

Synthesis and characterizations of the $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ solid solution ceramics

Y.-H. Bing · Z.-G. Ye

Published online: 11 September 2007
© Springer Science + Business Media, LLC 2007

Abstract We report a systematic study of the $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ (PSN–PT) solid solution in the form of ceramics with compositions at or near the morphotropic phase boundary (MPB) region ($0.35 \leq x \leq 0.50$). The PSN–PT ceramics have been synthesized by an improved two-step wolframite precursor method. The synthetic process has been optimized in terms of calcining and sintering conditions. Both dielectric permittivity measurements and differential scanning calorimetry (DSC) show a clear peak at T_C , at which the transition from the paraelectric to ferroelectric phase takes place. Interestingly, the solid solution of the MPB compositions displays a $T_C > 200$ °C, i.e. higher than the T_C of the $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ solid solutions, making the PSN–PT system very promising piezoelectric and ferroelectric materials for high-temperature applications. A dielectric maximum as high as 50,000 is obtained for the 0.65PSN–0.35PT ceramic with losses smaller than 0.05. The values of the remnant polarization and the strain level of the PSN–PT ceramics are comparable to those of the PZT ceramics.

Keywords $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ · Morphotropic phase boundary · Wolframite precursor method · Piezoelectric and ferroelectric properties

1 Introduction

Intensive studies of the $\text{PbZrO}_3-x\text{PbTiO}_3$ (PZT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN–PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN–PT) solid solution systems [1–3] have revealed that the outstanding dielectric and piezoelectric properties occur in the compositions at or near the so-called morphotropic phase boundary (MPB), making them excellent materials for applications as capacitors, sensors, actuators and other high-performance piezoelectric devices. The solid solution system of $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ (PSN–PT) has not been well studied compared with the PMN–PT and PZN–PT systems. The phase diagram of the PSN–PT system was first reported by Tennery et al. [4]. It shows a Curie temperature $T_C \approx 240$ – 260 °C (with compositions of $x \geq 0.35$), which is higher than that ($T_C < 170$ °C) of the PMN–PT and PZN–PT systems. This represents an important advantage for potential application in many areas that requires a broad temperature range, such as electromechanical transducers for ultrasonic medical imaging.

Only few studies were carried out on the PSN–PT solid solution. Yamashita [5–6] reported the PSN–PT and Nb-doped PSN–PT ceramics with a dielectric maximum (ϵ_{max}) of 39,100 and electromechanical coupling factors of $k_p = 71\%$ and $k_{33} = 76\%$ in the compositions around the MPB. The value of k_p was the highest found in any piezoceramics. It has been noticed from the earlier studies [4, 6] that the dielectric and piezoelectric properties of PSN–PT closely depend on the quality of the ceramics. The difficulties encountered so far in preparing high-quality PSN–

Y.-H. Bing · Z.-G. Ye (✉)
Department of Chemistry, Simon Fraser University,
8888 University Drive,
Burnaby, BC, V5A 1S6, Canada
e-mail: zye@sfu.ca

PT ceramics explain the inferior performance reported by most researchers. Moreover, the preparation of the pure perovskite phase of $(1-x)\text{PSN}-x\text{PT}$ is crucial for the phase analysis and thereby for the determination of the MPB phase diagram due to the complex phase mixture in the MPB region. It is expected that different phase components in the MPB region will affect the local structure and hence the properties of PSN–PT. Therefore, it is rewarding to systematically investigate the synthesis of the PSN–PT ceramics.

In this work, we report the synthesis of the $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ ceramics with compositions near or in the MPB region, i.e. $0.35 \leq x \leq 0.50$, and the characterizations of the $(1-x)\text{PSN}-x\text{PT}$ ceramics by means of differential scanning calorimetry (DSC), and dielectric, ferroelectric and piezoelectric measurements.

2 Experiment

2.1 Synthesis of $(1-x)\text{PSN}-x\text{PT}$ ceramics

The PSN–PT ceramics with the compositions of $x=0.35, 0.37, 0.38, 0.39, 0.40, 0.41, 0.42, 0.45,$ and 0.50 were synthesized by the wolframite precursor method. The two B-site oxides, Sc_2O_3 (99.99%) and Nb_2O_5 (99.99%), were pre-reacted to form a wolframite compound ScNbO_4 . The ScNbO_4 powder was then mixed with PbO (99.99%) and TiO_2 (99.99%) in stoichiometric amounts to form the complex perovskite compound. A 2% excess of PbO was introduced into the mixture powder to compensate for the PbO loss. In addition, the mixture is placed into an alumina crucible covered with an alumina lid. The PSN–PT powders were calcined at 840°C for 2 h. Polyvinyl alcohol (PVA) of 3–7 wt% of the total weight of the PSN–PT powder was added before the mould pressing. The disk-shaped pellets with a diameter of 15 mm were obtained. The pellets were then heated up at a rate of $200^\circ\text{C}/\text{h}$ and kept at 800°C for 1.5 h to remove the PVA binder in order to avoid the presence of porous structure in the resulting ceramic samples. The PSN–PT pellets were sintered at $1270\text{--}1280^\circ\text{C}$ for 8 h for further densification in a PbO -rich environment created within a sealed Al_2O_3 crucible. Under these sintering conditions, the resulting PSN–PT ceramics show a shrinkage of about 13% in diameter. The relative density of the ceramics measured by the Archimedes method is higher than 95% (of the theoretical value).

After sintering, the ceramic pellets were polished with diamond paste (9 μm) and cleaned in an ultrasonic bath. To eliminate the possible strains caused by polishing and cleaning, the samples were annealed at 700°C for 2 h. For X-ray diffraction, selected ceramic pieces were slowly ground into fine powder in order to obtain a better averaging of the data.

2.2 Characterization procedures

X-ray diffraction (XRD) was performed on a Philips diffractometer with $\text{Cu K}\alpha$ radiation. The data were collected with step scans at 0.02° intervals over an angular region from 10° to 80° and a count time of 2 s. Temperature dependences of the heat flow of the $(1-x)\text{PSN}-x\text{PT}$ ceramics were measured on a differential scanning calorimeter (DSC6200, Seiko Exstar). Approximately 60 mg of small crushed pieces of ceramics of each sample were used as specimens and a $10^\circ\text{C}/\text{min}$ heating and cooling rate was employed.

The dielectric permittivity as a function of temperature at various frequencies (from 10 to 100 kHz) was measured from 400°C down to 10°C at $2\text{--}3^\circ\text{C}$ intervals by means of an Alpha High Resolution Dielectric/Impedance Analyzer (NovoControl). The stabilization of temperature was within 0.1°C . For the dielectric, ferroelectric and piezoelectric measurements, the circular surfaces of the samples were sputtered with gold layers as electrodes and two gold wires were attached to the electrodes with silver paste.

3 Results and discussion

Figure 1 shows the XRD patterns of the $(1-x)\text{PSN}-x\text{PT}$ ceramics with the compositions of $x=0.35, 0.37, 0.38, 0.39, 0.40, 0.41, 0.42, 0.45,$ and 0.50 , from which we can draw the following conclusions: (1) all ceramics show a clean perovskite phase; (2) for the composition $x=0.45$, the tetragonal splits are visible on the cubic (100), (110), (200) (210) and (112) peaks, and these splits become more clear for the composition $x=0.50$; (3) for $x=0.42$, a broadened peak with asymmetrical profile is observed for the cubic (200), (210) and (112) reflections; (4) apparently, the symmetry of the phase gradually changes from rhombohedral to tetragonal upon increasing the Ti-content from $x=0.35$ to $x=0.50$.

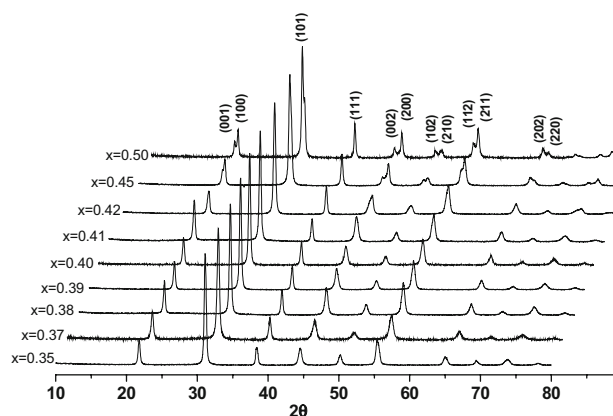


Fig. 1 XRD patterns of the $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ ceramics with compositions around the MPB

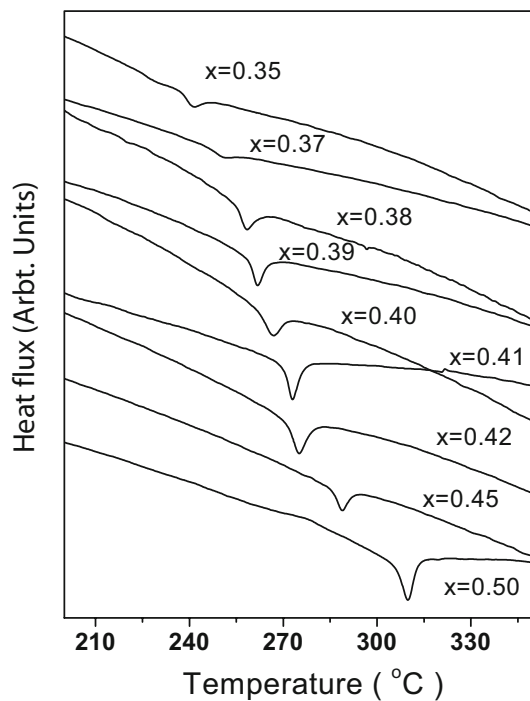


Fig. 2 DSC curves for the $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ ceramics with the compositions of $x=0.35-0.50$

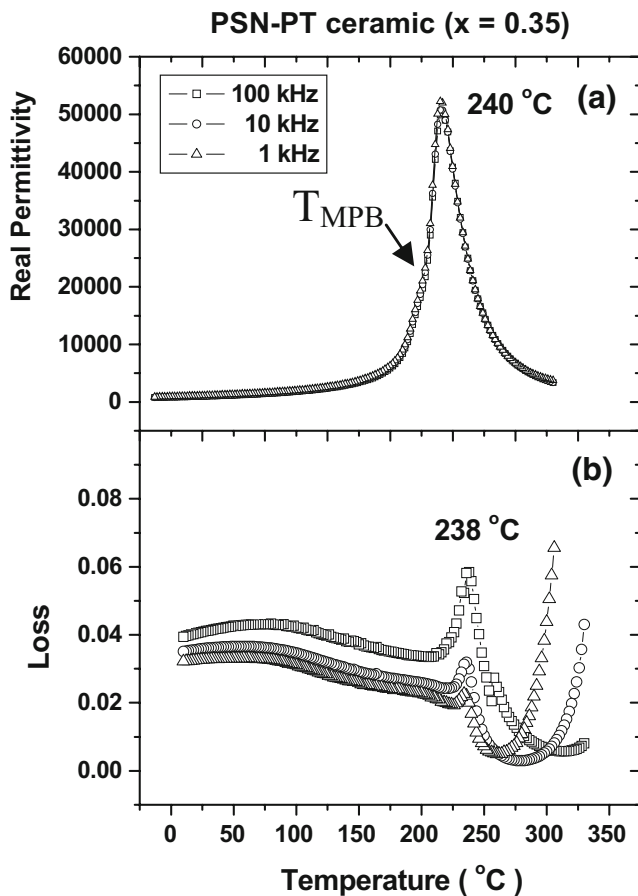


Fig. 3 The real permittivity (a) and losses (b) at the measured frequencies of 1, 10, and 100 kHz for a 0.65PSN–0.35PT ceramic

Figure 2 shows the plots of the DSC measurements upon heating. The thermal events detected by the DSC measurements with a sharp anomaly indicate a structural phase transition for all the samples studied. An additional weak anomaly is observed on the low temperature side of the major DSC peak for $x=0.35$, which corresponds to the morphotropic phase transition temperature T_{MPB} , also observed in the dielectric permittivity measurements (see details in the following text).

The temperature and frequency dependences of the dielectric permittivity were measured on unpoled $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ ceramics. Figure 3 shows, as an example, the real permittivity and losses as a function of temperature at the frequencies of 1, 10, and 100 kHz for the

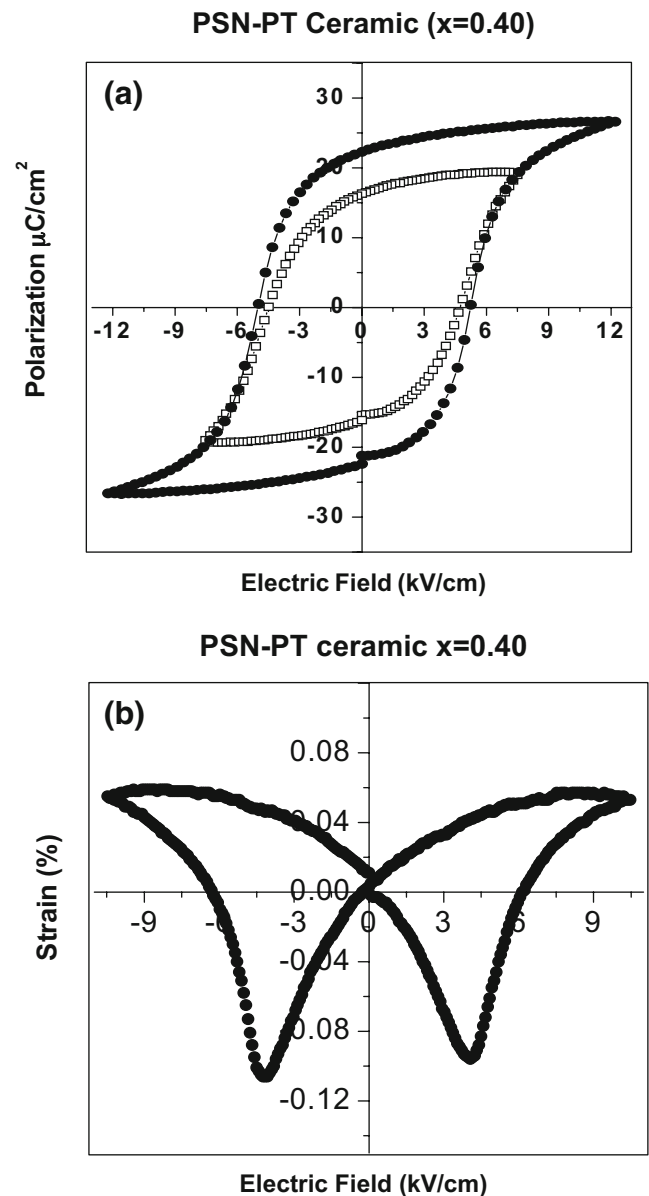


Fig. 4 (a) Typical P–E hysteresis loops and (b) strain–electric field variation, for a 0.60PSN–0.40PT ceramic under a bipolar drive

compositions of 35 mol% PbTiO₃. A sharp peak of the real permittivity appears at the ferroelectric Curie temperature, T_C (or T_{\max})=240 °C, which is higher than the T_C of PMN–PT or PZN–PT of MPB compositions. No frequency dispersion of the real permittivity can be observed in the whole temperature range near and below the dielectric maximum (T_{\max}), indicating that the PSN–PT ceramics with compositions $x>0.35$ behave mostly like normal ferroelectrics.

The sharp transition also points to the high-quality of the ceramics. However, frequency dispersion in the loss data can be observed. This suggests that PSN–PT with compositions near or in the MPB region still retains some degrees of relaxor characters. A slight change in the slope of the real permittivity can be noticed, which indicates a possible phase transition related to the presence of MPB. This shoulder-like anomaly appears at a lower temperature in other compositions ($0.35\leq x\leq 0.42$). More detailed investigation of the complex phase transition behaviour around MPB is underway. The T_C obtained from the dielectric measurements for all the compositions studied is in good agreement with that obtained from DSC (Fig. 2) and, as expected, it increases linearly as a function of the PbTiO₃ content.

PSN–PT samples with compositions near or in the MPB are confirmed to be ferroelectric at room temperature by the polarization-electric field measurements. Typical hysteresis loops are displayed in 0.60PSN–0.40PT at different applied electric fields (± 7.5 and ± 12 kV/cm), as shown in Fig. 4(a). The remnant polarization reaches $P_r\approx 22$ $\mu\text{C}/\text{cm}^2$ under a drive of $E\approx\pm 12$ kV/cm with a coercive field of $E_C\approx 5$ kV/cm. Fig. 4(b) shows the variation of strain as a function of bipolar electric field for the same sample. It displays a symmetric “butterfly” loop, resulting from the bipolar ferroelectric switching behaviour. A peak-to-peak strain value of 0.15% is obtained at $E=\pm 10$ kV/cm.

4 Summary

The solid solution of $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3-x\text{PbTiO}_3$ (PSN–PT) with compositions near or in the morphotropic phase boundary (MPB) region ($0.35\leq x\leq 0.50$) has been synthesized in the pure perovskite phase by an improved two-step wolframite precursor method. These materials are found to be promising candidates for high- T_C and high-performance piezoelectrics. The dielectric permittivity measurements and the differential scanning calorimetry (DSC) show a clear peak at T_C , at which the transition from the paraelectric to ferroelectric phase takes place upon cooling. The characterization of the dielectric, piezoelectric and ferroelectric properties shows that the performance of the PSN–PT ceramics is comparable with the PZT ceramics. More interestingly, the T_C (≥ 240 °C) of the MPB compositions is higher than that of the PMN–PT and PZN–PT systems, making the PSN–PT system particularly promising as high- T_C and high-performance piezoelectric materials.

Acknowledgement This work was supported by the U.S. Office of Naval Research (N00014-06-1-0166).

References

1. B. Jaffe, W.R. Cook, H. Jaffe, *Piezoelectric Ceramics* (Academic Press, London, 1971)
2. J. Kuwata, K. Uchino, S. Nomura, *Ferroelectrics* **37**, 579 (1981)
3. S.W. Choi, T.R. Shrout, S.J. Jang, A.S. Bhalla, *Ferroelectrics* **100**, 29 (1989)
4. V. J. Tennery, K. W. Hang, and R. E. Novak, *J. Am. Ceram. Soc.* **51**(12), 671 (1968)
5. Y. Yamashita, *Jpn. J. Appl. Phys.* **33**, 5328 (1994)
6. Y. Yamashita, *Jpn. J. Appl. Phys.* **33**, 4652 (1994)