

# Phase formation, microstructure and physical properties of lead iron scandium niobate

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Received 21 August 2004; received in revised form 16 November 2004; accepted 26 November 2004

Available online 19 January 2005

## Abstract

Lead iron scandium niobate,  $\text{Pb}(\text{Fe}_{1/4}\text{Sc}_{1/4}\text{Nb}_{1/2})\text{O}_3$  (PFScN), ceramics with pure perovskite phase were produced by conventional solid-state reaction method via a B-site oxide mixing route. Attention is focused on synthesis conditions, where sintering temperature exhibits a pronounced effect on phase formation, density, microstructure and physical properties of the sintered PFScN ceramics. Large bulk density (>95% of the theoretical density) and optimized dielectric properties can be obtained under sintering conditions of 1140–1180 °C for 2 h. Although synthesis conditions have been tailored to optimization, strong frequency dispersion of the dielectric behavior is observed in the sintered PFScN ceramics, which is considered correlating with the possible existence of residual semi-conductive  $\text{FeNbO}_4$  and/or  $\text{ScNbO}_4$  compounds and the thermally activated space-charge polarization resulted from the partial reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions during sintering. © 2004 Elsevier Ltd. All rights reserved.

*Keywords:*  $\text{Pb}(\text{Fe}, \text{Sc}, \text{Nb})\text{O}_3$ ; Sintering; Microstructure; Dielectric properties; Ferroelectric properties

## 1. Introduction

Relaxor ferroelectrics have attracted intensive research attention due to the high and nearly temperature insensitive dielectric and excellent piezoelectric properties, which make them applicable in the multi-layer capacitors, transducers and actuators applications.<sup>1–3</sup> The main structural feature of relaxors, which undergoes structural phase transition during thermal cycle, is the random occupation of equivalent crystallographic positions by different heterovalent ions. This chemical disorder results in the destruction of normal ferroelectric phase transition and the appearance of physical properties similar to those of disordered magnets.<sup>4</sup> The associated dielectric behavior exhibits broad and frequency-dispersive dielectric peaks where the temperature of dielectric maximum ( $T_m$ ) decreases with frequency accompanied with strong di-

electric dispersion at temperatures around and below the  $T_m$ . The relaxor states are then characterized by the frustration of local polarizations, which can prevent long-range ferroelectric ordering from developing completely.<sup>4</sup> The relaxor behavior is usually attributed to the polar clusters and/or the nanoscopic inhomogeneity induced by short-range occupational ordering on the equivalent crystallographic positions of the perovskite structure.<sup>2,5</sup>

Among lead-based complex perovskite relaxors, 1:1-type compounds  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) and  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PScN) attract our interest. PFN exhibits large dielectric constant and low-temperature sintering capability, which crystallizes into rhombohedral structure (space group  $R3m$ ,  $a = 4.0123 \text{ \AA}$  and  $\alpha = 89.98^\circ$ )<sup>6</sup> and undergoes a diffused phase transition at 112 °C to cubic structure (space group  $Pm3m$ ,  $a = 4.010 \text{ \AA}$ ).<sup>7</sup> Although PFN is compositionally disordered ferroelectric, it does not exhibit apparent dispersion of the  $T_m$  with frequency albeit discontinuous change in dielectric constant appears in the relaxor-type diffused dielectric constant peak. PScN is typical ferroelectric relaxor with the  $T_m$  at around 90 °C,<sup>8–10</sup> which deserves special investiga-

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tion since the degree of ordering of the B-site cations can be controlled by thermal treatment.<sup>4</sup> The arrangement of heterovalent cations, their electrostatic interactions and the stabilized structure greatly influence dielectric behavior and electromechanical response, which provide promising directions for future experimental and theoretical research. In the  $(1-x)\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 - x\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  solid solution, a morphotropic phase boundary (MPB) exists at an appropriate composition. The structure of MPB is considered to be a mixing of two adjacent ferroelectric phases and materials with compositions near to the boundary are of major importance from fundamental as well as technological viewpoints, since materials with the MPB composition are expected to exhibit enhanced dielectric constant and electromechanical-coupled factor, which are stable over a wide temperature range. An up-to-date investigation discovers a third phase with a lower symmetry (monoclinic and orthorhombic phases) existing around the MPB boundary in the relaxor-based ferroelectrics, which completely changes the MPB picture since the polarization vector is no longer constrained to lie along a symmetry axis, as in rhombohedral and tetragonal structures, but instead can rotate within a monoclinic plane.<sup>4,5,11–13</sup> Such structure character loosens polarization and softens material, leading to the extraordinary enhanced dielectric and piezoelectric response.<sup>5</sup>

In this paper, we report the synthesis, phase structure and characterization of  $\text{Pb}(\text{Fe}_{1/4}\text{Sc}_{1/4}\text{Nb}_{1/2})\text{O}_3$  (PFScN) ceramics fabricated by conventional ceramic processing via a B-site oxide mixing route. A technological problem correlating with the iron-contained compounds is to control dielectric loss. Since dielectric loss is sensitive to many variables, i.e., chemical composition, microstructure, processing history, trace impurities and measuring condition, intensive effort has been undertaken on critical processing variables, including high-purity raw materials, modified columbite/wolframite precursor technique and controlled firing profiles, in order to obtain excellent electronic ceramics.

## 2. Experimental procedure

PFScN ceramics were prepared by conventional ceramic processing via a B-site oxide mixing route. The B-site oxide mixing route technique is a modified columbite/wolframite precursor method, where all oxides of the B-site positions of the perovskite structure are pre-calcined together instead of preparing different columbite/wolframite precursors, respectively.<sup>14,15</sup> Such technique exhibits superior behavior in suppressing pyrochlore phases, stabilizing perovskite structure and improving the amount of perovskite phase as compared to the straight calcination and the columbite/wolframite precursor methods.<sup>14,15</sup> High-purity oxides,  $\text{PbO}$  (>99.9%),  $\text{Fe}_2\text{O}_3$  (>99.99%),  $\text{Sc}_2\text{O}_3$  (>99.9%) and  $\text{Nb}_2\text{O}_5$  (>99.9%) were used as raw materials. To maintain stoichiometric the raw materials were dried before weighing and the synthesized B-site precursors were weighed and in-

troduced into the batch calculation. The B-site oxides (according to the formula composition) were ground and pre-calcined at 1200 °C for 3 h. No free  $\text{Nb}_2\text{O}_5$  retains in the obtained B-site precursors (JCPDS files 27-1311 and 37-1468) confirmed by X-ray diffraction measurement (XRD, Rigaku RINT-2200VS Diffractometer). Stoichiometric  $\text{PbO}$  was added to the synthesized B-site precursor, and the mixed powder was calcined at 900 °C for 2 h. XRD measurement confirmed that the calcined powder is of pure perovskite phase. The perovskite powder was then isostatically pressed into pellets with the addition of 1 wt.% polyvinyl alcohol (PVA) binder and sintered between 1100 and 1220 °C with an interval of 40 °C for 2 h accompanied with a slow binder burning out heating process. The disk pellets were buried under an equiweight mixed raw oxides (with the same composition) in a covered crucible to minimize the volatilization of lead during sintering.

XRD measurement was undertaken on calcined powders and on sintered pellets, which confirms that no additional pyrochlore phases form. Bulk density of the sintered PFScN ceramics was measured geometrically using well-polished specimens. Micro-morphology of the PFScN ceramics sintered at different temperatures was observed by a scanning electron microscope (SEM, HITACHI S-4500 Scanning Electron Microscope) using free surfaces of the specimens after thermal etching at 825 °C for 30 min. For physical property measurement, sintered disk pellets were fine polished to obtain flat and parallel surfaces and silver paste was coated at 650 °C for 15 min on both surfaces as electrodes. Dielectric property was measured using a computer-interfaced Impedance/Gain-phase Analyzer, under a weak oscillation level (NF Electronic Instruments 2340 LCZ Meter). The samples were placed in a Pfeiffer Vacuum Test Chamber connected with a CTI-Cryogenics 8200 Compressor (HELIX Technology Corp.), which operated between 20 and 560 K. The temperature was monitored by a platinum resistance thermometer through a LTC-20 Temperature Controller (CONDUCTUS Inc.) with an accuracy of  $\pm 0.1$  °C. Dielectric hysteresis loop measurement was characterized by a laboratory modified Sawyer-Tower circuit. Low frequency sinusoidal waveform was generated by a G5100 Programmable Function Generator (TEX, Korea). A Model 10/10B High Voltage Amplifier (Trek Inc.) was used as the voltage source and a TDS 210 (two channel) Digital Real-time Oscilloscope (Tektronix Inc.) was attached to record the polarization electric field behavior ( $P-E$ ). Specimens were immersed in silicon oil to prevent arcing.

## 3. Results and discussion

The synthesized PFScN ceramics are of pure perovskite phase without detectable impurity, which proves again the efficiency of the B-site oxide mixing route in the synthesis of complex perovskite compounds. XRD patterns of the pre-calcined B-site precursor, calcined perovskite powder and

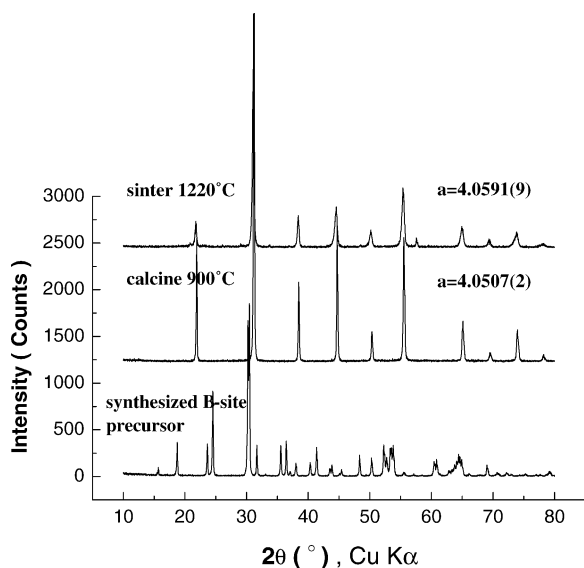


Fig. 1. XRD patterns of the pre-calcined precursor of the B-site oxides, calcined PFScN powder and 1220 °C-sintered PFScN ceramic. Lattice parameters with denomination Å are calculated by the XRD Pattern Processing Software (Materials Data Inc.) using high-purity silicon powder (NIST, 99.999%) as external standard.

sintered disk pellet are shown in Fig. 1. The obtained B-site precursor is solid solution composed of  $\text{FeNbO}_4$  and  $\text{ScNbO}_4$  (JCPDS files 16-0358 and 24-1013). Although pure perovskite phase is maintained during calcination and sintering (in all sintering temperatures) process, great difference is observed in the XRD patterns of the calcined powder and the sintered ceramics. It is astonishing that the calcined precursor shows better crystallization and the diffraction peaks present sharper as compared to those of the sintered ceramics. Superlattice diffraction peak is observed in the sintered specimens, indicating the increase of degree of ordering of the arrangement of B-site elements. PFScN crystallizes into pseudocubic structure and the cell parameters expands slightly from 4.0507 Å for the calcined sample to 4.0591 Å for the 1220 °C-sintered ceramics, which is considered correlating with the variation of microstructure and the growth of grain size during sintering process.

A technological important problem associated with the processing of lead-based ferroelectrics is the control of evaporation of PbO during sintering stage, since the evaporation of lead produces A-site vacancies and leads to the decomposition of perovskite into pyrochlore phase, which deteriorates physical properties of the obtained ceramics. The B-site oxide mixing route technique exhibits a superior behavior in suppressing the evaporation of raw materials since the weight loss during sintering stage is relatively low. The weight loss, induced mainly from the evaporation of PbO, can be calculated by recording weight change of the pellets before and after sintering (PVA binder was burned out in a separate stage), which is present in Fig. 2 accompanied with the variation of bulk density and cell parameters as a function of sintering temperature. In general, the weight loss increases with sin-

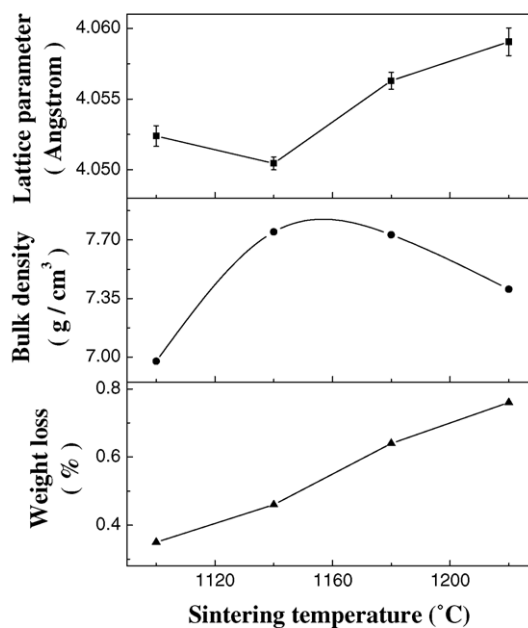


Fig. 2. Variation of the weight loss, apparent bulk density and lattice parameters as a function of sintering temperature of the PFScN ceramics.

tering temperature; the level of lead loss can be effectively minimized by employing the B-site oxide mixing route synthesis technique and the raw oxides atmosphere (with the same composition) since the weight loss is less than 1 wt.% in all sintering temperatures. Apparent bulk density of the sintered PFScN ceramics varies with sintering temperature and the maximum density occurs under sintering temperature between 1140 and 1180 °C. (Bulk density of the 1140 °C-sintered ceramics is 7.748 g/cm<sup>3</sup>, which is 94.87% of the theoretical density.) The variation of density is considered relating to weight loss induced by evaporation, elimination of porosity, grain size growth and distribution, and densification of ceramics with the increase of sintering temperature, which is confirmed by the SEM microanalysis. The decrease of density of the 1220 °C-sintered ceramics can be attributed to the slightly large value of weight loss and the abnormal growth of grain size. It is interesting to notice that the lattice parameters of sintered ceramics show a tendency to expand with sintering temperature, which can not be interpreted now.

The appropriate sintering temperature can be determined based on the analysis of weight loss, bulk density and physical properties. In general, grains grow up with the increase of sintering temperature, which produces large dielectric constant; however, too high sintering temperature does not favor the occurrence of perovskite phase as a consequence of the loss in volatile PbO from composition and results the formation of pyrochlore phase. Furthermore, higher sintering temperatures associate with larger values of dielectric loss, which are generally regarded as disadvantages in the majority of electronic applications. Therefore, the ultimate choice of sintering temperature will depend on collective assessment of the desired physical properties, fabrication cost and material requirements.

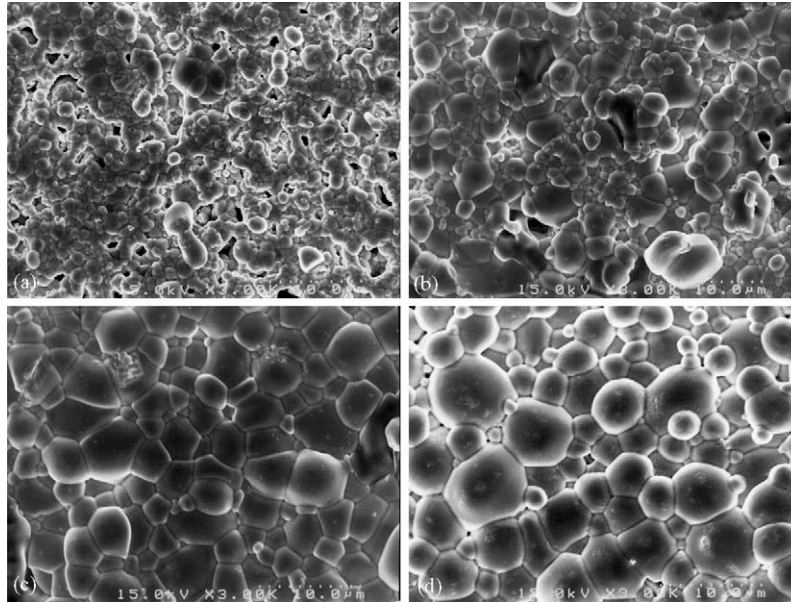


Fig. 3. SEM microphotographs of the free surfaces of the as-fired PFScN ceramics sintered at (a) 1100 °C, (b) 1140 °C, (c) 1180 °C and (d) 1220 °C for 2 h after thermal etching at 825 °C for 30 min.

SEM microphotographs of the as-fired PFScN ceramics sintered between 1100 and 1220 °C are illustrated in Fig. 3. For 1100 °C sintering, the fabricated PFScN ceramics are of rather uniform microstructure composed of fine grains accompanied with large part of closed pores. With the increase of sintering temperature, grain size tends to increase, porosity gradually eliminates, microstructure becomes dense as indicated by the grain packing and the increase in boundary thickness, and strong inter-granular bond develops, which increases the bulk density and strength of the ceramics. At 1180 °C sintering temperature, no remanent gas pore is observed, proving well densification of the ceramics and the bulk density reaches 7.730 g/cm<sup>3</sup>, which is 95.06% of the theoretical density. Abnormal growth of grains appears in the 1220 °C-sintered ceramics, accompanied with sub-micrometer grains, which can be attributed to the evaporation of PbO and the formation of pyrochlore phase although XRD measurement denies its existence. Liquid-phase sintering mechanism may take partial effect in the densification of the PFScN ceramics due to the round grain morphology. Even higher sintering temperatures are attempted, which result in critical sintering where the weight loss is unacceptable large, the Pb<sub>3</sub>Nb<sub>4</sub>O<sub>13</sub>-type pyrochlore phases form largely and the ceramics deteriorate with molten scars.

Temperature dependence of the dielectric constant and loss of the PFScN ceramics sintered at different temperatures is displayed in Fig. 4, where the dielectric constant is normalized by the value of dielectric constant at 300 K and divided by the bulk density of the ceramics in order to eliminate the influence of sintering conditions on dielectric response. The dielectric peaks appeared around 400 K can be attributed to the pseudo-cubic ferroelectric-cubic paraelectric phase transition. The value of dielectric maximum increases with sin-

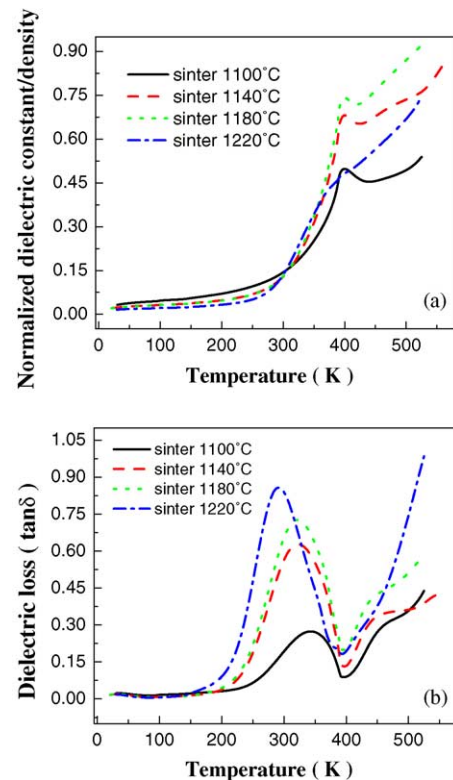


Fig. 4. Temperature dependence of the dielectric constant (a) and loss tangent (b) at 10 kHz upon heating of the PFScN ceramics sintered at different temperatures. The dielectric constant is normalized by the value of dielectric constant at 300 K and divided by the bulk density of the specimens to eliminate the influence of sintered conditions on dielectric response.

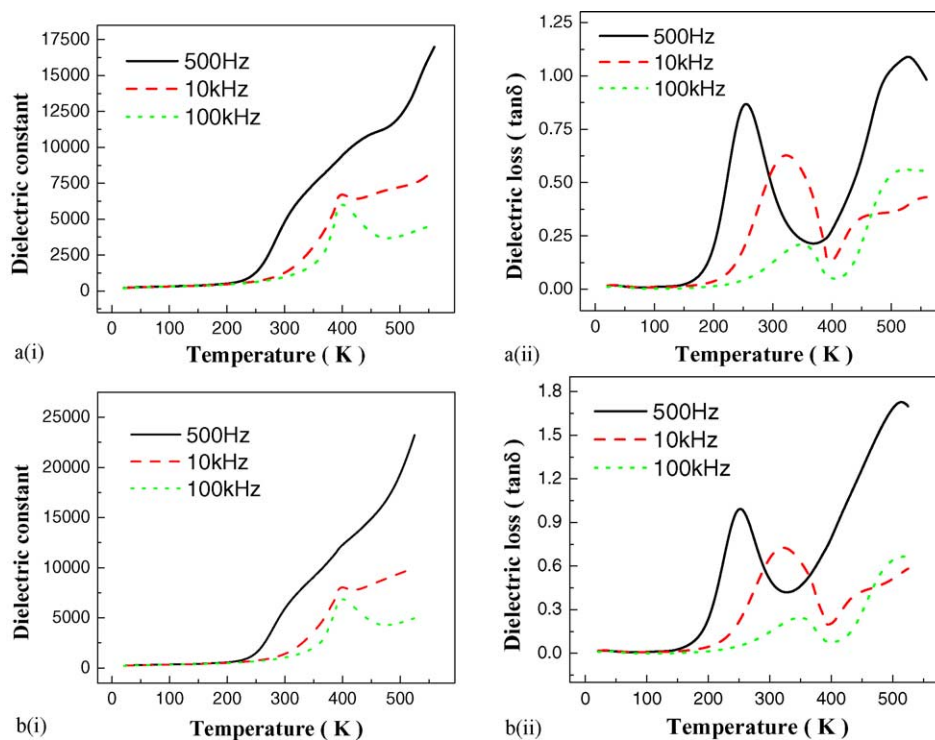


Fig. 5. Variation of the dielectric constant (i) and loss tangent (ii) as a function of temperature upon heating at several frequencies of the PFScN ceramics sintered at 1140 °C (a) and 1180 °C (b) for 2 h.

tering temperature up to 1180 °C (while the  $T_m$  retains unchangeable), then decreases for the 1220 °C-sintered ceramics, where the dielectric peak is indiscernible. The dielectric loss increases systematically with sintering temperature accompanied with the decrease of temperature of the dielectric loss maximum. Such character of dielectric behavior is considered correlating with the variation of densification, grain size and morphology, microstructure and conductivity of the ceramics sintered at different temperatures.

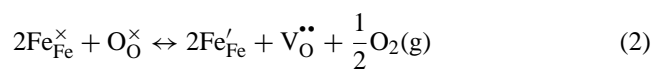
Optimized dielectric properties can be obtained in the PFScN ceramics with sintering temperature between 1140 and 1180 °C, which is given in Fig. 5 as temperature dependence of the dielectric properties. PFScN sintered at different temperatures exhibits similar dielectric behavior except that the value of dielectric maximum is slightly large in the 1180 °C-sintered ceramics. Dielectric constant peaks are indiscernible for the low-frequency measurement data. Such character and the recurrent increase of dielectric constant in the paraelectric phase accompanied with the tremendous increase of dielectric loss are usually observed in the iron-contained lossy ferroelectrics.<sup>16–18</sup> Dielectric loss exhibits strong frequency dispersion in a wide temperature range (down to below 150 K), and the temperature of loss maximum moves sharply to high temperature with the increase of frequency (more than 110 °C between 500 and 100 kHz) accompanied with the decrease of value of the dielectric loss.

Although the synthesis conditions for the PFScN ceramics have been tailored to optimization, strong frequency dispersion of the dielectric properties at low frequencies and the

relatively large dielectric loss cannot be improved by modifying ceramic processing. Such anomalous phenomena are considered relating to the nature of the iron-contained compounds, which results in peculiar conduction mechanism at higher temperatures. Existence of residual  $\text{FeNbO}_4$  and/or  $\text{ScNbO}_4$  in the sintered PFScN ceramics is possible although XRD measurement detects no impurity. These compounds exhibit semi-conductive properties, which could be responsible for the frequency dispersion and the large value of dielectric loss.<sup>19</sup> Another mechanism deserving consideration correlates with the partial reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions during sintering, which is highly sensitive to sintering temperature. Using the Kröger-Vink symbol, the defect reaction can be written as below:



The co-existence of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  cations on equivalent crystallographic sites gives rise to finite hopping/jump type of conduction mechanism, tending to take effect at lower frequencies. Such mechanism affords thermally activated space-charge polarization, which would be consistent with the strong frequency dependence of dielectric response. To compensate charge neutrality oxygen vacancies are produced:



This reaction can be suppressed at lower sintering temperatures as confirmed by the experimental work carried out here.

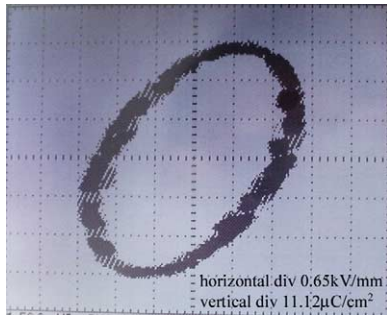


Fig. 6. Typical  $P$ – $E$  hysteresis loop of the PFScN ceramics sintered at  $1180\text{ }^{\circ}\text{C}$  for 2 h.

Based on above discussion sintering in oxygen will restrain the reaction of reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions, which results in the decrease of concentration of  $[\text{Fe}_{\text{Fe}}]$ , leading to the improvement of dielectric dispersion behavior. Alternatively, chemical doping introduced oxygen vacancies extrinsically also suppresses above reaction, which engineers a degree of non-stoichiometry in the obtained PFScN products. These considerations provide future study directions for further tailoring physical properties of the iron-contained compounds.

Typical dielectric hysteresis loop of the PFScN ceramics sintered at  $1180\text{ }^{\circ}\text{C}$  for 2 h is shown in Fig. 6. The  $P$ – $E$  hysteresis loops of PFScN exhibit similar patterns for all sintering temperatures. The polarization may not saturate due to the existence of large magnitude of space charge and the small electric field used in the experiment. With the increase of sintering temperature, the remanent polarization increases gradually from  $12.49\text{ }\mu\text{C}/\text{cm}^2$  ( $1100\text{ }^{\circ}\text{C}$ ), to  $22.01\text{ }\mu\text{C}/\text{cm}^2$  ( $1140\text{ }^{\circ}\text{C}$ ),  $27.79\text{ }\mu\text{C}/\text{cm}^2$  ( $1180\text{ }^{\circ}\text{C}$ ) and then  $31.42\text{ }\mu\text{C}/\text{cm}^2$  ( $1220\text{ }^{\circ}\text{C}$ ). Such variation of the remanent polarization can be attributed mainly to the increase of dielectric constant with sintering temperature, indicating that physical properties of ceramics not only depend on composition, but also rely largely on porosity, grain size and distribution and microstructure. The later usually takes significant effect in the synthesis of ceramics, which provides the feasibility to tailor ceramic properties by modifying sintering conditions.

#### 4. Conclusions

High quality PFScN ceramics with pure perovskite phase were synthesized by conventional ceramic processing via a B-site oxide mixing route. The weight loss is relatively low as compared to the direct calcination and the columbite/wolframite precursor methods, which effectively prohibits the formation of parasitical pyrochlore phase. With the increase of sintering temperature, crystal lattice of the polycrystalline PFScN ceramics exhibits a tendency to expand accompanied with the variation of bulk density. Grain size also grows up from sub-micrometer for the PFScN ceramics sintered at  $1100\text{ }^{\circ}\text{C}$  to  $3\text{--}7\text{ }\mu\text{m}$  for those sintered at

$1180\text{ }^{\circ}\text{C}$ . High densification ( $>95\%$  of the theoretical density) and optimized dielectric/ferroelectric properties can be obtained for the PFScN ceramics under the sintering temperature  $1140\text{--}1180\text{ }^{\circ}\text{C}$ . Strong frequency dispersion of the dielectric response accompanied with relatively large dielectric loss is observed, which can be attributed to the possible existence of residual semi-conductive  $\text{FeNbO}_4$  and/or  $\text{ScNbO}_4$  compounds and the thermally activated space-charge polarization resulted from the partial reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions during sintering.

#### Acknowledgment

The authors would like to thank the Satellite Venture Business Laboratory of Utsunomiya University, Japan, for financial support.

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