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Dielectric and piezoelectric properties of relaxor $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ thin films

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Pure perovskite $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ thin films without pyrochlore phase were prepared by the sol-gel method on $\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates. Films exhibited (111) preferred orientation and columnar microstructure. Diffuse phase transitions with permittivity maximum decreasing in value and shifting toward higher temperature with increasing frequency and slim polarization-electric field hysteresis loops typical for relaxors were observed. The maximum field-induced piezoelectric d_{33} coefficient measured with ac electric field of 14 kV/cm was 58 pm/V. The d_{33} -dc electric field relation is virtually hysteresis free. © 2003 American Institute of Physics.

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Relaxor ferroelectrics and their solid solutions with ferroelectric PbTiO_3 (PT) have lately been the focus of intense research interests in view of their application potential and interesting scientific phenomena.¹ Device oriented applications include microelectromechanical systems (MEMS) such as microactuators, microsensors, image transducers, pyroelectric devices, decoupling capacitors, and memory applications such as high-speed nonvolatile solid-state memories.² Relaxor-based thin films are of interest because they exhibit very high dielectric permittivity over a wide temperature range, large electrostrictive strains, and field induced piezoelectric coefficients that are comparable to those of lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) films, in particular, with much smaller hysteresis loss.³⁻⁶

Complex perovskite $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PSN) is a well-known relaxor ferroelectric. PSN with B-cation disorder exhibits a spontaneous ferroelectric-relaxor phase transition around 100 °C and frequency dependent maximum of permittivity ≈ 15 °C above this temperature. If the concentration of lead vacancies is relatively high ($\approx 2\%$) the maximum in permittivity ϵ_{max} is lower ($\epsilon_{\text{max}} = 15\,000$) with respect to stoichiometric disordered material ($\epsilon_{\text{max}} = 40\,000$), the spontaneous transition into ferroelectric phase becomes smeared and less pronounced. The lead deficiency also decreases temperatures of ϵ_{max} and spontaneous phase transition into the ferroelectric phase.⁷ Recently, PSN was shown to be an attractive model material with potential to exhibit interesting engineered properties. Using first-principle calculations, Iniguez and Bellaiche⁸ have shown that large enhancement of the piezoelectric and dielectric properties may be obtained at certain special arrangements of Sc and Nb atoms.

In general, thin films of relaxor materials, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) (Refs. 4 and 5) and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST),⁹ exhibit properties that are inferior

to those of bulk materials, although relaxor characteristics are preserved. Thus, investigation of the thin film relaxor is of interest as it can shed light on the physical and chemical origins of relaxor phenomena. However, preparation of Pb-based thin relaxor films is difficult due to the tendency of these materials to form pyrochlore phases, lose lead, and because these materials generally require very high processing temperatures that are incompatible with silicon-based technologies.⁶

In this letter, we report on preparation of pure PSN thin films without any second phases. The crystal structure and microstructure of the films are examined and are found to be of critical importance for obtaining good electromechanical properties. Field induced piezoelectric effect and dielectric properties are investigated.

PSN thin films were prepared on $\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates by a modified sol-gel method. The precursor solutions were prepared under a controlled inert gas atmosphere [$\text{Ar}(g)$ of 99.998% purity] using Schlenk tubes and vacuum line techniques. Lead acetate trihydrate [$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$], scandium acetate hydrate [$\text{Sc}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$] and niobium ethoxide [$\text{Nb}(\text{C}_2\text{H}_5\text{O})_5$] were used as precursor materials and purified anhydrous 2-methoxyethanol as solvent. Anhydrous lead acetate was prepared by refluxing with anhydrous 2-methoxyethanol. To compensate the lead loss during thermal annealing, 15 mol % excess lead was added to the precursor solution. Anhydrous scandium acetate was obtained by refluxing with acetic anhydride and drying under vacuum and niobium ethoxide was purified by vacuum distillations. First, anhydrous scandium acetate and niobium ethoxide were separately dissolved in solvents and combined at room temperature. Anhydrous lead acetate was dissolved in anhydrous 2-methoxyethanol. This lead solution and Sc-Nb mixed solution were continuously reacted to a final concentration of 0.35 M by refluxing and multiple distillations.

The PSN thin films were deposited on

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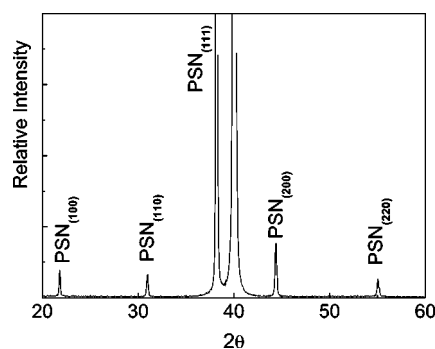


FIG. 1. X-ray diffraction pattern of a 720-nm-thick PSN thin film crystallized at 700 °C for 1 min on $\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrate.

$\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates via spin coating. A 5-nm-thick TiO_2 seed layer was sputter deposited on a Pt bottom electrode. After two-step pyrolysis heat treatment at 220 °C for 2 min and 380 °C for 2 min, the films were subjected to rapid thermal annealing in two steps: densification at 670 °C for 10 min after annealing at 700 °C for 1 min. The orientation and microstructural analysis of the films were conducted by x-ray diffraction (XRD) and scanning electron microscopy (SEM). For electrical measurements, Pt top electrodes (590 μm in diameter) were deposited by the sputtering method at room temperature and annealed at 650 °C for 15 min. The polarization–electric field (P – E) curves were measured using a commercial system. To measure the dielectric constants, an impedance analyzer and a chamber with controlled heating and cooling rates were used. During the measurements, the temperature of the sample was detected with a Pt 100 probe. The piezoelectric coefficient was investigated using a modified Mach–Zender laser interferometer.¹⁰

Figure 1 shows the XRD pattern of a 720-nm-thick PSN film crystallized at 700 °C for 1 min on a $\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrate. PSN films have the (111) preferred orientation of about 90% and present, within detection limit of XRD, a pure perovskite phase without the presence of pyrochlore and PbO_x phases. The addition of 15 mol % excess lead acetate in precursor solution appears suitable to successfully compensate most of the lead loss during crystallization. Even though the TiO_2 seed layers were used to reduce the temperature of phase formation, pure perovskite PSN films were obtained between 670 and 800 °C, which is somewhat higher than the phase formation temperature (about 600–650 °C) of PZT thin films on the same substrate.

Examination of films using SEM did not reveal traces of PbO_x and pyrochlore phases, as shown in SEM micrographs of the plan- and cross-sectional views, Fig. 2. Dense columnar microstructures without cracks and pores are observed. Distribution of grain size is about 150–500 nm. The columnar growth suggests that nucleation and growth of a perovskite phase start from the interface between the PSN film and TiO_2/Pt substrate. As shown in the Figs. 1 and 2, a 5-nm-thick TiO_2 seed layer may enhance the low temperature nucleation and (111)-oriented columnar growth.¹¹

Figure 3 shows the temperature dependence of the relative permittivity and dielectric loss of a 720-nm-thick PSN thin film at various frequencies. Measurements were made at

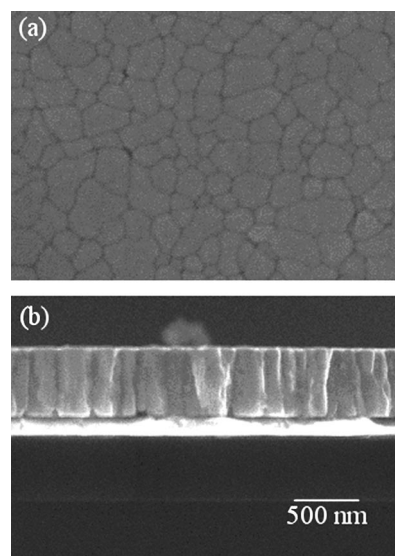


FIG. 2. Scanning electron micrographs of the (a) plan-view and (b) cross-sectional view of a (111)-oriented PSN thin film.

1 kV/cm. The Pt top electrode was postannealed in oxygen at 650 °C for 15 min to assure a good adhesion between PSN films and electrodes and reduce the frequency dispersion above T_{max} .⁵ Relaxor-like behavior is clearly indicated, including diffuse permittivity maximum, frequency dispersion of the dielectric permittivity below the temperature where permittivity reaches maximum (T_{max}), shift of the ϵ_{max} to higher temperatures with increasing frequencies, and deviation from the Curie–Weiss law above T_{max} (Fig. 3). Even though PSN films show evident relaxor behavior, T_{max} is shifted to lower temperature (about 10 °C at 1 kHz) and the maximum permittivity of PSN films ($\epsilon_{\text{max}}=3450$) is lower than in bulk PSN. The dielectric loss factor decreases monotonically and does not exhibit a peak at T_{max} , as observed in bulk material.⁷ The reasons for different behaviors of thin films and bulk materials is presently not clear. It may result from undetected small amounts of residual pyrochlore or PbO_x phase or defects in surface and within films that can reduce the permittivity even if they are not detected by XRD, SEM, and transmission electron microscopy (TEM); clamping of the thin films by the substrate (strain effect),¹² “dead”

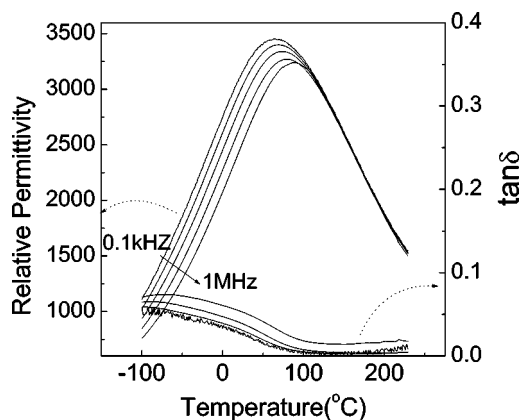


FIG. 3. Temperature dependence of the relative permittivity and dielectric loss of a 720-nm-thick PSN thin film crystallized at 700 °C for 1 min on a $\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrate at various frequencies (Measurements were made at 1 kV/cm).

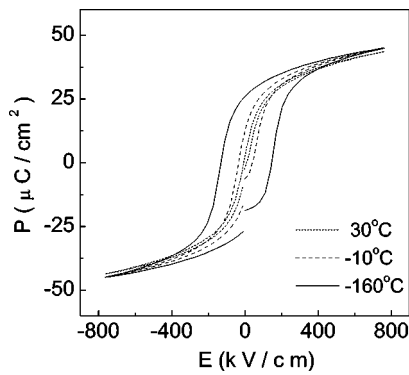


FIG. 4. Polarization–electric field hysteresis loops of 720-nm-thick PSN thin films measured at various temperatures during cooling.

layer between PSN film and substrate,¹³ the lower sintering temperature in films (700 °C) compared to that of the bulk materials (1500 °C), which may have an effect on different distribution of atoms throughout the thin film and bulk material. In the case of PSN, it is tempting to attribute lower permittivity, reduction in T_{\max} and apparent absence of spontaneous ferroelectric-relaxor phase transition to presence of lead vacancies, as observed in bulk materials.⁷ However, these effects in thin films appear to be very large and further studies are needed to verify whether they can be explained solely on the basis of increased concentration of lead vacancies.

Polarization hysteresis loops of 720-nm-thick PSN thin films as a function of ac electric field (E_{ac}) at various temperatures during cooling are displayed in Fig. 4. At room temperature, well-saturated slim hysteresis loops are observed indicating typical relaxor behavior. As the temperature decreases, the loop opens up and the remnant polarization (P_r) and coercive field (E_c) increase. A ferroelectric hysteresis loop with P_r of 27 $\mu\text{C}/\text{cm}^2$ and E_c of 149 kV/cm is observed at -160°C . The applied electric field of PSN thin films (750 kV/cm) is much higher than one of the bulk capacitors (7 kV/cm). However, these results indicate the presence of long-range cooperation between polar regions and the macrodomain ferroelectric state at low temperatures.⁷

Even though relaxors are centrosymmetric in the nonferroelectric state, a large piezoelectric response may be induced by application of external dc electric field.¹⁴ Figure 5 shows the dc electric field (E_{dc}) induced piezoelectric coefficient (d_{33}) of 720-nm-thick PSN thin films. The ac field (14 kV/cm) used for measurements of d_{33} was applied as the dc bias field changed from -13 to 13 MV/m. The d_{33} – E_{dc} curve exhibits a slim hysteresis loop, as expected for a material without ferroelectric domains. The maximum d_{33} value is 58 pm/V, comparable to that in PZT films. Strong asymmetry of the d_{33} – E_{dc} curve is probably a consequence of the self-polarization, as already observed in other relaxor films.^{5,14} A relatively low value of d_{33} for a relaxor material is directly related to the low dielectric permittivity and film clamping by the substrate.⁵

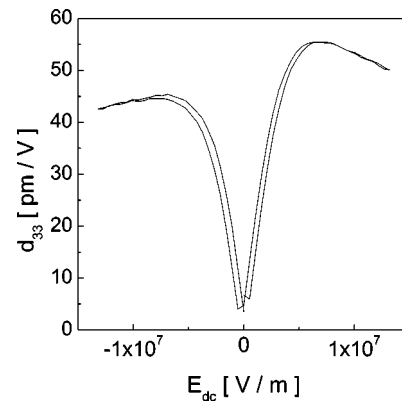


FIG. 5. Piezoelectric coefficient (d_{33}) vs dc electric field (E_{dc}) for a 720-nm-thick PSN thin film crystallized at 700 °C for 1 min on a $\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrate. The ac field (amplitude=14 kV/cm and frequency=1 kHz) used for measurements of d_{33} was superposed on the various dc biases.

In summary, using the strict control of heat treatments (two-step pyrolysis and annealing) and oxide seed layer (a 5-nm-thick TiO_2), it was possible to prepare second-phase-free perovskite PSN thin films with (111) preferred orientation on $\text{TiO}_2/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates by modified sol-gel processing. PSN thin films showed the typical and well-developed relaxor-like behavior. However, the values of permittivity and piezoelectric coefficient are inferior to those in bulk material, which is a common feature of all relaxor thin films reported so far. The reasons for this are presently not clear and further studies are in progress to answer these questions.¹⁵

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