.6PMW as a function of mechanical activation time.

centered at 384 cm^{-1} clearly demonstrates that the degree of ordering decreases with increasing mechanical activation time. This is in agreement with what has been indicated by the XRD. The band at 384 cm^{-1} cannot be eliminated by extension in mechanical activation time, although its intensity decreases dramatically at the initial 5 h of mechanical activation. Further extension in mechanical activation time up to 20 h led to little change in the bandwidth and intensity. The same band was also reported in disordered PST quenched from an elevated temperature, where the B site ordering domains of <3 nm were observed by dark field TEM image [16]. They were too small to be shown in XRD diffraction due to the broadening of superlattice peaks. The survival of broaden Raman peak at 384 cm^{-1} suggests the occurrence of tiny ordered microdomains in the mechanical activated 0.4PMN–0.6PMW, which are below the XRD coherence length.

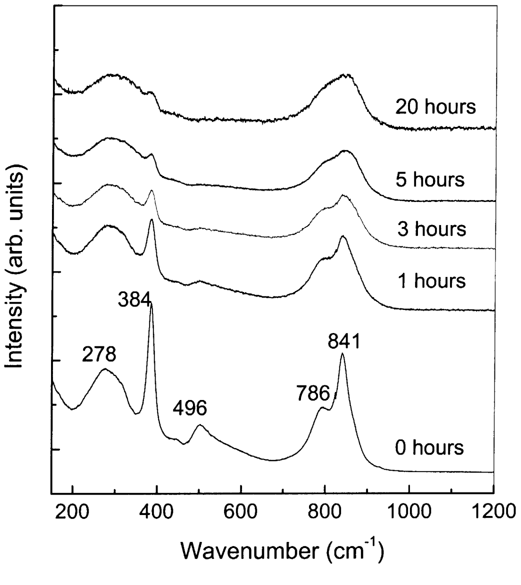

Fig. 3. Raman spectra of 0.4PMN–0.6PMW subjected to various periods of mechanical activation, showing the decrease of intensity in 384 and 841 cm^{-1} bands.

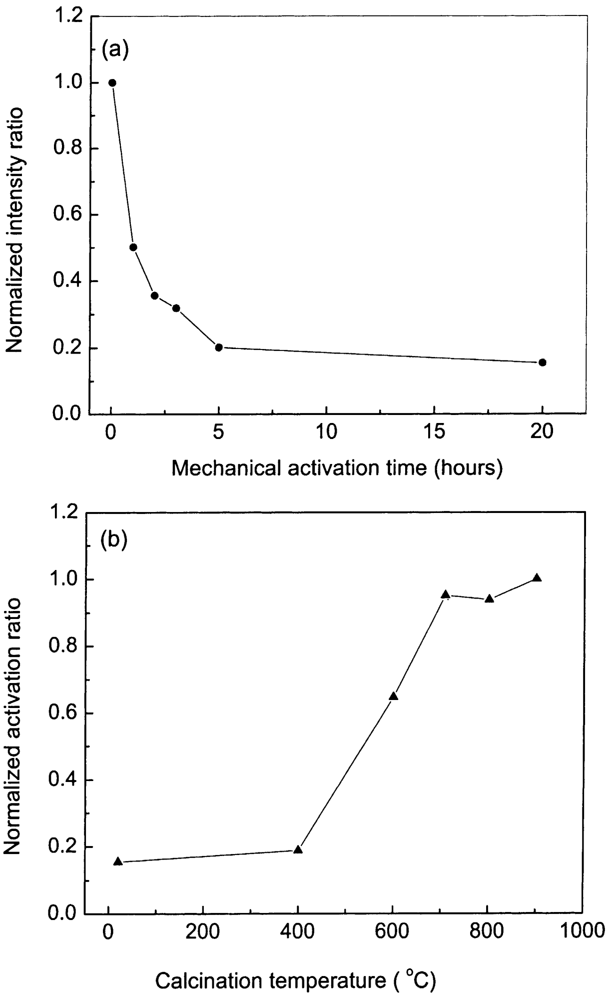

Fig. 4. The normalized intensity ratios of (I_{384}/I_{278}) for 0.4PMN–0.6PMW as a function of (a) mechanical activation time and (b) calcination temperatures. All the intensity ratios are normalized by dividing the intensity ratio of the unactivated 0.4PMN–0.6PMW.

The degree of ordering can be calculated with the intensity ratio of 384 to 278 (I_{384}/I_{278}). The intensity ratio of I_{384}/I_{278} for 0.4PMN–0.6PMW as a function of mechanical activation time and as a function of calcination temperature was shown in Fig. 4(a) and (b), respectively. Raman intensity ratio decreases with increasing mechanical activation time from 1 to 5 h, due to the fall in the degree of B site ordering at the initial stage of mechanical activation. Further extension in mechanical activation time leads to little change in the intensity ratio. Fig. 4(b) demonstrates the temperature dependence of the intensity ratios of the Raman spectra, which exhibits a steady increase in degree of ordering from 500 to 700 °C. In comparison, the Raman intensity ratio shows a larger extent of ordering than that from XRD

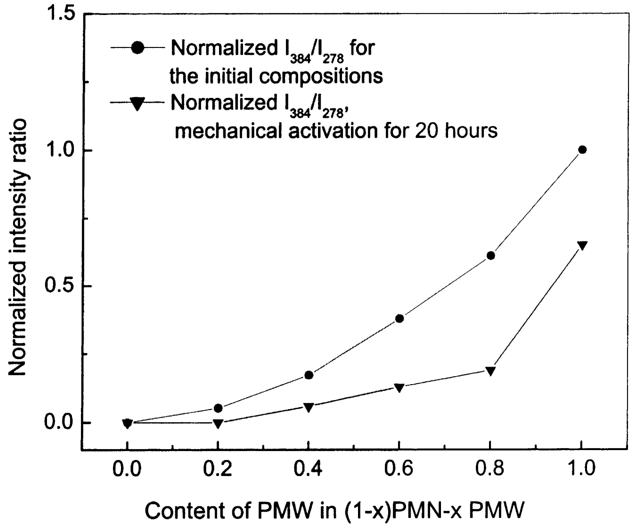

Fig. 5. Normalized Raman as a function of PMW content in $(1-x)$PMN $- x$PMW solid solutions for the activated and unactivated compositions, respectively. To normalize the intensity ratios, the intensity values were divided by the intensity ratio of unactivated PMW.

diffraction at low temperatures, owing to the sensitivity of Raman in small domains.

The composition dependence of ordering for the unactivated and activated compositions calculated from Raman intensity ratio (I_{384}/I_{278}) is shown in Fig. 5. In order to give a comparison, the intensity ratios were normalized by dividing the intensity ratios with that of the unactivated PMW. For the unactivated compositions, the intensity ratio increases with increasing PMW content, similar to that shown by XRD results. For the mechanically activated compositions, the degree of ordering is dramatically reduced by the mechanical activation, but remains in the compositions more than 0.4 mol PMW, and increases with increasing PMW content at the same time. We also observed the degree of ordering from the Raman spectra for mechanically activated compositions exhibit a larger value than that from the XRD results. This discrepancy can be ascribed to the limitation of XRD in extremely small ordering domains, as discussed above.

The order–disorder transition in PMN–PMW is a complicated process and it can be affected by several structure and composition parameters. A similar order–disorder transition triggered by mechanical activation was also reported in FeAl alloy [17], where the shearing-induced glide causes the dwindling of ordered domains and thermal diffusion recovers the ordering. Although shear-induced glides may not occur in oxide-based ceramic materials at room temperature, they have, however, been observed in a number of ceramic materials, including perovskite structures at elevated temperatures [18]. In particular, they occur when the crystallite size is in nanometer scales, where the surface-related phenomena dominate both the thermodynamic and kinetic processes [19]. On the one hand, the repeated mechanical impacts and shearing during mechanical activation fragmented the crystallites and ordered domains of PMN–PMW. As clearly illustrated by the Raman spectra shown in Fig. 3, there exist ordered microdomains in the activated 0.4PMN–0.6PMW. On the other hand, thermal diffusion at the collision point can lead to the recovery in superlattice ordering, where the in situ temperature is estimated to be 400–500 °C [2]. Therefore, the observed preservation of ordered microdomains in the mechanically activated PMN–PMW compositions is a result of the equilibrium between the mechanical destruction of crystallites and domains, and the recovering of ordering in association with the in situ temperature at the collision points.

4. Conclusions

B site disordering in PMN–PMW triggered by mechanical activation were investigated using both XRD and Raman spectroscopy. In 0.4PMN–0.6PMW, B site ordering is steadily reduced by mechanical activation, while it is recovered by thermal activation. At the initial stage of mechanical activation, refinements in ordered domain size and crystallite size take place simultaneously. Further mechanical activation reduces the ordering to out of the XRD detectable range, but the small degree of ordering can still be observed by Raman spectroscopic study. This order–disorder transition triggered by mechanical activation also exhibits a composition-dependent. After long duration of mechanical activation, a considerable degree of ordering still remains in the compositions contenting more than 0.4 mol PMW. The preservation of microdomains can be accounted for by the competition between the mechanical destruction and the recovering of ordering by thermal diffusion.

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