

Nanocrystalline PbTiO_3 powders from an amorphous Pb-Ti-O precursor by mechanical activation

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Abstract

Mechanical activation is investigated for its efforts in triggering PbTiO_3 nanocrystallites from an amorphous Pb-Ti-O precursor, which was synthesized by co-precipitation. In this study, the amorphous precursor and the compositions that were subjected to mechanical activation for various time periods were investigated using Raman spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). A single perovskite PbTiO_3 phase was readily formed in the amorphous Pb-Ti-O precursor by mechanical activation, where a nanocrystalline feature is retained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous Pb-Ti-O ; Nanocrystalline; Scanning electron microscopy; Raman spectroscopy

1. Introduction

Lead titanate, PbTiO_3 (PT) is a perovskite-type ferroelectric material with excellent dielectric, pyroelectric and piezoelectric properties [1,2]. Its large pyroelectric coefficient and electro-mechanical coupling factor make it a good candidate material for a number of demanding applications, such as in sensors, capacitors, piezoelectric actuators, and integrated non-volatile memories [3]. Mechanical activation has recently been successfully applied to synthesize nanometer-sized PbTiO_3 particles from mixed oxides at room temperature [4]. This is particularly interesting to the lead-based electroceramic material, as calcination involved in the conventional solid state reaction often leads to loss of volatile lead oxide at elevated temperatures. Furthermore, the conventional ceramic synthesis by solid state reactions at high temperatures almost always results in the unwanted particle coarsening and aggregation, which are detrimental to the subsequent sintering. Most of the wet-chemistry-based synthesis routes also involve a post-precursor calcination step at an elevated temperature, in order to realize the precursor to ceramic conversion. Unfortunately, the calcination will ruin the sintering reactive nature of the precursor, again as a consequence of the undesirable crystallite coarsening and particle aggregation at the calcination temperature. In this paper, we report on the formation of nanocrystalline PT phase by mechanical activation from an amorphous Pb-Ti hydroxide precursor derived from co-precipitation.

2. Experimental

To prepare the amorphous precursor for mechanical activation, co-precipitation of Pb-Ti hydroxides was carried out by slowly adding a mixed nitrate solution of Pb^{2+} and Ti^{4+} into an ammonia solution of pH 9. The resulting co-precipitates were aged for 1 h in the supernatant liquid before being recovered by filtration and dried at 90°C for 2 h in an oven. The dried precursor powder was thermally treated at 300°C for 2 h, which is for partially dehydrating the precursor, and at the same time, preserving the amorphous nature of the Pb-Ti hydroxide precursor. Mechanical activation was then carried out in a SPEX mill operated at 900 rpm for 10, 20 and 30 h. The resulting samples were characterized for phases using both an X-ray diffractometer (X'Pert, Philips) and a Raman spectrometer (ISA T64000 triple grating system). Both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were employed for characterization of the particle size and morphologies of powders derived from various periods of mechanical activation.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized precursor and the compositions that were mechanically activated for 10, 20 and 30 h. When the precursor was thermally treated at 300°C for 2 h, only one broadened hump ranged from 2θ of 25° to 35° can be observed, indicating its

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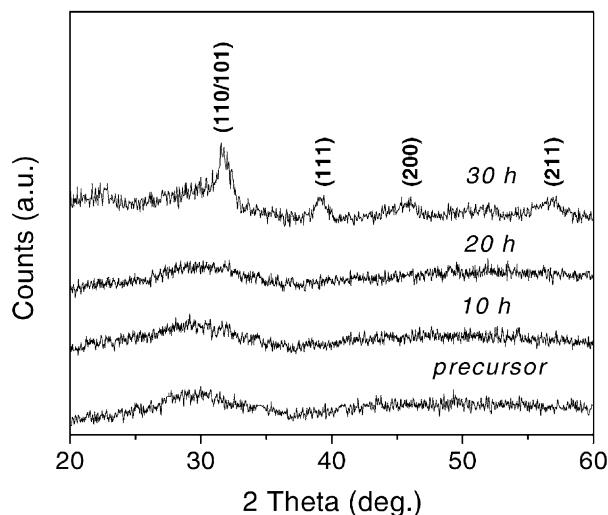


Fig. 1. XRD patterns of the as-synthesized precursor and those subjected to 10, 20 and 30 h of mechanical activation.

highly amorphous nature. There is no significant difference between the XRD pattern of the precursor and that of the composition mechanically activated for 10 h, implying that little crystalline phase was triggered by 10 h of mechanical activation. Similarly, little further change was observed in the XRD trace of the composition was mechanically activated for 20 h, although the hump over the 2θ range of $25\text{--}35^\circ$ was slightly sharpened by the continued mechanical activation. Upon mechanical activation for 30 h, four peaks at 2θ angles of 32.1° , 39.3° , 46.1° and 57.5° , were well established, corresponding to the (101/110), (111), (200) and (211) planes of the crystalline PbTiO_3 perovskite structure [5]. The appearance of these diffraction peaks demonstrates that the perovskite nanocrystallites of PbTiO_3 can be triggered to form in the highly amorphous Pb–Ti–O precursor by mechanical activation at room temperature. This is in agreement with what has been observed in several other Pb-based ferroelectric compositions, where nucleation and subsequent growth of nanocrystallites can take place in the highly activated matrices [6–8].

As indicated in Fig. 1, the hump centered at 2θ of 32.1° in XRD trace was sharpened with increasing mechanical activation, suggesting the nucleation and subsequent growth of PbTiO_3 nanocrystallites. This was supported by the studies using high resolution TEM. Fig. 2 shows a TEM micrograph for the composition that was mechanically activated for 20 h. There occur nanocrystallites of <10 nm in dimensions in an amorphous matrix. Identification of d-spacing suggests the spherical crystallite shown in Fig. 2 corresponds to the (101) plane of PbTiO_3 phase. This demonstrates that nanocrystallites of perovskite PbTiO_3 phase was triggered in the amorphous Pb–Ti–O precursor by 20 h of mechanical activation, although it was not shown by the phase analysis using X-ray diffraction (XRD). This can be accounted for by the resolution limit of conventional XRD in identifying nanocrystallites as a result of the size effect.

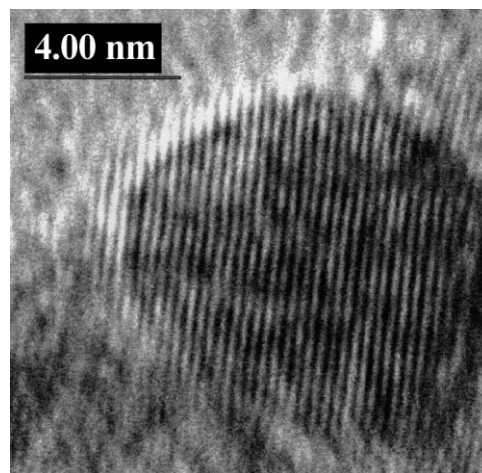


Fig. 2. A TEM micrograph showing the nanocrystallites of PbTiO_3 in the precursor that was mechanically activated for 20 h.

To further identify the nanocrystallites triggered by mechanical activation in the amorphous matrix, Raman spectrometer was employed to study the compositions that were mechanically activated for various time periods up to 30 h. Fig. 3 shows the Raman spectra of the as-synthesized PT precursor and that was mechanically activated for 10, 20 and 30 h of mechanical activation. As expected, no nanocrystalline phase was observed in the as-synthesized PT precursor, although it was deliberately thermal treated at 300°C . A broadened hump occurs in the composition that was mechanically activated for 10 h, which was centered at $\sim 300\text{ cm}^{-1}$ suggesting the occurrence of nanocrystallites of PbTiO_3 . It was further established in intensity when the mechanical activation time was extended to 20 h. This agrees with what has been demonstrated by the phase analysis of XRD that nucleation and subsequent growth of PbTiO_3 phase took

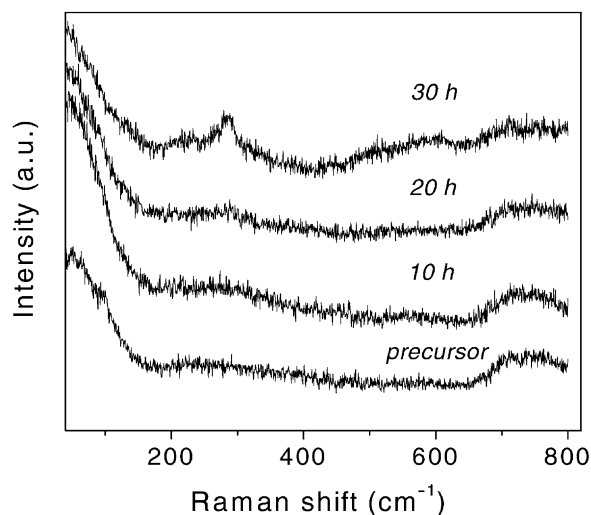


Fig. 3. Raman spectra of the as-synthesized precursor and those subjected to 10, 20 and 30 h of mechanical activation.

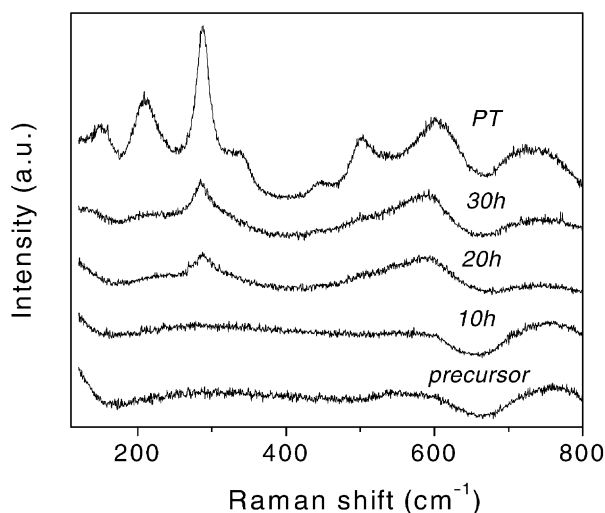


Fig. 4. Raman spectra of the as-synthesized precursor and those subjected to 10, 20 and 30 h of mechanical activation upon further calcination at 400 °C for 1 h. The spectrum on the top is recorded for a standard PbTiO_3 powder, for comparison.

place with increasing mechanical activation time. Raman peaks were well established in the PT precursor that was mechanically activated for 30 h, centered at ~ 300 , ~ 500 and $\sim 600 \text{ cm}^{-1}$ [9]. In comparison with the phase identification using XRD, the occurrence of nanocrystalline PbTiO_3 phase was clearly shown by the Raman band centered at $\sim 300 \text{ cm}^{-1}$ in the compositions that were mechanically activated for more than 10 h.

As shown by the peak broadening in XRD trace of Fig. 1, the crystallite size of PbTiO_3 triggered by mechanical activation is $< 10 \text{ nm}$. Growth in crystallite size was expected when the mechanically activated precursors were subjected to further thermal annealing with increasing temperature. Fig. 4 shows the Raman spectra of the compositions that were mechanically activated for various periods up to 30 h, followed by thermal annealing at 400 °C for 1 h. Little change was induced by the thermal annealing at 400 °C for the as-synthesized amorphous precursor that was not subjected to any prior mechanical activation and that mechanically activated for 10 h. However, the thermal annealing led to an apparent sharpening of the Raman peaks centered at ~ 300 and $\sim 590 \text{ cm}^{-1}$ for the composition that was mechanically activated for 20 h, prior to the thermal annealing at 400 °C for 1 h. A similar change was observed for the composition that was mechanically activated for 30 h. This suggests that the annealing at such a low temperature resulted in growth of PbTiO_3 crystallites, which were triggered in the amorphous matrix by mechanical activation. However, the thermal treatment was unable to trigger the nucleation of PbTiO_3 nanocrystallites in the as-synthesized precursor and that was mechanically activated for 10 h.

As expected, crystallite coarsening and aggregation took place with increasing annealing temperature, following the

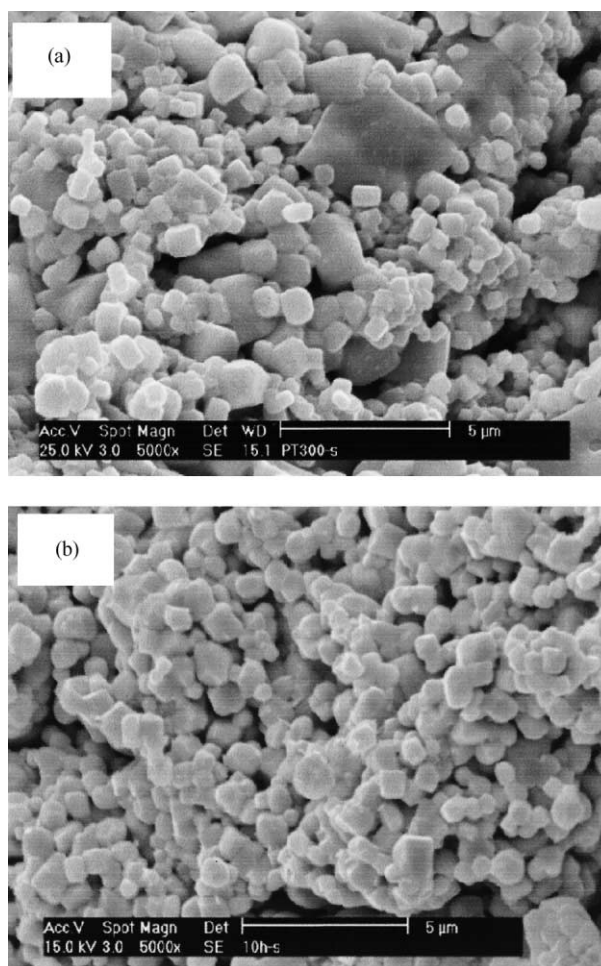


Fig. 5. SEM images of the PbTiO_3 particles derived from calcination at 650 °C for 20 h. (a) From the as-synthesized precursor without prior mechanical activation and (b) from the precursor that was mechanically activated for 10 h prior to calcination.

prior mechanical activation for various time periods. Interestingly, mechanical activation has an apparent impact on the PbTiO_3 powders derived from the amorphous precursor. Fig. 5(a) and (b) show the SEM micrograph of PbTiO_3 powder derived from calcination at 650 °C for 20 h of the PT precursor without and with 10 h of prior mechanical activation, respectively. The PbTiO_3 particles of perovskite structure derived from 10 h of mechanical activation are more uniform (300–500 nm) in sizes than those derived from calcination without prior mechanical activation of the amorphous precursor. The latter consists of PbTiO_3 particles of $\sim 500 \text{ nm}$ in sizes, together with some much coarsened particles of 4–5 μm , apparently due to the particle coarsening at the calcination temperature. It was also observed that the average particle size of PbTiO_3 showed an apparent decrease with increasing mechanical activation, prior to calcination at 650 °C for 20 h. For example, an average particle size of $\sim 250 \text{ nm}$ was observed for the material derived from 20 h of mechanical activation, while the average particle size of the PbTiO_3 derived from 30 h of mechanical

activation was further reduced to about 100 nm. On the basis of these observations, the effects of mechanical activation on the amorphous PT precursor can be considered as follows: (i) The initial stage of mechanical activation (up to 10 h) refines and re-disperses the co-precipitated precursor such that the differential coarsening and particle aggregation are minimized, upon calcination at 650 °C, as a result of the homogenization. This is supported by the observation that the two PbTiO₃ powders shown in Fig. 5(a) and (b) shows similar particle sizes, although the calcination without prior mechanical activation led to formation of some much coarsened particles. (ii) Extended mechanical activation, e.g. up to 20 h and above, triggered the occurrence of PT nuclei, which underwent growth upon calcination at 650 °C. The existence and competition of these nanocrystallites at the calcination temperature refine the resultant particle size, which are demonstrated by the decreasing particle size with increasing mechanical activation time from 20 to 30 h.

4. Conclusions

Mechanical activation at room temperature led to the formation of nanocrystallites of PbTiO₃ of perovskite structure in an amorphous Pb–Ti–O precursor synthesized by co-precipitation. The resultant PbTiO₃ nanocrystallites are

<10 nm in sizes and rounded in morphology. The initial stage of mechanical activation (up to 10 h) refines and re-disperses the co-precipitated precursor such that the differential coarsening and particle aggregation are minimized, upon further calcination at 650 °C. Extended mechanical activation, e.g. up to 20 h and above, triggered the occurrence of PbTiO₃ nanocrystallites, which significantly refined the particle size of PbTiO₃ powder derived from the amorphous precursor by further calcination.

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