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The B-site order-disorder transformation in $Pb(Sc_{1/2}Ta_{1/2})O_3$ triggered by mechanical activation

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Having pioneered mechanical activation on Pb-based relaxor ferroelectrics, we describe a unique order-disorder transformation phenomenon brought about by mechanical activation in Pb-based relaxor ferroelectrics of complex perovskite. B-site disorder in $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) which is traditionally tailored by thermal annealing after sintering at elevated temperatures, can be triggered by mechanical activation. The B-site disorder in $Pb(Sc_{1/2}Ta_{1/2})O_3$ triggered by mechanical activation can well be retained in sintered $Pb(Sc_{1/2}Ta_{1/2})O_3$, leading to an unique ferroelectric transition behavior (e.g., from a normal ferroelectric to relaxor) and a shift in the Curie temperature.

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1. Introduction

B site cation orders in complex perovskites has attracted long interest because of their strong effects on the electric properties [1]. $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) has been used for investigation into B site structural order, where the degree of order can be modified by thermal annealing following sintering at high temperature, allowing studies of the relationship between the structural order and ferroelectric properties [2–4]. Ordered PST shows a normal ferroelectric phase transition at 300 K, while the disordered PST exhibits a relaxor to normal ferroelectric phase transition at ∼280 K [5, 6]. The latter also demonstrates a glassy like dielectric relaxor behavior, which can be fitted to a Vogel-Fulcher relationship, and can be affected by applying an external bias electric field [7–9].

To tailor the degree of B site order in sintered PST, combination of a high temperature sintering (1500°C) and long time annealing at relatively low temperature was commonly practiced. However, this results in loss of volatile PbO [9]. In this paper, we report a completely different approach, where mechanical activation is employed to generate B site disorder. Fabrication of PST with various degree of order is realized by combination of a pre-sinter mechanical activation and subsequently sintering at a temperature of ∼1200°C.

2. Experimental procedures

Commercially available PbO (99% in purity, J. T. Baker Inc.), Sc_2O_3 (99.6% in purity, J. T. Baker Inc.), and Ta_2O_5 (99% in purity, Aldrich, USA) were used as starting materials. PST powder of perovskite structures was synthesized by using the Wolframite precursor method [10], which was then mechanically activated for various time periods from 0–20 h in order to investigate the order-disorder transformation triggered by mechanical activation. PST derived from mechanical activation were then sintered in closed crucibles with a PbO rich atmosphere by powder bedding, in order to avoid the likely loss of PbO by evaporation at the sintering temperatures.

The degree of order in PST was characterized by using an X-ray diffraction (XRD, Cu K_α), where the degree of long-range order (LRO) was calculated on the basis of peak intensity of (200) plane of the perovskite phase and that of the superlattice (111) diffraction peak. Raman spectroscopic studies were employed to further examine the structure disorder. Microstructures of sintered PST ceramics were characterized by scanning electron microscope (SEM, Philips, XL 30). Dielectric properties of sintered PST were characterized using a precision LCR meter (HP 4284A), where silver paste was applied on both side surfaces of PST pellets as electrodes prior to dielectric measurements.

3. Results and discussions

XRD traces of the PST powder derived from the Wolframite route and they subjected to various hours of mechanical activation are shown in Fig. 1a. The diffraction peak at 2θ of 21.7° corresponds to (002) plane the perovskite structure, while the peak at 2θ of 18.8° is from the (111) superlattice plane indicating B site structural order. The superlattice peak decreases gradually in intensity with increasing mechanical activation time, and it has almost completely disappeared upon mechanical activation for 10 h. More interestingly, as shown

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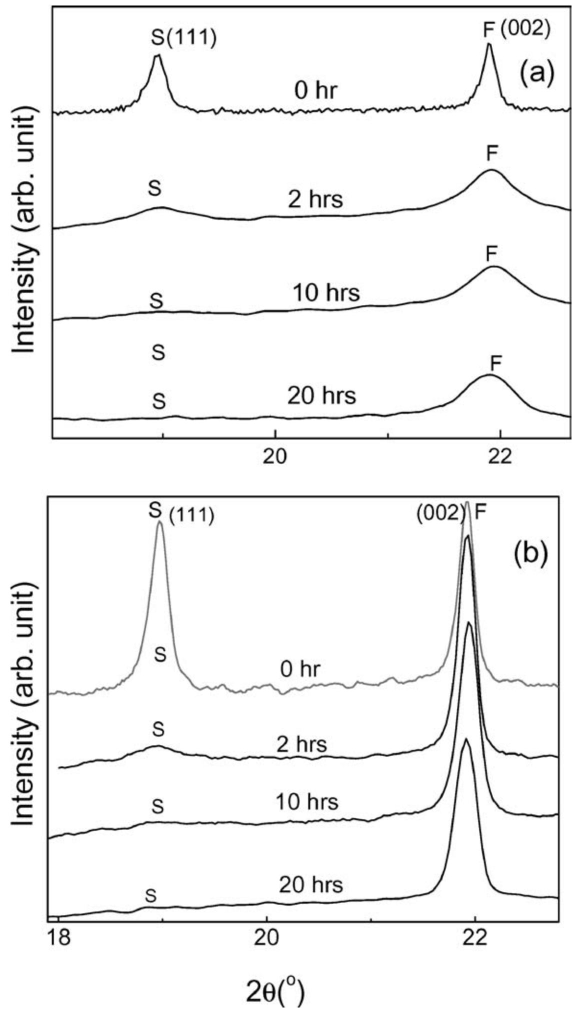

Figure 1 XRD diffraction patterns for PSTs (a) subjected to mechanical activation for various times, and (b) subsequently sintered at 1200°C for 4 h. S: denotes the (111) superlattice diffraction peak from B site cation order; F is the fundamental diffraction patterns of the perovskite structure.

in Fig. 1b, where the B-site disorder created by mechanical activation cannot be eliminated by sintering for 10 h at 1200°C, as indicated by the peak intensity of superlattice. The retention of B-site disorder in sintered PST creates an excellent opportunity for synthesizing PST with a designed degree of B-site disorder for specific ferroelectric and dielectric behaviors, through an appropriate combination of mechanical activation and subsequent sintering at the normal sintering temperature.

Fig. 2 plots the dielectric constant as a function of temperature for PST sintered at 1200°C subjected to various durations of mechanical activation prior to sintering. PST of ordered structure, which is not subjected to any pre-sinter mechanical activation, exhibits a sharp dielectric peak at 20°C, indicating a normal ferroelectric phase transition. With increasing mechanical activation time, an apparent enhancement in frequency dispersion and a sharp rise in peak dielectric constant were observed. The enhanced frequency dispersion and the broadened dielectric peak brought about by mechanical activation demonstrate a relaxor behavior in association with the structural disorder in PST, as confirmed by XRD. At the same time, a relaxor to normal ferroelectric (R-nFE) phase transition is also observed in the PSTs that was subjected to mechanical activation prior to sintering at 1200°C, as indicated by the onset of a sharp drop in dielectric constant at temperatures of ~10°C. This indicates that the dielectric relaxation induced by mechanical activation is closely related to the structural order.

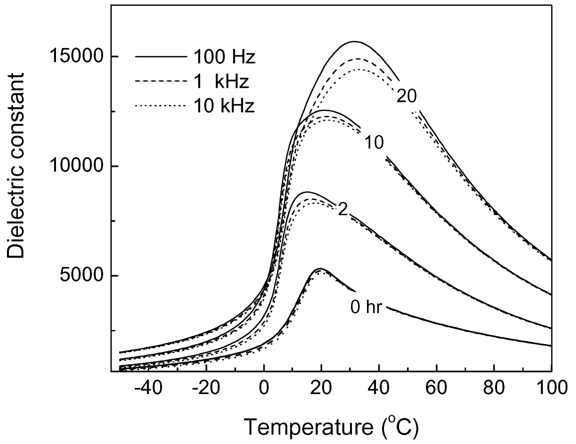

Figure 2 Dielectric constant of the PST derived from mechanical activation and subsequently sintering at 1200°C for 4 h. The dielectric constant varies with the pre-sinter mechanical activation time. Number in each curve denotes mechanical activation time prior to sintering.

The observed retention in B site order of PST is rather different from that in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Pb(Mg_{1/2}W_{1/2})O_3$ (PMN-PMW) [11], where the structure disorder can easily eliminated by thermal annealing. To further examine the stability of structure disorder triggered by mechanical activation, sintered PST derived from 10 h of mechanical activation was further annealed at 1000°C for 10 h. As shown in Fig. 3, the superlattice diffraction peak reappears after the long time annealing. However, it is not fully recovered, indicating a very slow recovery in structural order at the annealing temperature. The observed slow rate of recovery in B-site order suggests a low thermal exchange rate in B site cations in PST, which is governed by B site ordering driving force [4]. Indeed, the driving force for ordering in PMW is much stronger than that of PST,

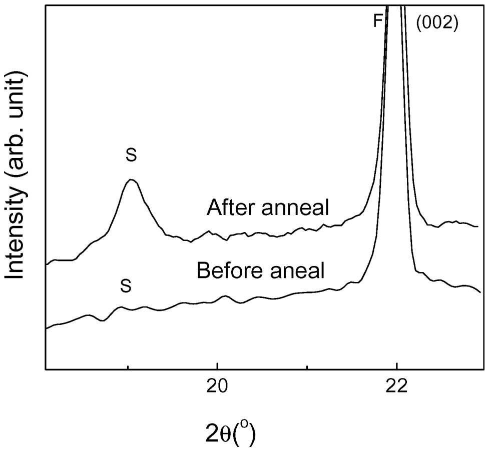

Figure 3 XRD diffraction pattern for PSTs before and after annealing at 1000°C for 10 h, derived from mechanical activation and then sintered at 1200°C.

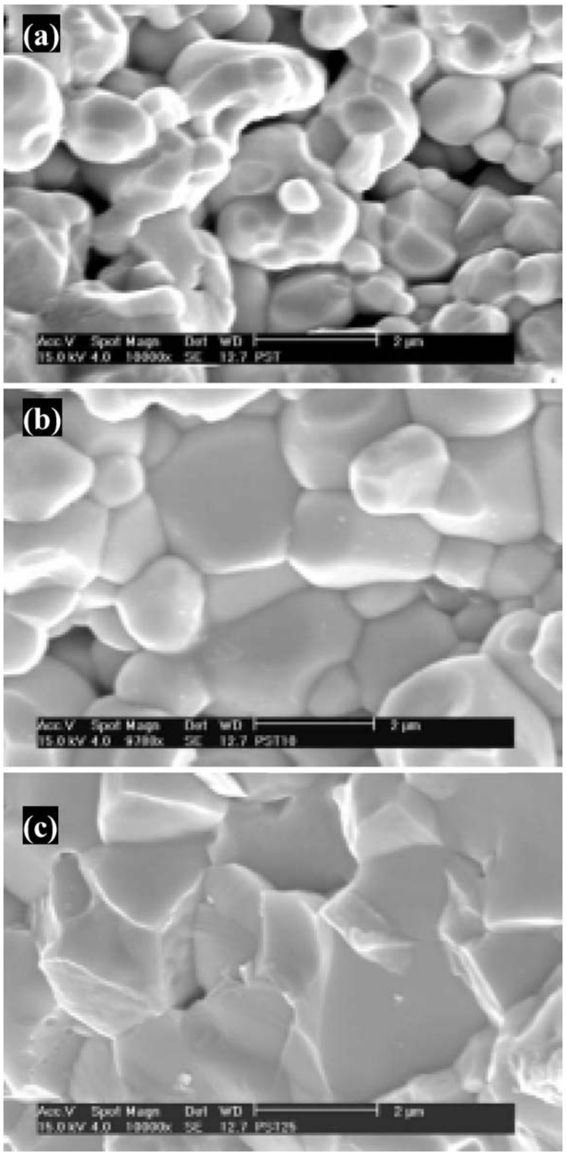

Figure 4 SEM images showing PST subjected to various degree of pre-sinter mechanical activation and then sintered at 1200°C for 4 h: (a) 0 h, (b) 10 h, and (c) 20 h.

because the former has a large charge difference among B site cations. As a result, a much longer annealing time at 1000°C is required to eliminate the structure disorder initially introduced by mechanical activation in PST [4, 11].

Fig. 4 are SEM micrographs showing the fracture surface of PSTs subjected to various hours of pre-sinter mechanical activation. An average particle size of 1.7, 2.2, 3.5 μm was measured for the PST sintered at 1200°C that was indicating mechanically activated for 0, 10, 20 h, respectively, prior to sintering. The sintered density of PST increases monotonously with rising mechanical activation time. A sintered density of 93.1% theoretical was measured for PST subjected 20 h of pre-sinter mechanical activation, compared favorably with 83.5% theoretical for PST without any mechanical activation. The enhancement in sinterability of PST by mechanical activation is attributed to the refinements in particle sizes and creation of structural defects, which greatly enhance the sintering reactivity, leading to an obvious improvement in sintering density of PST.

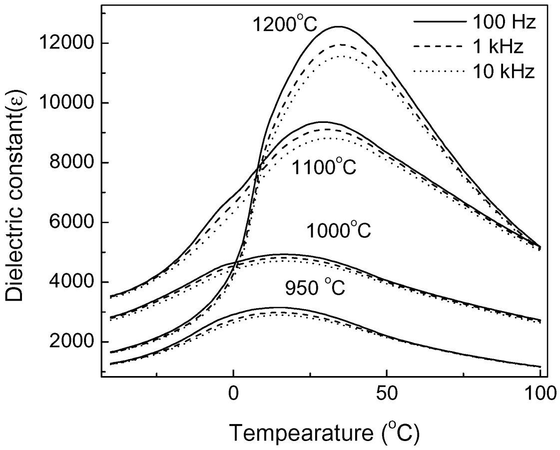

Figure 5 Dielectric constant as a function of temperature for PSTs derived from mechanical activation for 20 h and then sintered at various temperatures.

Dielectric properties of PST can be strongly affected by the microstructural parameters. For example, when the particle size is refined into a nanometer scale, its ferroelectric properties are altered dramatically [12]. However, the grain sizes of the sintered PSTs sintered at 1200°C are far beyond the nanoscale range. Therefore the observed relaxor behavior in association with mechanical activation, are not due to the particle size effect. Instead, the relaxor behavior is due to the disorder structure triggered by mechanical activation.

Fig. 5 plots the dielectric constant as a function of temperature for PST sintered at temperatures at the range of 950 to 1200°C. When sintered at 1200°C, it shows a typical R-nFE phase transition, similar to that in Fig. 2. As the sintering temperature decreases to 1100°C, its dielectric behavior changes significantly. The sharp dielectric drop at around 9.4°C, corresponding to the R-nFE phase transition, has disappeared, and at the same time the dielectric peak at around 34°C is broadened and shifts downwards to 29°C. Further lowering the sintering temperature depresses the dielectric peak and shifts it further downwards. The PST sintered below 1100°C shows a completely relaxor ferroelectric transitions instead of a R-nFE phase transition. Such an R-nFE to relaxor transformation can also occur in partially ordered PST, when grain size is small enough ($\sim$110 nm) [12], suggesting that grain size plays an important role in determining the order disorder transformation and dielectric behaviors.

4. Conclusions

Mechanical activation triggers B site order to disorder transformation in $Pb(Sc_{1/2}Ta_{1/2})O_3$. The structural disorders induced by mechanical activation in PST are rather stable against thermal activation at high sintering temperatures, thereby they can be retained in the electroceramics sintered at 1200°C. PST without any pre-sinter mechanical activation demonstrates a normal ferroelectric transition, while the PST derived from mechanical activation exhibit a relaxor behavior and a R-nFE transition. A designed degree of structure order can then be obtained by an appropriate combination of pre-sinter mechanical activation and sintering at a high temperature.

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