

Mechanically Activating Nucleation and Growth of Complex Perovskites

John Wang,¹ J. M. Xue, D. M. Wan, and B. K. Gan

Department of Materials Science, Faculty of Science, National University of Singapore, Singapore 119260

Received October 21, 1999; in revised form May 4, 2000; accepted May 26, 2000; published online August 30, 2000

Mechanical activation of the constituent oxides at room temperature led to the formation of nanocrystalline Pb-based relaxor ferroelectrics and piezoelectrics of complex perovskite structure. The activation-triggered occurrence of complex perovskites, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $0.9[0.4\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.6\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3] - 0.1\text{PbTiO}_3$, and $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, in the mixed oxide compositions and in an amorphous precursor derived from coprecipitation proceeds via a process involving nucleation and subsequent growth of perovskite crystallites with increasing degree of mechanical activation. This is fundamentally different from the one or more interfacial reactions and diffusions responsible for a thermally activated solid state reaction occurring at an elevated temperature. Nucleation occurs in a highly activated state, where a degree of amorphization has taken place, and the subsequent growth proceeds as a result of the constant collisions and rearrangement of perovskite nuclei. © 2000 Academic Press

Key Words: mechanical activation; nucleation; crystallite growth; lead magnesium niobate; perovskites; lead zirconate titanate.

INTRODUCTION

Mechanically activated processes are among the earliest phenomena created by humankind and the use of flint to trigger fires is perhaps the best known example (1). Mechanochemical reactions have been devised and employed for synthesis and fabrication of nanocrystalline and nanostructured metallic and ceramic materials (2–4). There are a number of unique phenomena associated with mechanical activation, including refinement in crystallite size (5), creation of point, surface, and lattice defects (6, 7), amorphization of crystalline phases (8, 9), phase transformations (10, 11), and crystallization from an amorphous state and chemical reactions (12–14). The high rates and complex natures involved have, however, precluded the establish-

ment of the exact mechanisms behind most of the activation-triggered reactions, and therefore they are much less investigated and understood than their thermally activated counterparts (1, 15). Mechanochemical reactions at the interface in microsecond or nanosecond duration of shock and collision (16), local temperature-facilitated solid state reactions (17), and the nucleation at interfaces and subsequent growth of crystallites (15, 18) are among the very few suggestions that have been made so far.

Several PbO-based ferroelectrics and piezoelectrics of perovskite structure, including $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT), have been successfully synthesized in the authors' laboratory by mechanically activating mixed oxide compositions. On one hand, this has a significant technological implication that the currently employed multiple steps of phase-forming calcination for ceramic materials can be skipped. More importantly, on the other hand, several unique phenomena have been observed in association with mechanical activation. They create an opportunity for us to investigate the mechanisms behind the activation-triggered reactions. On the basis of conclusive evidences, we show that the occurrence of nanocrystalline perovskites in the highly activated oxide mixtures proceeds via a process involving nucleation and subsequent growth with increasing degree of mechanical activation, instead of the previously suggested interfacial reactions (16, 18).

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is a well-established relaxor-type ferroelectric of perovskite structure, owing to its excellent dielectric and electrostrictive properties for numerous applications in electronics industry (19). There is a big family of PMN-based relaxor ferroelectrics, including those solid solutions in the systems of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{PbTiO}_3$. It is however impossible to synthesize a single phase of PMN and PMN-based relaxor ferroelectrics of perovskite structure from the constituent oxides by a one-step of solid state reaction at high temperatures (20). The solid state reaction of PbO , MgO , and Nb_2O_5 at high temperature always results in one or more transitional pyrochlore phases (notably $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ and $\text{Pb}_2\text{Nb}_2\text{O}_7$), which

¹To whom correspondence should be addressed. Fax: (65) 7763604. E-mail: maswangj@nus.edu.sg.

are thermodynamically stable over a wide range of temperatures, prior to the perovskite PMN phase. This is a consequence of the difference in reactivity among the three oxides over a wide range of temperatures. Also, there apparently exists a much larger interfacial area between any two of these three oxides than the common contact area where all three oxides are present, creating opportunities for the preferred interfacial reaction between PbO and Nb₂O₅ to take place (21). The Columbite method (20), whereby MgO and Nb₂O₅ are first mixed and reacted together at temperatures of around 1000°C to form a columbite MgNb₂O₆ phase, prior to being mixed and reacted with PbO in a second step of calcination, is the only viable technique for single phase PMN. Therefore, it has been dominating the fabrication of PMN and PMN-based relaxor ferroelectrics over the past 15 years. In remarkable contrast, we are able to synthesize a nanocrystalline PMN powder of perovskite structure by a single step of mechanical activation of mixed oxides at room temperature.

Lead zirconate titanate, Pb(Zr_{1-x}Ti_x)O₃ (PZT), is a well-established piezoelectric, which is widely employed in a large number of sensing and actuating devices (22). It is traditionally prepared by solid state reaction among the constituent oxides at elevated temperatures. Due to the difference in reactivity among the three oxides, transitional PbTiO₃ (PT) and PbZrO₃ (PZ) phases occur prior to the perovskite PZT phase. Therefore it is rather difficult to synthesize a single phase PZT of high chemical homogeneity and stoichiometry in composition by the conventional solid state reaction. In a remarkable success, we have synthesized a single perovskite phase of PZT by mechanically activating the constituent oxides at room temperature. Furthermore, we have observed that the transitional PT and PZ phases are not involved in mechanical activation prior to the formation of perovskite PZT. As will be discussed later, this is due to the very different phase-formation process triggered by mechanical activation in comparison to that in the conventional solid state reaction.

EXPERIMENTAL PROCEDURE

The starting oxides were commercially available PbO (>99% in purity, J. T. Baker, USA), MgO (>99% in purity, Aldrich, USA), Nb₂O₅ (>99% in purity, Aldrich, USA), ZnO (>99% in purity, J.T. Baker), ZrO₂ (>99% in purity, MEL, Manchester, UK), and TiO₂ (>99% in purity, Merck, Germany). They exhibited a particle size distribution covering the range of submicrons to tens of microns. Appropriate amounts of the constituent oxides, as required by the stoichiometric Pb(Mg_{1/3}Nb_{2/3})O₃, 0.9[0.4Pb(Mg_{1/3}Nb_{2/3})O₃-0.6Pb(Zn_{1/3}Nb_{2/3})O₃]-0.1PbTiO₃ (PMN-PZN-PT), and the mixed oxide composition equivalent to a mixture consisting of equal amounts of Pb(Zr_{0.52}Ti_{0.48})O₃ and PbO, respectively, were weighed out and placed in a laboratory

plastic ball mill, together with an appropriate amount of ethanol and zirconia balls of 5.0 mm diameter as the milling media. They were each milled for 48 hours, followed by drying the slurry at ~80°C in an oven. The as-dried powder mixtures were ground using an agate mortar and pestle to eliminate large powder lumps and was then passed through 40 mesh sieves.

A modified coprecipitation technique was used to synthesize an amorphous PZT precursor in this work, where commercially available Pb(NO₃)₂ (>99% in purity, Merck, Germany), TiCl₄ (>99% in purity, Hayashi Pure Chemical Industries Ltd., Japan), and a ZrO(NO₃)₂ aqueous solution (20 wt% ZrO₂, MEL Limited, Manchester, UK) were used as the starting materials. It was started by slowly adding chilled (~4°C) deionized water into a cool TiCl₄ solution with stirring. A preweighted amount of ZrO(NO₃)₂ solution was blended into the TiCl₄-water mixture, before a desirable amount of cold ammonia solution (12 wt%) was added into the mixed solution. The addition of ammonia solution resulted in the formation of Zr-Ti-hydroxide hydrate precipitates. To remove the Cl⁻ ions, the gelatinous precipitates were filtered and washed repeatedly using deionized water until the pH of filtrate was close to 7.0 and no trace of Cl⁻ was detected using AgNO₃. A Zr-Ti-oxynitrate aqueous solution (10 wt%) was prepared by dissolving the white precipitates into an appropriate amount of 3.0 M HNO₃. A precalculated amount of Pb(NO₃)₂ was first dissolved in deionized water and then combined into the Zr-Ti-oxynitrate solution, in order to prepare a nitrate solution containing Pb²⁺, Zr⁴⁺, and Ti⁴⁺ ions in the molar ratio of 1:0.52:0.48. The coprecipitation of Pb-Zr-Ti-hydroxides was carried out by slowly adding the mixed nitrate solution into an ammonia solution of pH 9, which was checked and maintained by adding a few drops of concentrated ammonia solution during the coprecipitation process. The precipitates were then aged for 1 hour in the supernatant liquid before being recovered by filtration and dried at 90°C for 2 hours in an oven. The dried precursor powder was thermally treated at 400°C for 2 hours, with both heating and cooling rates being fixed at 5°C/minute. Phase analysis using XRD indicated that the PZT precursor is highly amorphous and therefore the perovskite phase was not in existence prior to the mechanical activation.

A batch of 6 grams of each of the above powder mixtures was then loaded into a wear-resistant cylindrical vial of 40 mm diameter and 40 mm in length together with a stainless steel ball of 12.7 mm diameter. Mechanical activation of these powders was carried out in a shaker mill operated at ~900 rpm for various time periods in the range of 0 to 35 hours (23). The resulting powders were then characterized for phases present using an X-ray diffractometer (X'Pert, Philips) and a Raman spectrometer (Spex 1702/04 Raman spectrometer). The crystallite size of the nanocrystalline perovskite phases was estimated on the basis of peak

broadening of XRD traces using the Scherrer equation (24). Their specific surface areas and equivalent particle sizes were measured using a BET surface area analyzer (NOVA-2000, Quantachrome, USA). A transmission electron microscope (TEM, JEOL 100CX) and a high-resolution transmission electron microscope (HRTEM, Philips CM300 FEG) were then employed to study their particle and crystallite characteristics.

RESULTS AND DISCUSSION

Figure 1 shows the XRD traces of mixed oxides of PbO, MgO, and Nb₂O₅ upon mechanical activation for 5, 10, and 20 hours, respectively, together with that of the powder mixture that was not subjected to any mechanical activation. Sharp peaks of crystalline PbO, MgO, and Nb₂O₅ are observed for the starting powder mixture, indicating that little or no reaction took place during mixing milling in the conventional ball mill. A few broadened peaks were observed when the oxide mixture was mechanically activated

for 5 hours. The strongest one at 2θ angle of $\sim 29.1^\circ$ corresponds to the PbO (111) peak, which was seen as a sharp peak before the mechanical activation. This implies that the initial 5 hours of mechanical activation led to a significant refinement in particle and crystallite sizes together with a degree of amorphization of the constituent oxides. It is supported by a rise in the specific surface area from 1.20 m²/g for the oxide mixture that was not subjected to mechanical activation to 9.52 m²/g for the powder subjected to 5 hours of mechanical activation. The second strongest broadened peak at 2θ angle of $\sim 31.2^\circ$ and peaks at 2θ angles of 44.7 and 55.5° are newly formed. They are assigned to perovskite PMN (110), (200), and (211) peaks, respectively. This suggests that nanocrystallites of the perovskite PMN phase have been formed as a result of the initial 5 hours of mechanical activation. The intensities of the perovskite PMN (110), (200), and (211) peaks increase with increasing mechanical activation time, apparently at the expenses of the PbO (111) peak, although there is little further increase in the specific surface area (e.g., 10.13 m²/g at 10 hours of mechanical activation). In the powder mechanically activated for 20 hours, nanocrystalline PMN is the only XRD-detectable phase, as suggested by the well-defined peaks at 2θ angles of 21.9, 31.2, 38.5, 44.7, 50.2, 55.5, and 65.0°, respectively. There is also an apparent sharpening in the PMN (110), (111), (200), (210), and (211) peaks when the mechanical activation time is extended to 20 hours, suggesting that there is an increase in the crystallinity of the perovskite PMN phase. It was calculated using the Scherrer equation (24) on the basis of peak broadening of the perovskite (110) peak that the PMN nanocrystallites exhibited an average crystallite size of ~ 15 nm after 20 hours of mechanical activation, in comparison to ~ 9 nm for the powder that was mechanically activated for 5 hours. This clearly demonstrated that the perovskite nanocrystallites of lead magnesium niobate underwent a steady growth with increasing degree of mechanical activation, while the pyrochlore phases are apparently not involved in the process, prior to the formation of perovskite phase.

The above experimental results of phase analysis and specific surface area clearly demonstrate the significant refinement in particle and crystallite sizes together with a degree of amorphization at the initial stage of mechanical activation. This is followed by the occurrence and then growth of perovskite PMN nanocrystallites in the highly activated oxide mixture. The absence of intermediate pyrochlore phases, e.g., Pb₃Nb₄O₁₃ and Pb₂Nb₂O₇ which have always been observed as interfacial reaction products in the temperature-driven solid state reaction (20, 21), suggests that the occurrence of perovskite nanocrystallites triggered by mechanical activation is not a result of one or more interfacial reactions as stated by the Roller model (18). Instead, they occur via a nucleation process involving all three oxides in a highly activated oxide matrix, where a

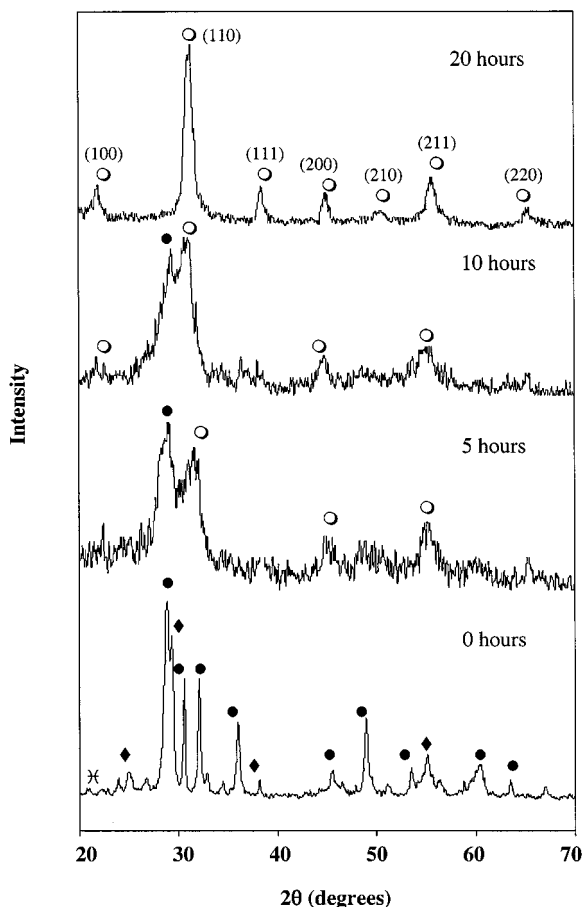


FIG. 1. XRD traces of the mixed oxides of PbO, MgO, and Nb₂O₅ when subjected to mechanical activation for 0, 5, 10, and 20 hours (○, perovskite; ●, PbO; ⊖, MgO; ◆, Nb₂O₅).

significant refinement in particle and crystallite sizes together with a degree of amorphization have taken place. As mentioned earlier, there is a much smaller amount of common contact areas involving all three oxides in the powder mixture than the interfacial contact areas between any two of the three oxides, e.g., between PbO and Nb₂O₅ particles. On one hand, this, together with the high reactivity between PbO and Nb₂O₅, ensures the involvement of transitional pyrochlore phases in the conventional solid state reaction when mixed oxides of PbO, MgO, and Nb₂O₅ are calcined at elevated temperatures. On the other hand, it is very unlikely that the formation of nanocrystallites of the perovskite PMN phase triggered by mechanical activation is a result of the interfacial reactions involving all three oxides without first going through any of the transitional pyrochlore phases. The subsequent steady growth of PMN nanocrystallites of perovskite structure with increasing degree of mechanical activation is a consequence of the equilibrium between the activation-driven build-up and destruction involving the entire masses of perovskite nuclei (15). Constant collisions and rearrangement of perovskite nuclei provided by mechanical activation create opportunities for two or more of these nuclei to meet at favorable positions leading to growth in the crystallite size. At the same time, there is also a probability that the perovskite nanocrystallites are distorted and fragmented by the mechanical activation.

To support the suggested nucleation and subsequent growth of perovskite crystallites in activated oxide compositions, mechanical activation was carried out on the following two more types of oxide mixtures: (i) mixed oxides of PbO, MgO, ZnO, TiO₂, and Nb₂O₅ equivalent to the stoichiometric composition of 0.9[0.4Pb(Mg_{1/3}Nb_{2/3})O₃-0.6Pb(Zn_{1/3}Nb_{2/3})O₃]-0.1PbTiO₃ (PMN-PZT-PT), and (ii) mixed oxides of PbO, ZrO₂, and TiO₂ equivalent to a mixture consisting of equal amounts of PbZr_{0.52}Ti_{0.48}O₃ and PbO. The two oxide mixtures were prepared by mixing the constituent oxides in a conventional ball mill and were then subjected to mechanical activation for various time periods from 0 to 20 hours, followed by phase analysis using X-ray diffraction. The choice of the multicomponent 0.9[0.4Pb(Mg_{1/3}Nb_{2/3})O₃-0.6Pb(Zn_{1/3}Nb_{2/3})O₃]-0.1PbTiO₃ composition would maximize the involvement of several transitional phases prior to the perovskite PMN-PZT-PT nanocrystallites, if the phase formation triggered by mechanical activation proceeded via one or more interfacial reactions. In other words, it would be almost impossible not to go through one or more transitional phases if the phase formation of the activation-triggered perovskite nanocrystallites is controlled by one or more interfacial reactions. In fact, it is almost impossible to concurrently involve all five oxides at an interfacial location in order to form the designed PMN-PZN-PT phase by the interfacial reaction. As shown in Fig. 2, however, a consider-

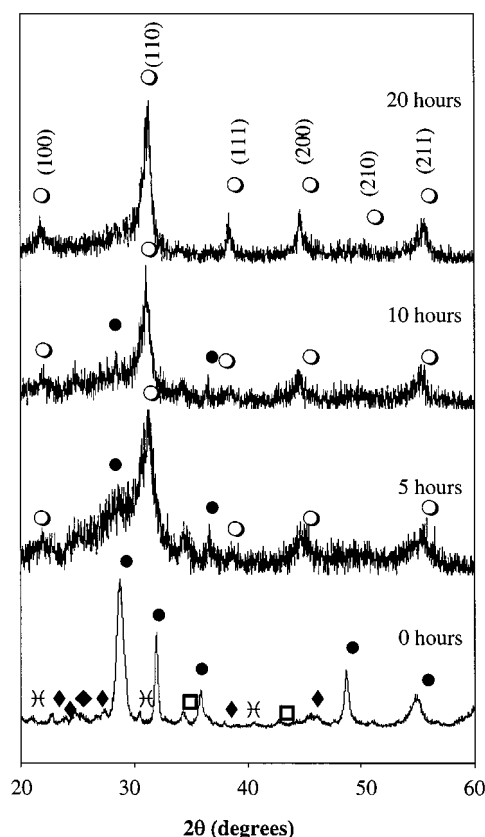


FIG. 2. XRD traces of the mixed oxides of PbO, ZnO, MgO, TiO₂, and Nb₂O₅ when subjected to mechanical activation for 0, 5, 10, and 20 hours (○, perovskite; ●, PbO; ×, MgO; ◆, Nb₂O₅; □, ZnO; ■, TiO₂).

able amount of perovskite PMN-PZT-PT phase was observed at 5 hours of mechanical activation and a single perovskite phase was obtained at 20 hours of mechanical activation. No any intermediate phases were involved prior to the nanocrystalline PMN-PZN-PT phase with increasing mechanical activation time.

Figure 3 is an HRTEM micrograph together with the selected area diffraction patterns showing the nanocrystallites of perovskite PMN-PZN-PT in an amorphous matrix triggered by 10 hours of mechanical activation. They are well-established perovskite crystallites of 5 to 10 nm in dimension dispersed in an amorphous oxide matrix. The occurrence of a faint halo and multiple spotty rings of the selected area diffraction pattern demonstrates that the powder consists of nanocrystallites and an amorphous matrix. The three apparent rings correspond to perovskite (110), (200), and (211) planes, respectively. As expected, the faint halo largely overlaps with the perovskite (110) plane, due to the domination of PbO in composition. Measurement of lattice spacing (e.g., $d_{110} = 2.87$ Å) also confirms that these nanocrystallites are perovskite PMN-PZN-PT. As further illustrated by the Raman spectrum in Fig. 4 for the

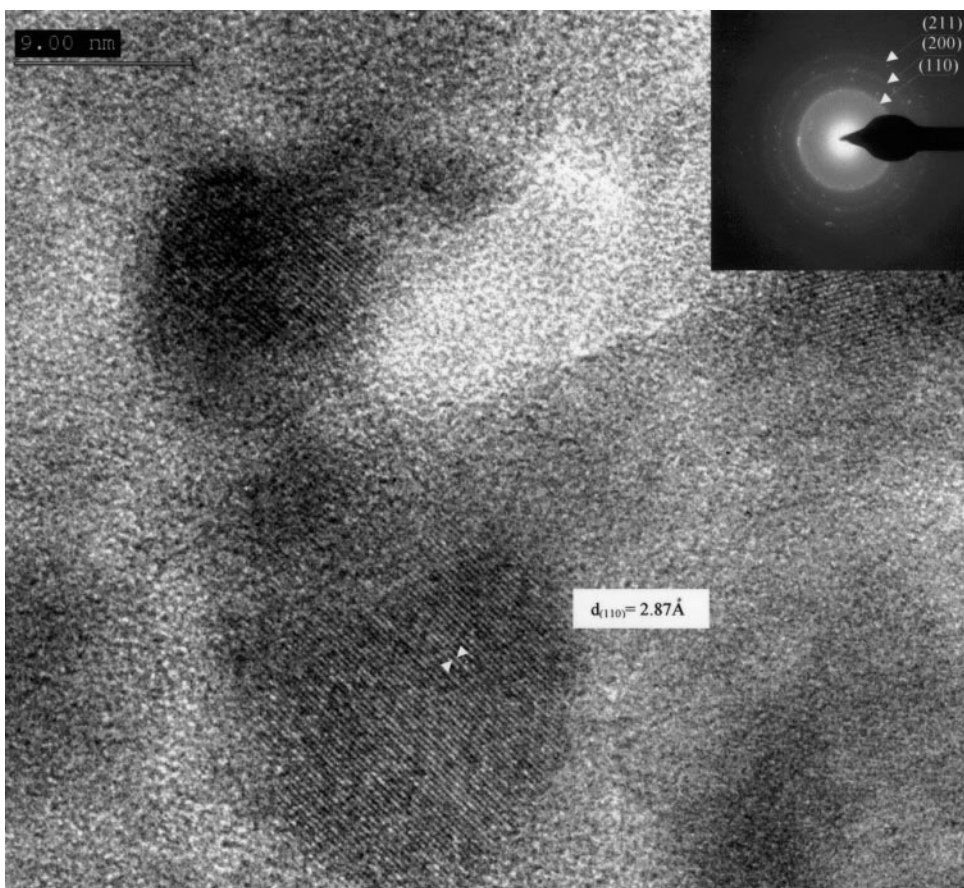


FIG. 3. HRTEM micrograph and corresponding selected area diffraction pattern showing the nanocrystallites of perovskite structure in an amorphous matrix, derived from mechanical activation for 10 hours of mixed oxides of PbO, MgO, ZnO, TiO₂, and Nb₂O₅.

mixed oxides of PbO, ZnO, MgO, TiO, and Nb₂O₅ subjected to 10 hours of mechanical activation, the nanocrystalline PMN–PZN–PT phase of perovskite structure is the predominant crystalline phase as indicated by the bands centered at 138, 270, and 788 cm⁻¹. Apparently, no any transitional pyrochlore phases are involved when the mixed oxides are subjected to an increasing degree of mechanical activation. This agrees with what has been shown by the phase analysis using X-ray diffraction as shown in Fig. 2, which demonstrated that the activation-triggered perovskite nanocrystallites underwent a growth in crystallinity with increasing mechanical activation time.

Figure 5 shows the XRD traces of mixed oxides of PbO, ZrO₂, and TiO₂ equivalent to a mixture consisting of equal amounts of Pb(Zr_{0.52}Ti_{0.48})O₃ and PbO upon mechanical activation for various time periods from 0 to 20 hours. Again, the choice of constituent oxides for PZT in a large amount of excess PbO matrix would maximize the involvement of transitional PT and PZ phases prior to PZT, if the activation-triggered occurrence of PZT nanocrystallites was due to the interfacial reactions as in the conventional solid

state reaction. As expected, the starting oxide mixture consists of crystalline PbO, ZrO₂, and TiO₂ after the conventional ball milling. An initial 5 hours of mechanical activation resulted in a significant refinement in particle and crystallite sizes, together with a degree of mechanical activation of mixed oxides, as indicated by the peak broadening in XRD trace. A significant amount of nanocrystalline PZT phase can be observed at merely 5 hours of mechanical activation, although there is a large amount of excess PbO in the mixed oxide composition as shown by a strong and broadened peak at the 2θ angle of 29.1°. The amount of perovskite PZT phase in the excess PbO matrix increases with increasing mechanical activation time. Surprisingly, however, transitional PbTiO₃ (PT) and PbTiO₃ (PZ) phases are not observed at any stage of mechanical activation, although TiO₂ and ZrO₂ are dispersed in such a large amount of excess PbO matrix, favoring the interfacial reactions between PbO and TiO₂ and between PbO and ZrO₂. In other words, ZrO₂ and TiO₂ have been preferably picked out during mechanical activation from the highly activated oxide matrix, leading to the formation of a nanocrystalline

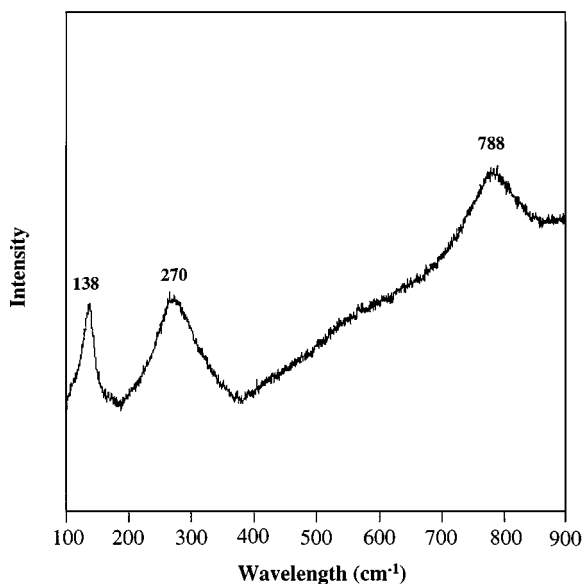


FIG. 4. Raman spectrum of the oxide composition subjected to 10 hours of mechanical activation. The starting materials were mixed oxides of PbO, MgO, ZnO, TiO₂, and Nb₂O₅ equivalent to 0.9[0.4Pb(Mg_{1/3}Nb_{2/3})O₃-0.6Pb(Zn_{1/3}Nb_{2/3})O₃]-0.1PbTiO₃ in composition.

PZT phase in the PbO matrix. This clearly demonstrates that the activation-triggered formation of PZT nanocrystallites is not a result of the interfacial reactions. As a comparison, Fig. 6 shows the XRD trace of the mixed oxide composition equivalent to the mixture consisting of equal amounts of Pb(Zr_{0.52}Ti_{0.48})O₃ and PbO upon calcination at 700°C for 1 hour. Both PT and PZ were formed at the calcination temperature. This is expected for the conventional solid state reaction, where the process is controlled by the interfacial reactions between PbO and TiO₂ and between PbO and ZrO₂, resulting in little PZT phase present at the calcination temperature.

The activation-triggered nucleation and subsequent growth of nanocrystallites of perovskite structure are further supported by the mechanical activation of a PZT precursor derived from coprecipitation. Five hours of mechanical activation led to a steady formation of PZT nanocrystallites in an essentially amorphous PZT precursor, where interfacial reactions cannot possibly occur as none of the individual oxide phases existed in the homogeneous precursor prior to mechanical activation. Figure 7 shows the XRD traces of the coprecipitated precursor powder upon mechanical activation for 5, 15, and 35 hours, respectively, together with that of the amorphous powder that was not subjected to any mechanical activation. Only one strong and broadened peak is observed over the 2θ angle of 28° to 35° for the starting precursor powder, indicating its amorphous nature. A total weight loss of ~10% was observed in the TGA curve when the precursor powder was

heated to ~600°C, suggesting that the decomposition of coprecipitated hydroxides was not completed by the thermal treatment at 400°C and an amorphous nature was thus retained for the thermally treated precursor. A few sharpened peaks are observed for the precursor powder mechanically activated for 5 hours. The strongest one at the 2θ angle of ~31.2° corresponds to the PZT (110) peak, showing that fine crystallites of perovskite PZT phase have been formed as a result of the mechanical activation for the initial 5 hours. In fact, the nanocrystalline PZT has become the predominant phase at merely 5 hours of mechanical activation. The intensity and sharpness of perovskite PZT (110), (100), (111), (200), (210), (211), and (220) peaks were further established when the mechanical activation was extended to 15 hours and then 35 hours. Again, transitional PT and PZ phases were not observed with increasing degree of mechanical activation. It was estimated, using the Scherrer equation

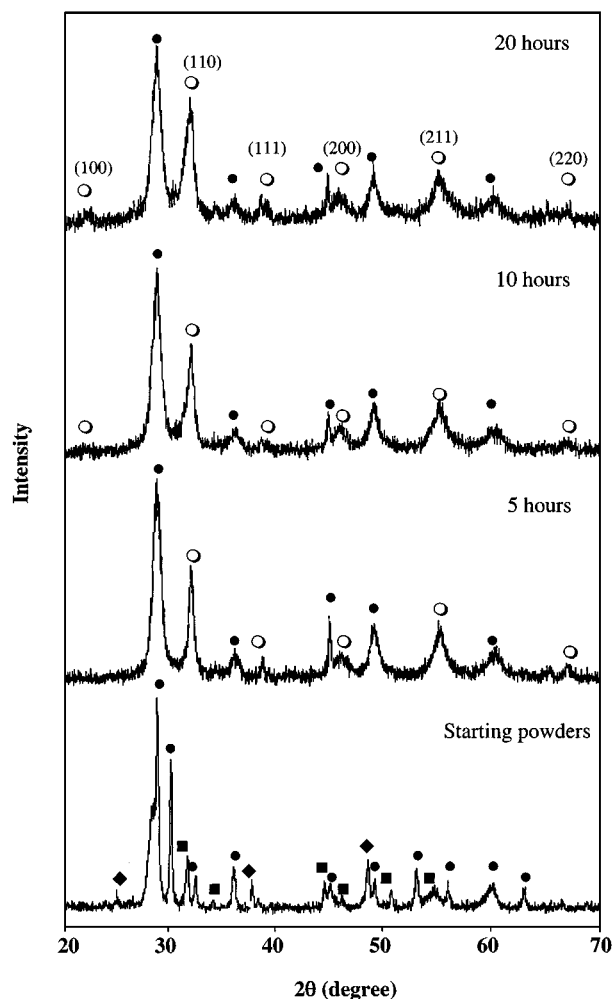


FIG. 5. XRD traces of mixed oxides of PbO, ZrO₂, and TiO₂ equivalent to the composition consisting of equal amounts of PbZr_{0.52}Ti_{0.48}O₃ and PbO upon mechanical activation of various time periods from 0 to 20 hours (●, PbO; ■, ZrO₂; ◆, TiO₂; ○, PZT).

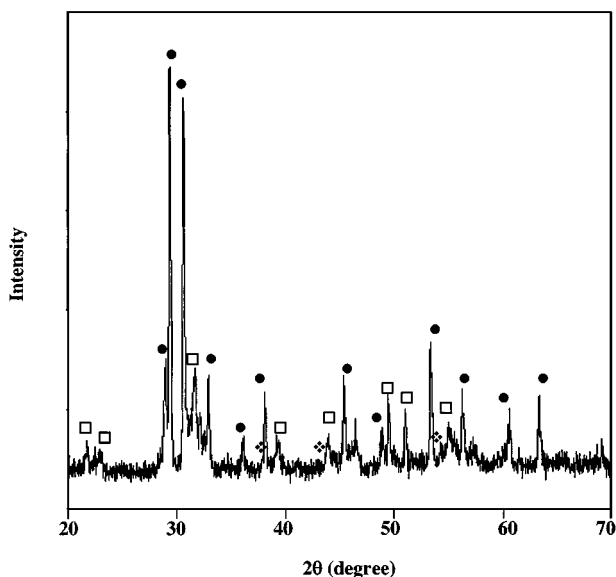


FIG. 6. XRD trace of the mixed oxide composition equivalent to a mixture consisting of equal amounts of $\text{PbZr}_{0.48}\text{Ti}_{0.52}\text{O}_3$ and PbO upon calcination at 700°C for 1 hour (●, PbO ; □, PbTiO_3 ; ◆, PbZrO_3).

(24) on the basis of the half-width of PZT (110), that the nanocrystallites of the PZT phase in the powder mechanically activated for 35 hours are ~ 20 nm in size, in contrast to ~ 9 nm for the powder subjected to the initial 5 hours of mechanical activation. As shown in Fig. 8, the PZT powder derived from 35 hours of mechanical activation of the coprecipitated precursor consists of particle agglomerates of varying size and morphology. A detailed study at high magnifications confirmed that they are comprised of nanosized PZT particles, which are more or less spherical in morphology. Figure 9 is a bright-field TEM micrograph, together with the selected area diffraction pattern, for the powder derived from 35 hours of mechanical activation. PZT particles of 30 to 50 nm in size are observed, although they form irregularly shaped aggregates. Its polycrystalline nature is clearly demonstrated by the multiple spots observed in the selected area diffraction pattern.

In a separate study of triggering perovskite $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) nanocrystallites in the mixed oxides of PbO , ZnO , and Nb_2O_5 , an *in-situ* temperature of $< 500^\circ\text{C}$ at the collision points is clearly indicated (25). It is therefore unlikely that the growth of perovskite crystallites in the activated oxide matrix is a result of the thermally activated diffusions as in the temperature-driven solid state reactions. Rather, it is a result of the equilibrium between the activation-driven build-up and destruction involving the entire masses of perovskite nuclei. Constant collisions and rearrangement of perovskite nuclei provided by mechanical impact, shock, shear, and deformation create opportunities

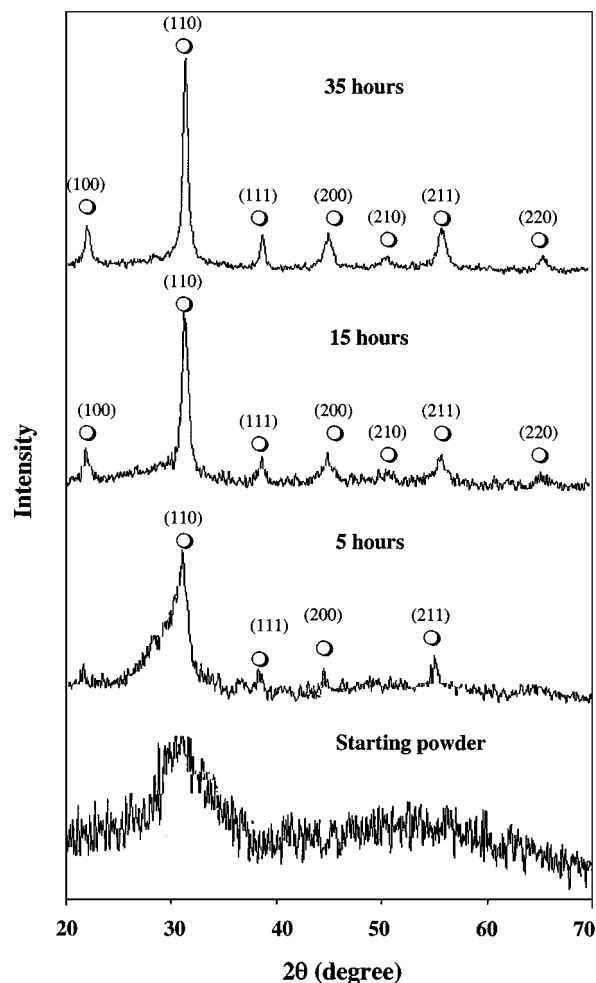


FIG. 7. XRD traces of the PZT precursor derived from coprecipitation when mechanically activated for various times ranging from 0 to 35 hours (○, PZT).

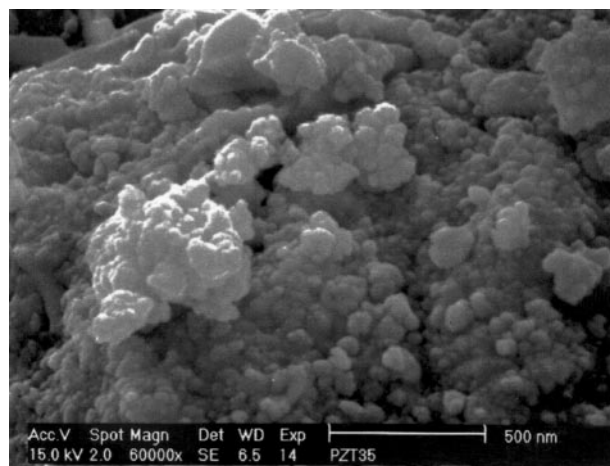


FIG. 8. SEM micrograph showing the PZT powder derived from 35 hours of mechanical activation of the coprecipitated precursor.

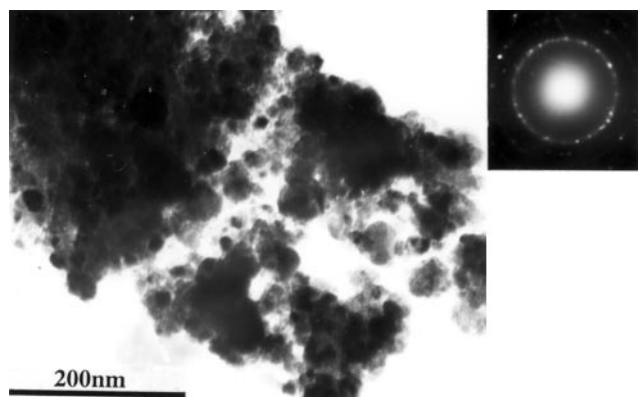


FIG. 9. TEM micrograph and the corresponding selected area electron diffraction pattern shown the PZT powder derived from 35 hours of mechanical activation of the coprecipitated precursor.

for two or more nuclei to meet at favorable positions leading to the growth in crystallite size. At the same time, there is also a probability that the perovskite nanocrystallites are distorted and fragmented by the mechanical activation.

CONCLUSIONS

The mechanical activation of mixed oxide compositions at room temperature led to the formation of nanocrystalline PMN, PMN-PZN-PT, and PZT phases of perovskite structure. Transitional phases, such as pyrochlores, PT, and PZ, which have commonly been observed in the conventional solid state reactions, are not involved in the mechanical activation. The phase-forming reactions triggered by mechanical activation of mixed oxides proceeds via a route completely different from that in the conventional solid state reactions, where the process is controlled by one or more interfacial reactions and diffusions. They involve nucleation and the subsequent growth of perovskite nanocrystallites with increasing degree of mechanical activation, as has been demonstrated in PMN, multicomponent PMN-PZN-PT system, mixed oxide composition equivalent to a mixture consisting of equal amounts of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and PbO , and an amorphous PZT

precursor derived from coprecipitation. Nucleation of the perovskite nanocrystallites occurs in a highly activated state, where a significant refinement in particle and crystallite sizes together with a degree of amorphization has taken place at the initial stage of mechanical activation. The subsequent growth proceeds as a result of the constant collisions and rearrangement of the perovskite nuclei.

REFERENCES

1. P. G. McCormick and F. H. Froes, *JOM* **11**, 61 (1998).
2. J. G. Baek, T. Isobe, and M. Senna, *J. Am. Ceram. Soc.* **80**, 973 (1997).
3. D. Michel, F. Fraudot, E. Gaffet, and L. Mazerolles, *J. Am. Ceram. Soc.* **76**, 2884 (1993).
4. A. K. Giri, *Adv. Mater.* **9**, 163 (1997).
5. E. Gaffet, D. Michel, L. Mazerolles, and P. Berthet, *Mater. Sci. Forum* **235-238**, 103 (1997).
6. U. Steinike, D. C. Uecker, K. Menning, and B. Rosner, in "Proceedings of the InCoMe'93" (K. Tkacova, Ed.), p. 121. Cambridge Interscience, Cambridge, 1993.
7. T. G. Shen, C. C. Koch, T. L. McCormick, R. J. Nemanich, J. H. Huang, and J. G. Huang, *J. Mater. Res.* **10**, 139 (1995).
8. H. J. Fecht, *Nature* **356**, 133 (1992).
9. G. J. Fan, F. Q. Guo, Z. Q. Hu, M. X. Quan, and K. Lu, *Phys. Rev. B* **55**, 11010 (1997).
10. B. Bokhonov, I. Konstanchuk, E. Ivanov, and V. Boldyrev, *J. Alloys Compds.* **187**, 207 (1992).
11. B. Bokhonov, I. Konstanchuk, and V. Boldyrev, *J. Non-Cryst. Solids* **153 & 154**, 606 (1993).
12. M. L. Trudeau and R. Schulz, *Phys. Rev. Lett.* **64**, 99 (1990).
13. H. Chen, Y. He, G. J. Shiflet and S. J. Poon, *Nature* **367**, 541 (1994).
14. J. J. Gilman, *Science* **274**, 65 (1996).
15. N. N. Thadhani, *J. Appl. Phys.* **76**, 2129 (1994).
16. V. V. Boldyrev, *Mater. Sci. Forum* **225-227**, 511 (1996).
17. L. Takacs, *Appl. Phys. Lett.* **69**, 436 (1996).
18. A. N. Dremin and O. N. Breusov, *Russ. Chem. Rev.* **37**, 392 (1968).
19. S. L. Swartz, T. R. Shrout, W. A. Schulze, and L. E. Cross, *J. Am. Ceram. Soc.* **67**, 311 (1984).
20. S. L. Swartz and T. R. Shrout, *Mater. Res. Bull.* **17**, 1245 (1982).
21. T. R. Shrout and A. Halliyal, *Am. Ceram. Soc. Bull.* **66**, 704 (1987).
22. D. Berlincourt, *Ferroelectrics* **10**, 111 (1976).
23. J. Wang, D. M. Wan, J. M. Xue, and W. B. Ng, Singapore Pat. No. 9801566-2, 1998.
24. H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials", pp. 491-538. Wiley, New York, 1954.
25. W. B. Ng, M.Sc. Thesis, National University of Singapore, 1999.