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Dielectric and Piezoelectric Properties of $Pb(Sc_{1/2}Nb_{1/2})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Ternary Ceramic Materials

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Abstract

The dielectric and electrical properties of x*Pb* *$(Sc_{1/2}Nb_{1/2})O_3$–*y*$Pb(Ni_{1/3}Nb_{2/3})O_3$–*z*$PbTiO_3$ (PSNNT 100*x*/100*y*/100*z*) ternary ceramic materials near the morphotropic phase boundary (MPB) were investigated. The MPB follows on almost linear region between PSNNT 58/00/42 and PSNNT 00/68/32 of the binary systems. The maximum electromechanical coupling factor* kp = *70·7% was found at PSNNT 36/26/38, where $\varepsilon_{33}{}^T/\varepsilon_0 = 3019$ and* Tc = *210°C were obtained. These values are similar to those of the $Pb(Sc_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ system and better than those of PZT.*

Keywords: $Pb(Sb_{1/2}Nb_{1/2})O_3$, dielectric properties, piezoelectric properties, perovskites.

1 Introduction

In recent years, a new approach to the development of piezoelectric materials based on the $Pb(B_1B_2)O_3$ relaxor–$PbTiO_3$ (PT) systems (where, $B_1 = Mg^{2+}$, Ni^{2+}, Zn^{2+}, $B_2 = Nb^{5+}$, Ta^{5+}) has attracted peculiar attention. The advantages of relaxor–PT materials compared with conventional $Pb(Zr,Ti)O_3$ (PZT) are a diversity of compositions, good mechanical properties, and reduced PbO evaporation during the firing process.[1] Another important advantage of relaxor–PT system is the case with which single crystals of MPB compositions can be grown.[2]

Perovskite lead scandium niobate, $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) is a typical relaxor ferroelectric material and has a Curie temperature of about 90°C.[3] Recently, the authors have reported the dielectric and piezoelectric properties of the PSN based relaxors–PT systems such as $Pb(Sc_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PSMNT)[4] and $Pb(Sc_{1/2}Nb_{1/2})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PSZNT).[5] However, their properties of $Pb(Sc_{1/2}Nb_{1/2})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PSNNT) system has not elucidated so far. The purpose of this work is to study dielectric and piezoelectric properties of this ternary system in the vicinity of the MPB in detail. Furthermore, the advantages and disadvantages of these systems compared with PZT system are also discussed.

2 Experimental

Details of the procedure used to prepare ceramic samples are described as shown in Fig. 1. Calcination was performed in two steps. In the first step, scandium niobate ($SbNbO_4$) and nickel niobate ($NiNb_2O_6$) were prepared using the columbite process.[6] After wet-mixing the starting materials using a plastic ball mill with 5 mm ZrO_2 balls, the slurry was dried. In the second step, the mixture was calcined at 800~850°C for 2 h in air. The calcined cake was then ball-milled in the same mill for 24 h. Pellets 12–18 mm in diameter and 1·5~3 mm in thickness were pressed at 200 MPa cm^{-2}. After burnout the binder, the samples were sintered at a temperature of 1050~1250°C in the Al_2O_3 crucible.

The fired density was measured using the Archimedes method. Grain size was determined by the linear intercept method on the fired surface as observed by a scanning electron microscope (SEM). The crystallography was performed by X-ray diffraction (Monochromatized CuK_α radition). Capacitance was measured using same impedance analyzer at room temperature. The dielectric constant was calculated from the capacitance at a frequency of 1 kHz. For the electrical and piezoelectric measurements,

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disk specimens 18 mm in diameter and 1·0 mm in thickness were formed from the sintered ceramics and Au- or Ag-coated at 700°C for 5 min. The specimens were immersed in silicone oil and poled in a 2·5–4·0 kV mm^{-1} D.C. field. The electric field was applied at a temperature of 125°C for 15 min, and the specimens were cooled to 30°C in the field. After 24 h of aging at room temperature, electromechanical coupling factors were measured using an impedance analyzer (HIP-4192A) by the resonance–antiresonance frequency method. The standards of the Electronic Materials Manufactures Association of Japan (EMAS-6100)[7] were adopted in these measurements.

3 Experimental Results

3.1 Crystal structure

Figure 2 shows the MPB line as determined from crystal structure and electrical properties in the PSNNT ternary system. The MPB locates almost linear region between PSNNT 58/00/42 (PSNT) and PSNNT 00/68/32 (PNNT 68/32) compositions in each binary systems. Among the MPB, an almost 100% perovskite phase is obtained. The densities are better than 97% of theoretical values as calculated from the lattice constants. Fired grain size are 3–5 microns.

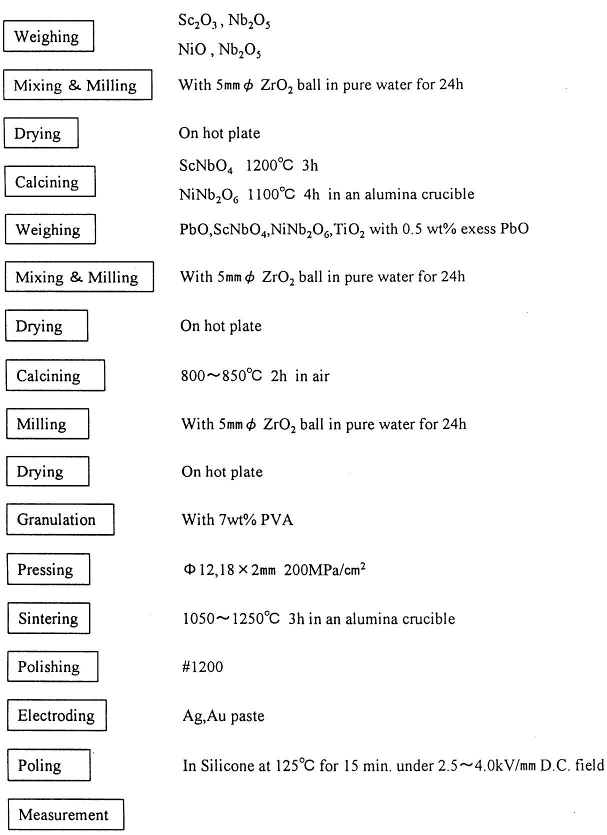

Fig. 1. Flow chart of sample preparation.

Figure 3 represents X-ray diffraction (XRD) patterns for PSNNT 29/100*y*/100*z* ceramics. Fired PSNNT 29/33/38 indicates a rhombohedral (R) phase, while PSNNT 29/26/45 has a tetragonal (T) phase. However, compositions from PSNNT 29/33/38 to PSNNT 29/26/45 exhibit three different peaks, representing a mixture of the rhombohedral and the tetragonal phases.

3.2 Dielectric properties

Figure 4 shows dielectric properties of the PSNNT ceramics. The composition PSNNT 44/15/41 shows a large dielectric constant maximum of around 40 000. The dielectric properties of the MPB compositions have a very weak frequency dispersion of dielectric constant. These compositions have a first-order phase transition. As shown in Fig. 5, the Curie temperature varies from 170 to 210°C as a function of PT in the 0·29 PSN–$(1-y)$PNN–yPT system.

3.3 Piezoelectric properties

The electromechanical coupling factor k_p was observed in the 0·36 PSN-(1–*y*)PNN–*y*PT system

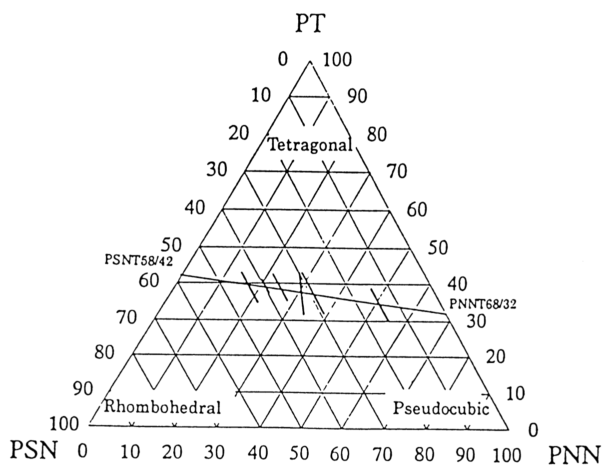

Fig. 2. Phase diagram of PSNNT system.

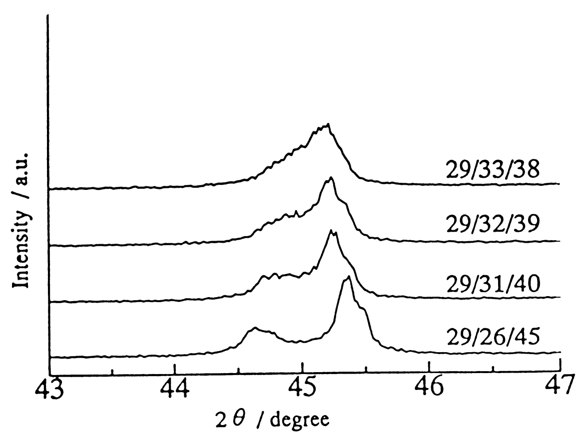

Fig. 3. X-ray diffraction patterns of PSNNT 29/100*y*/100*z* ceramics.

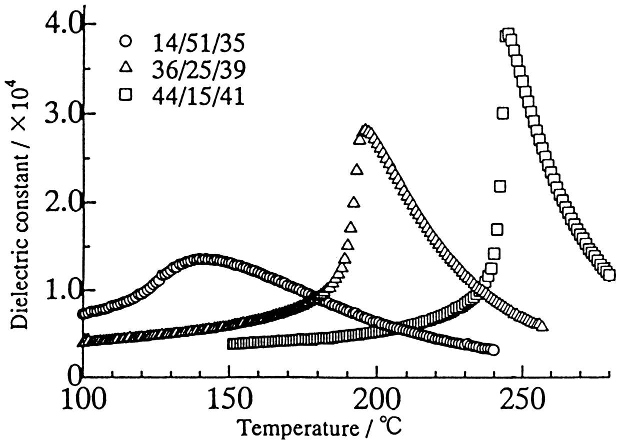

Fig. 4. Dielectric properties of PSNNT ceramic system at 1 kHz.

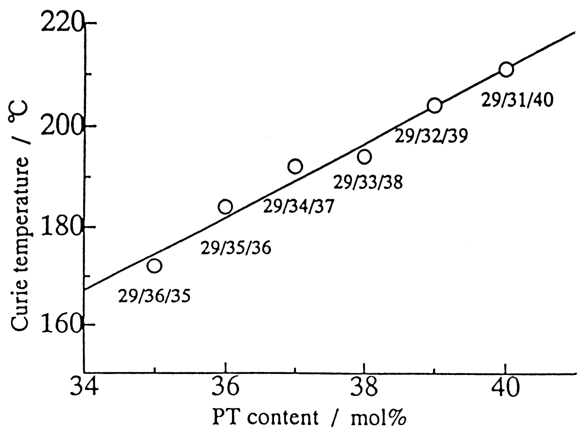

Fig. 5. Dependence of Curie temperature on PT content in the 0·29 PSN–(1−y)PNN–yPT system.

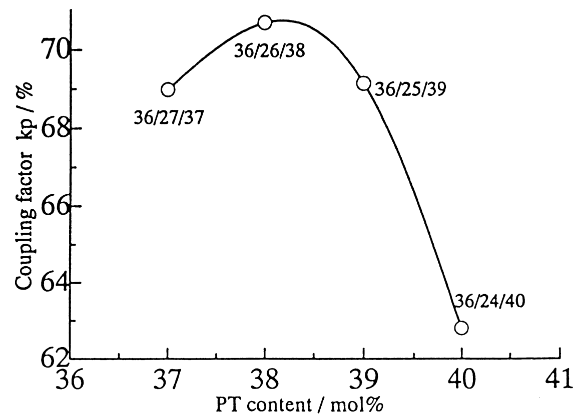

Fig. 6. The coupling factor k_p for 0·36 PSN–(1−y)PNN–yPT system.

Table 1. Comparison of PSNNT 36/26/38 and PSMNT 29/34/37

	PSNNT 36/26/38	*PSMNT 29/34/37*
Firing temperature (°C)	1250	1250
Density	7·95	7·72
Porosity (%)	1·5	3·1
Perovskite ratio (%)	100	100
Fired grain size (μm)	3·2	3·5
Phase	Mix of R and T	Mix of R and T
Dielectric constant maximum	29 500	33 000
Curie temperature (°C)	210	204
Dielectric constant after poling	3019	3000
E/M coupling factor k_p (%)	71	72

as found in Fig. 6. The largest value ($k_p = 70{\cdot}7\%$) was obtained in the composition of PSNNT 36/26/38 which is near the MPB region. Many parameters affect the final piezoelectric properties of ceramics including composition, impurities, phase purity, fired density, grain size, T_c, electrode material, poling condition and measurement procedure. A comparison of the PSNNT 36/26/38 and PSMNT 29/34/37 ceramics is listed in Table 1. Both materials are consisting of a complete perovskite structure with a mixture of rombohedral and tetragonal structures, and are characterized by high densities of more than 96% with almost the same grain size. The Curie temperatures are similar, as are the room temperature and maximum dielectric constants.

It is well known[8] that typical 52 mol% $PbZrO_3$–48 mol% $PbTiO_3$ (PZT 52/48) near the MPB has $k_p = 53\%$ and $T_c = 402°C$. PZT ceramics have advantages for higher Curie temperature, but their piezoelectric properties are lower than those of PSNNT system materials.

4 Conclusions

The multi-component material system consisting of $Pb(Sc_{1/2}Nb_{1/2})O_3$–$Nb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PSNNT) ternary ceramics near the MPB was investigated by the columbite process using $ScNbO_4$ and $NiNb_2O_6$. The physical and electrical properties were studied and the following conclusions were reached.

- Ternary system PSNNT ceramic materials fired at 1250°C have single-phase perovskite with more than 97% of the theoretical density.
- The MPB composition traces an almost linear region between the two MPB compositions of PSNNT 58/00/42 and PSNNT 00/68/32. The maximum electromechanical coupling factor $k_p = 70{\cdot}7\%$ is found at PSNNT 36/26/38, where $\varepsilon_{33}^T/\varepsilon_0 = 3019$ and $T_c = 210°C$ are obtained.
- PSNNT piezoelectric ceramics similar to PSMNT system are shown to be some of the

most suitable tranducer materials for a variety of applications. This material system offers high electromechanical coupling factors ($k_p > 65\%$) with Curie temperature ranging from 150 to 250°C.

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