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Non-relaxor responses of highly ordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ crystals

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Abstract

$\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ crystals have been grown by the top seeded solid solution technique, which present pure rhombohedral perovskite structure. The existence of superlattices and the calculation about the chemical order parameter confirm the high order degree of ions occupancy. Unlike previous reports, where $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ takes on typical relaxor behavior, here it exhibits non-relaxor ferroelectric behavior. The domain structure appears full extinction under crossed polarizers when the temperature is more than Curie temperature (68 °C), showing non-relaxor ferroelectric phase transition behavior. The temperature dependence of the dielectric permittivity shows a sharp peak around 70 °C without any trace of relaxor behavior. The conceive field and remnant polarization sharply drop down to zero when the temperature is more than 68 °C.

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1 Introduction

Relaxor ferroelectrics, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST), are characterized by the extraordinary dielectric response, exhibiting high dielectric maximum, broad peak and strong frequency dispersion as a function of temperature, which are different from those of normal ferroelectrics [1-8]. Their high dielectric properties make them suitable for industrial applications [8-10]. Several models have been proposed to explain their unusual dielectric response, including spin glasses, random field interactions and so on [1, 11-18]. According to these models, the compositional fluctuations of B-site cations result in the quenched inhomogeneity. Therefore, nanometer size of chemical order/disorder regions could be generated [8, 9], which persisting at temperatures over the temperature of the dielectric permittivity maximum, are often believed to be the origin of the relaxor behaviour [3, 19]. In $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$ perovskites, it is found that the chemical orders/disorders depend on both the valence and ionic radii differences of B' and B'' cations, which has been summarized as follows: (1) the chemical differences between B' and B'' are large enough for the cations order so as to form superstructure; (2) in some $\text{Pb}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$, 1:1-type compounds, the chemical differences between B' and B'' are close to the critical limit for B-site order/disorder occupancy to modify the degree of ordering by proper thermal annealing, quenching or crystal growth conditions; (3) the $\text{Pb}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$, 1:2 compounds, with smaller chemical differences usually exhibit long-range disorder occupancy [20-22].

As one of the 1:1-type compounds, $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PSN) with chemical

difference between Sc^{3+} (0.745 Å) and Nb^{5+} (0.64 Å) close to the critical limit for B-site order/disorder occupancy was suggested as a suitable starting candidate for studying the contribution of structure order/disorder to diffuse phase transition by Setter and Cross [23]. In the previous reports, PSN ceramics or crystals always exhibit chemical disorder or low degree of order of B-site occupancy, and relaxor dielectric response with broad maxima and frequency dispersion of dielectric permittivity [8-9, 24-30]. Actually, the degree of order of PSN can be changed by thermal annealing and quenching, which was first investigated by Stenger in 1980 [25]. Moreover, crystal growth technique and condition can also influence the order degree. Considering this point, we grew the PSN crystals and investigated their optical and electric responses, which exhibit the inherent non-relaxor ferroelectric response.

2 Experiments

PSN crystals with size of $19 \times 24 \text{ mm}^2$ have been obtained by the top seeded solid solution technique, as shown in Figure 1a. High purity chemicals, PbO , Sc_2O_3 (99.99%) and Nb_2O_5 (99.9%), were weighed according to the stoichiometric compositions of PSN. The mixture of PbO and H_3BO_3 (99.9%) with molar ratio of 3:2 was selected as a flux. Detailed process of crystal growth is the same as other systems reported in our previous works [3, 31-34].

X-ray powder diffraction (XRD) patterns were performed at room temperature by a Rigaku R-axis diffractometer equipped with $\text{Cu K}\alpha$ radiation and a graphite monochromator. The FEI Tecnai F20 FEG microscope was used for transmission electron microscopy (TEM) study. Moreover, fine crystal powder was needed, which

was dispersed in alcohol to form a dilute suspension. One droplet of the suspension was dropped onto a copper grid with carbon support film. A polarized light microscope (LV100POL, Nikon, Japan) equipped with Linkam THMS 600 E hot plate was employed to examine the domain structure and its evolution as the increase of temperature from room temperature (RT) to 200 °C. The optical crystal plates were cut from as grown crystal along [001] direction, which were then grinded and polished to 36 μm in thickness. A computer-controlled Alpha-A broadband dielectric/impedance spectrometer (NovoControl, GmbH) was used to measure dielectric properties. The measurements were carried out at a field of $1V_{\text{rms}}$ as a function of temperature upon heating from -50 °C to 200 °C. An aix-ACCT TF ANALYZER 2000 ferroelectric test system was employed to display the polarization–electrical field hysteresis loops.

3 Results and discussion

The XRD pattern of PSN crystals presents pure perovskite phase, as shown in Figure 1b, indicating the pure rhombohedral (R) perovskite symmetry, with cell parameters $a = 4.09$ Å, $\alpha = 89.96$ °. There are two extra peaks appearing at 18.7° and 36.5° in addition to the fundamental reflection, resulted from the B-site 1:1 order, which are marked by asterisks [25, 35]. These two peaks corresponding to d-spacing values twice as much as those of (111) and (311) major ones can be indexed as $(1/2\ 1/2\ 1/2)$ and $(3/2\ 1/2\ 1/2)$. The existence of superlattice reflections suggests that the prototypic crystal structure is an ordered perovskite with an effective unit cell ($2a_c \times 2a_c \times 2a_c$) doubled in size in all crystallographic axis directions of a simple cubic

perovskite cell ($a_c \times a_c \times a_c$). Here, the subscript “c” refers to the cubic perovskite basic cell. Moreover, the superlattice reflections are further identified by transmission electron microscopy. In the electron diffraction patterns with the $[-110]$, $[1-1-1]$ and $[001]$ zone-axes, as shown in Figure 2, the $(1/2 \ 1/2 \ 1/2)$, $(1/2 \ 0 \ 1/2)$ and $(1/2 \ 1/2 \ 0)$ superlattice diffractions are observed, further confirming the B-site 1:1 order.

The chemical order parameter S was calculated by dividing the ratio of the experimentally observed superlattice $(1/2 \ 1/2 \ 1/2)$ reflection intensity over the fundamental reflection (111) intensity from a parallel plane, by the corresponding calculated ratio for a perfectly ordered sample, that is [3, 23]:

$$S^2 = \frac{\left(\frac{I_{1/21/21/2}}{I_{111}} \right)_{\text{exp}}}{\left(\frac{I_{1/21/21/2}}{I_{111}} \right)_{S=1}}$$

Interestingly, the ratio of $I_{1/21/21/2}/I_{111}$ is calculated to be 0.169 for as grown PSN crystal, which is much higher than the theoretical value 0.102 for a complete ordered ceramic [25], indicating a highly ordered structure. It suggests that something like the density, the size of grain, the grain boundary and so on, may reduce the degree of order of PSN ceramics.

Viewed under crossed polarizers, the domains appear to be in extinction when their slow and fast vibrations direction along the vibration directions of polarizer (P) and analyzer (A). The domain structure and its extinction characterization in (001) PSN crystal plates as a function of temperature is shown in Figure 3. Under crossed polarizers, the field manifests full bright, while the objective table is rotated 45° , it presents all dark, confirming the rhombohedral symmetry of PSN crystal at room

temperature [36]. In optically uniaxial rhombohedral phase, the symmetry axis of spontaneous polarization is aligned along the [111] crystallographic directions. Accordingly, the extinction position (θ) in (001) plates is 45° in the rhombohedral phase.

By heated from room temperature to 200°C , the evolution of domain extinction is studied in the full bright field under crossed polarizers, which exhibits few change until 68°C . However, by continuous heating, the field instantly turns into all dark state, indicating the optical characterization of non-relaxor ferroelectrics. In the temperature range $69\text{--}200^\circ\text{C}$, no variation is found, which demonstrates the stable cubic phase.

The dielectric permittivity (ϵ') of the PSN crystal as a function of temperature at different frequencies (f) is shown in Figure 4. There are sharp dielectric peaks at Curie temperature (T_C) around 70°C with the maximum value about 1.2×10^4 , corresponding to the transition from ferroelectric phase to paraelectric one. The peak of dielectric permittivity is independent of frequency, indicating non-relaxor ferroelectric response. Above Curie temperature, the temperature dependence of the dielectric permittivity well obeys the Curie-Weiss law.

The polarization-electric field (P-E) hysteresis loops of PSN crystal are well developed at the frequency of 2 Hz at different temperatures, as shown in Figure 5a. At room temperature, the polarization reaches its saturation at a bipolar electric field of about ± 7 kV/cm, with almost vertical lines of the loop, indicating the sharp switching of macroscopic domains [37]. The conceive field (E_c) and remnant

polarization (P_r) are 2 kV/cm and 20 $\mu\text{C}/\text{cm}^2$, respectively. Meanwhile, the temperature dependence of ferroelectric parameter of E_c and P_r in PSN crystal is also displayed in Figure 5b. It is obvious that the E_c and P_r show a prompt reduction around 70 °C, indicating non-relaxor ferroelectric characterization.

Both superlattice reflections and chemical order parameter of as grown PSN crystals demonstrate high the order degree of B-site occupancy. Chemical bonding theory of single crystal growth indicates that crystal lattice occupancy is organized by their constituent chemical bonds in an anisotropic way, which experiences thermodynamic bonding formation on the growing interfaces during the growth stage [38-40]. It is believed that the disordered structure is formed first during the growth process of complex $\text{Pb}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$ compounds, which is a non-equilibrium one [41]. The change toward equilibrium phase is through cation diffusion process, which depends greatly on the temperature. If the crystallization temperature is high enough and the hold time is adequately long, the non-equilibrium phase could transform into the equilibrium one [41]. During the process of crystal growth by top seeded solid solution, the crystallization temperature exceeds 1000 °C, and the rate of cooling is small enough (1-2 °C/d). In this condition, the transformation from disorder to order can realize almost completely. Thus, high 1:1 B-site order is found in obtained PSN crystals. The evolution of extinction, dielectric and ferroelectric responses as a function of temperature confirms the absence of diffuse/relaxor behavior, indicating the highly ordered distribution of B-site ions.

4 Conclusions

PSN crystals have been obtained by the top seeded solid solution technique, which presents pure rhombohedral perovskite structure. The highly ordered distribution of B-site ions is confirmed by the existence of the superlattice peaks and the chemical order parameter, which is much larger than the theoretical value in the previous reports. The non-relaxor dielectric and ferroelectric behavior is quite different from the previous reports, where the dielectric and ferroelectric response takes on the relaxor behavior, demonstrating the inherent highly ordered structure of PSN crystals. In conclusion, the obtained PSN crystals are non-relaxor ferroelectrics with highly ordered B-site occupancies.

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Captions

Figure 1 One as-grown PSN Crystal (a) and the X-ray diffuse pattern of PSN crystals at room temperature (b).

Figure 2 Electron diffraction patterns of $(1/2\ 1/2\ 1/2)$ with the $[-110]$ zone-axis (a), $(1/2\ 0\ 1/2)$ with the $[1-1-1]$ zone-axis (b) and $(1/2\ 1/2\ 0)$ with the $[001]$ zone-axis (c).

Figure 3 Micrographs of the (001) PSN crystal plate under crossed polars (shown by arrows) at different temperatures.

Figure 4 Dielectric permittivity of the PSN crystal as a function of temperature at frequencies 1 Hz, 10 Hz, 100 Hz, 1 kHz, 10 kHz and 100 kHz.

Figure 5 Polarization-electric field hysteresis loops of PSN crystal at 2 Hz at different temperatures (a) and the conceive field and remnant polarization as a function of temperature (b).

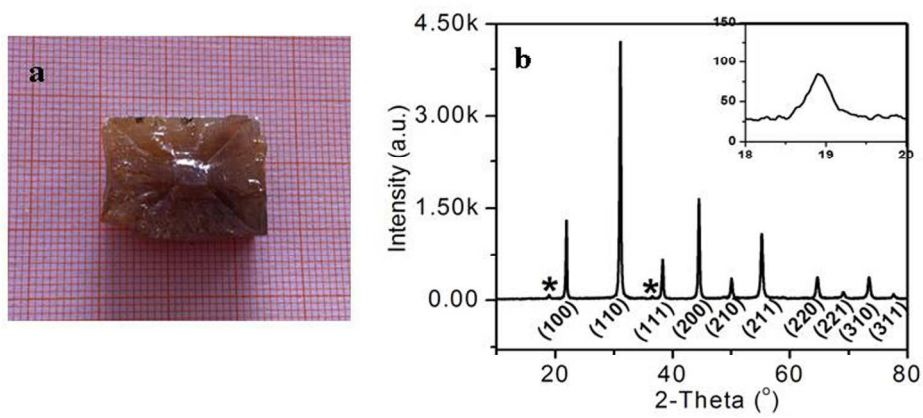
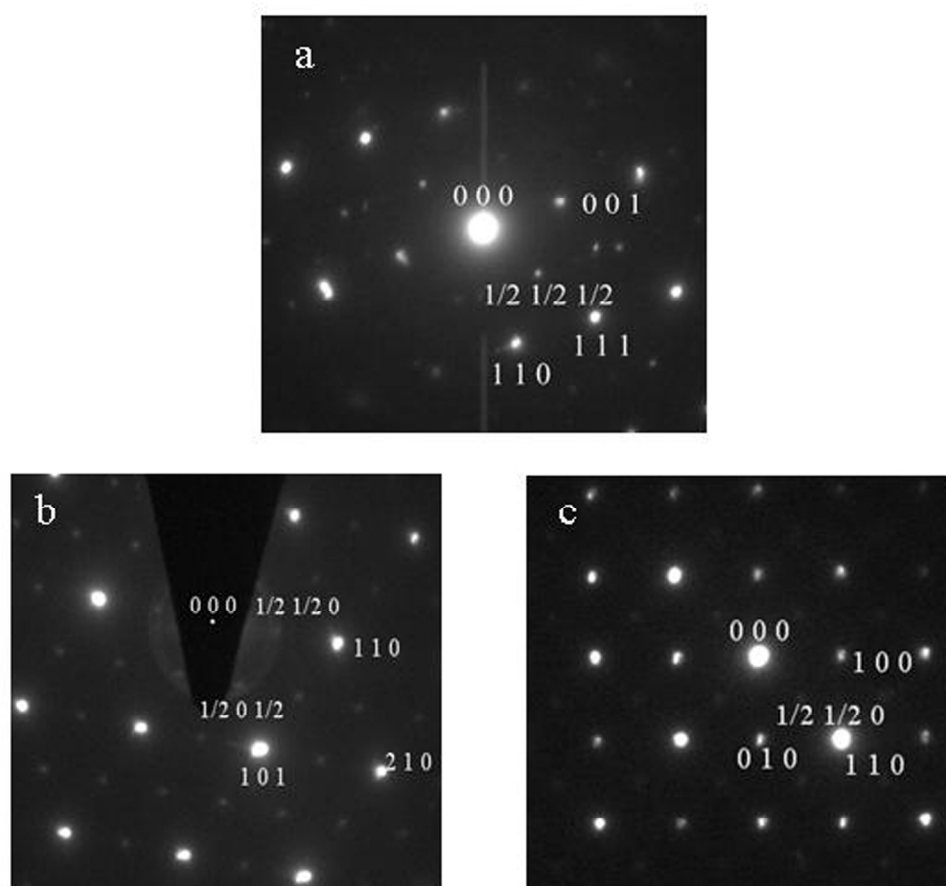
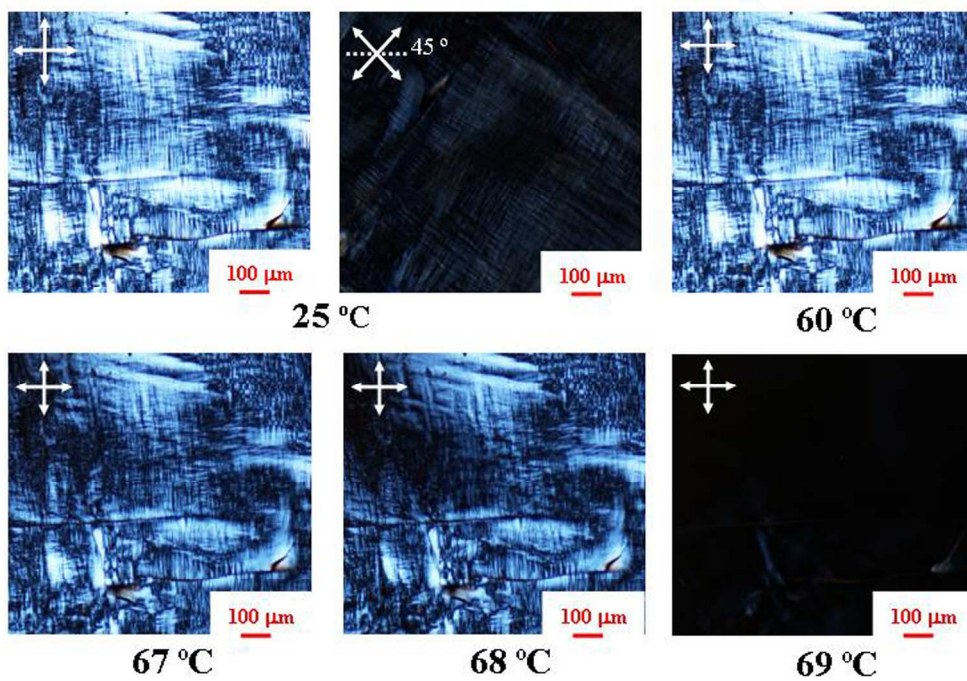


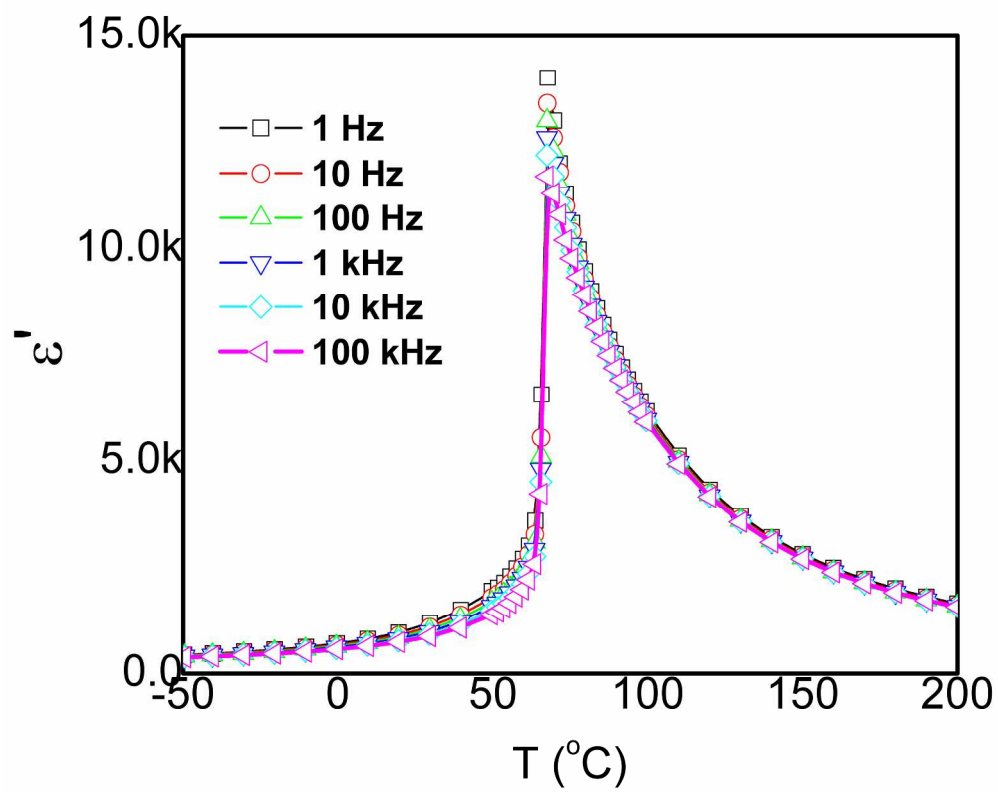
Figure 1 One as-grown PSN Crystal (a) and the X-ray diffuse pattern of PSN crystals at room temperature (b).
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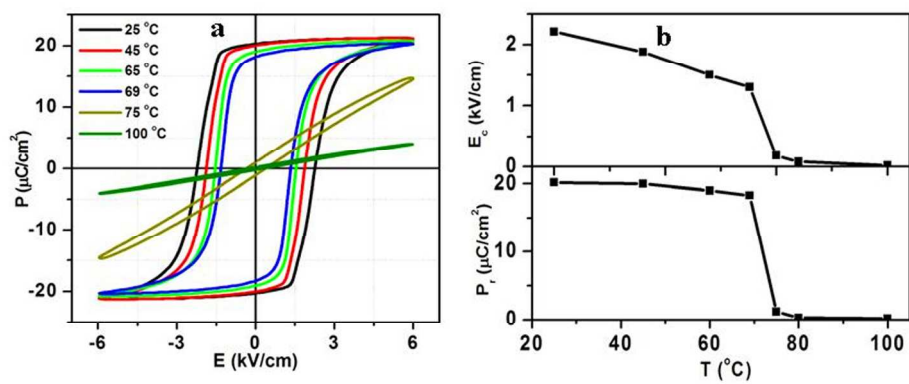
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135x92mm (600 x 600 DPI)



248x212mm (300 x 300 DPI)



105x45mm (600 x 600 DPI)