IMPROVEMENT OF MECHANICAL AND ELECTRICAL PROPERTIES OF PNN-PZT CERAMICS WITH STRONTIUM CONTENT

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Abstract

In this research, mechanical and electrical properties of ceramics from PSNN-PZT system have been investigated. The ceramics with formula of $Pb_{(1-x)}S_{rx}(Ni_{0.33}Nb_{0.67})_{0.5}Ti_{0.35}Zr_{0.15}O_3$ where x = 0.00, 0.02, 0.04, 0.06 and 0.08 were prepared by a conventional mixed-oxide method. There sults showed that with increasing Sr concentration, dielectric constant versus temperature curves become gradually broader. The degree of diffuse phase transition was enhanced with Sr dopant. The substitution of Pbion by Sr ion in the PSNN-PZT ceramics resulted in an improvement of their hardness, and fracture toughness. The maximum room temperature dielectric constant, hardness and fracture toughness were achieved from the sample with x = 0.06. This is considered as the optimized composition in this study.

Keywords : Piezoelectric, PNN-PZT, Dielectric, lowtemperature, PZT

Introduction

Piezoelectric and ferroelectric materials are widely used in various electronic devices, including multilayer capacitors, sensors, transducers and actuators (Jaffe *et al*., 1971; Fuda *et al*., 1997; Wakiya *et al*., 1999). For the past several years, Pb $(Zr_{1-x}- T_{ix})O_3$ (PZT) was reported to host exceptionally high dielectric and piezoelectric properties. The excellent properties were observed for compositions close to the morphotropic phase boundary (MPB) which locates around Pb TiO_3 : $PbZrO_3$ ~ 1 : 1 and separates the Ti-rich tetragonal phase from the Zr-rich rhombohedral phase (Fuda *et al*., 1997). Therefore, many commercial PZT ceramics have been designed in the vicinity of the MPB with many doping schemes in order to obtain superior properties (Jaffe *et al*. 1971). Several in vestigators have reported the properties of PZT or PZT based ceramics with cations substituted on A and B-sites. For example, Zheng *et al*. (2001 and 2002) reported that

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Sr-doping at A site of PZT ceramics resulted in higher dielectric and piezoelectric properties than those of the pure PZT. The substitutions of Sr also produced a shift of the MPB composition to wards the tetragonal phase, and reduced the Curietemperature (T_C) of the ceramic.

The Pb $(Ni1/_3Nb_2/_3)O_3$-$PbTiO_3$-$PbZrO_3$ (hereafter PNN-PT-PZ) ceramic is an attractive material for uses in many piezoelectric applications because it has a large electromechanical-coupling coefficient (k_{33}) for ceramics equal to 0.8 (Kondo *et al.,* 1997; Kondo *et al.*, 1998; Kondo *et al.,* 1998). Another feature of PNN-PT-PZ ceramics is that they can be sintered at relatively low temperatures.

In the present work, effects of Sr doping at A-site on dielectric and ferroelectric of $Pb_{(1-x)}$ Sr_x $(Ni_{0.33}$ $Nb_{0.67})_{0.5}$ $Ti_{0.35}$ $Zr_{0.15}$ O_3 ceramics were investigated. Dense ceramic specimens were fabricated by varying the concentration of Sr under the same sintered conditions. Various physical measurements were conducted. In this paper, the perovskite phase evolution and lattice constants as a function of the concentration of Sr have been reported and discussed. The temperature dependence of the dielectric constant as a function of the concentration of Sr was given. The remanent polarization and coercive field determined from *P–E* hysteresis loops the diffuseness parameter (δ) of sample were also introduced.

Materials and Method

Material Preparation

In this research, the investigated compositions were $Pb_{(1-x)}$ Sr_x $(Ni_{0.33}$ $Nb_{0.67})_{0.5}$ - $Ti_{0.35}$ $Zr_{0.15}$ O_3 where x = 0.00, 0.02, 0.04, 0.06 and 0.08 which were synthesized by the conventional mixed oxide method. Reagent grade metal oxide powders were used in this work. They were mixed and ball milled for 24h. The mixtures were dried and calcined at 850°C for 3h and then at 1100°C for 3h with heating and cooling rate of 10°C/min. An excess of 2 mol% PbO was added to all compositions. The calcined powders were wet-milled again for 24h After drying and sieving, a few drops of 5 wt% PVA (polyvinyl alcohol) were added to the mixed calcined powder as a binder and the powder was pressed into pellets with a diameter of 10 mm using a uniaxial pressing method at 1.5 ton. The binder was burned out at 500°C for 1h. The green discs were put in a covered Al_2O_3 crucible and weresinteredin an electric furnace at 1250°C for 2 h in an ambient atmospheric pressure.

Materials Characterizations

Phase for mation of the sample was studied by an X-ray diffraction (XRD) technique. The bulk density of sintered PSNN-PZT ceramic samples were measured by Archimedes'method. A scanning electron microscope (SEM, JEOL JSM5910LV) was used to observe the microstructure of ceramic samples. The mean linear intercept was used to evaluate grain size of the ceramic. For electrical property measurement, the sintered samples were ground to obtain parallel faces, which were then coated with silver as electrodes. The dielectric constants and dielectric loss of the sintered ceramics were measured as a function of temperature with an automated dielectric measurement system. The system consists of a LCR-meter and environment controlled chamber, where both temperature and dielectric properties were measured and recorded by computer. The ferroelectric properties were measured usinga Sawyer Tower circuit. The electrode specimens were poled in silicon oil bath at 50°C by applying a DC field of 3 kV/mm for 30 min. After 24h ageing, the poled specimens were characterized for piezoelectricproperties. The piezoelectric coefficients (d_{33}) were characterized using a KCF S5865d_{33} meter.

Resultsand Discussion

Figure 1 shows the XRD patterns of Sr-doped PSNN-PZT ceramics, each exhibitinga single perovskite phase with high purity according to the detection limit of the equipment. All

specimens contain no secondary phase. An increase in the mole fraction of Sr^{2+} did not show any evidence of a change in symmetry. With increasing Sr^{2+} contents, the density of the samples increases. The x = 0.06 sample has the highest density value as shown in Table 1. On the other hand, the grain size changed from 2.64 μm of x = 0.00 sample to 1.72 μm of x = 0.08 sample. It can be noted that the grain size of the sample decreased with increasing Sr^{2+} content as shown in the SEM micrographs of the correspond ceramics (Figure 2). Mechanical properties of the ceramics in terms of Vickers hardness (H_v) and fracture toughness (KIC) were investigated, and the results are shownin Figure 3. At low Sr^{2+} concentrations (x = 0.02-0.04), the hardness values are quite low and slightly decreased 9 Again, past or present you want for this sentence?) with increasing Sr^{2+}. An increaseof Sr^{2+} content from 0.02 to 0.06 mole rapidly increased the hardness value to ~4.31 GPa. The changes in hardness may be contributed to both grain size and their density values. Grain boundaries are known as stress concentration sites, which acted as effective obstacles to dislocation pile-up in the adjacent grains, leading to aharder material (Rice *et al.* 1977). That is why in several a ceramic with smaller grain size showed higher hardness value compared to those with larger grains. Fracture toughness result showed that an addition of 0.00–0.08 mole Sr^{2+} in to PSNN-PZT ceramic increased fracture toughness

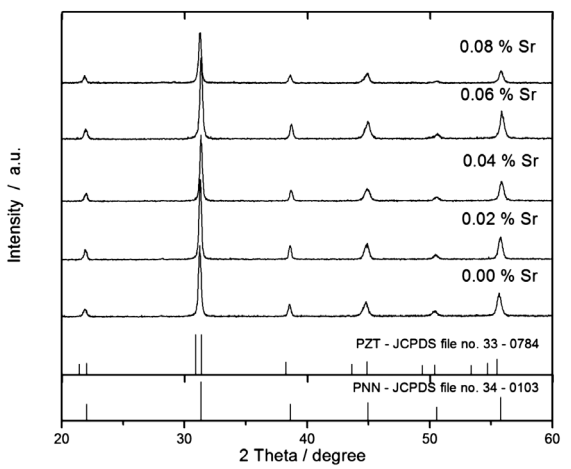

Figure 1. The XRD patterns of Sr-doped PSNN-PZT ceramics sintered at 1250°C

Table 1. The hardness, fracture toughness, density and grain size of PSNN-PZT ceramics

sample	H_v (GPa)	K_{IC} (MPa·m$^{1/2}$)	Density (g/cm^3)	Grain size (μm)
X = 0.00	2.95	0.33	7.41	2.64
X = 0.02	2.67	0.42	7.59	2.08
X = 0.04	2.94	0.58	7.54	2.49
X = 0.06	4.31	0.63	7.80	2.19
X = 0.08	4.08	0.48	7.64	1.72

values from 0.33 to 0.63 MP $am^{1/2}$, which maximum value was found at x = 0.06 (KIC∼ 0.63 $MPam^{1/2}$). This was supposed to be caused by adriving force for crack extension which was reduced in the ceramics containing smaller grains.

The experimental on dielectric measurements at room temperature for various Sr^{2+}

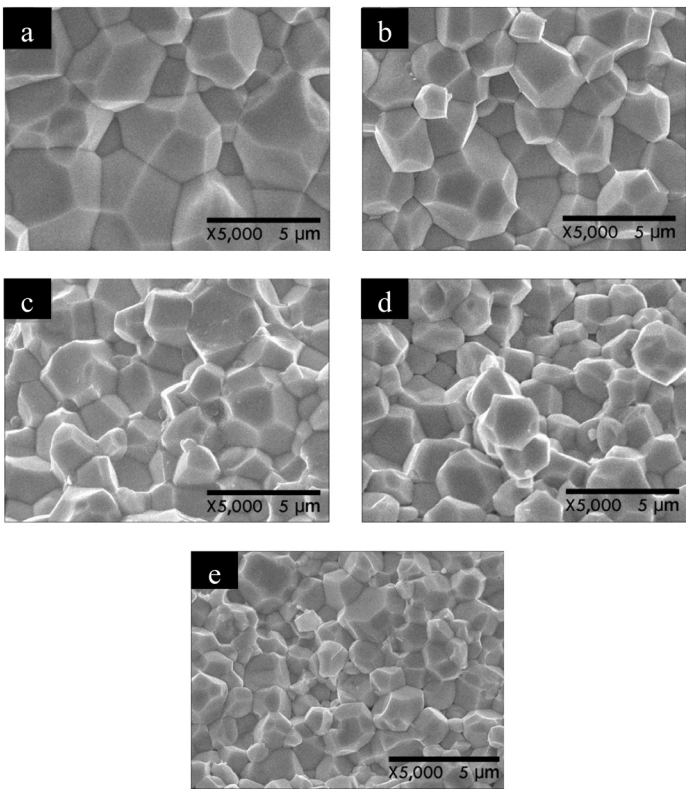

Figure 2. SEM micrographs of Sr-doped PSNN-PZT ceramics where (a) x = 0.00, (b) x = 0.02, (c) x = 0.04, (d) x = 0.06 and (e) x = 0.08

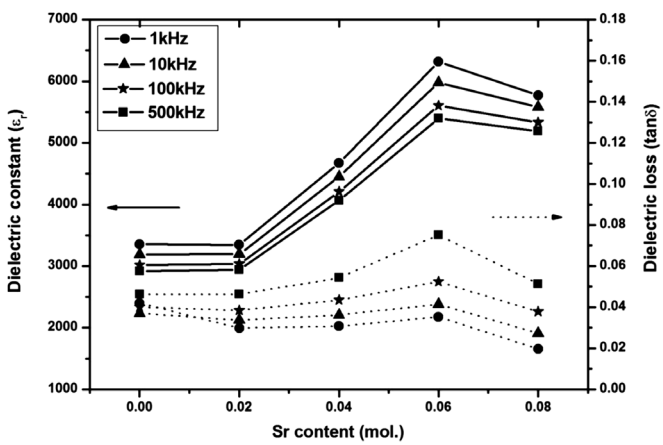

Figure 3. The Vickers hardness (H_v) and fracture toughness (K_{IC}) of PSNN-PZT ceramics

contents are graphically plotted in Figure 4. It can be clearly seen that dielectric constant (εr) increases with increasing Sr^{2+} (x) reaching a maximum value at x = 0.06. Further addition of Sr^{2+} slightly decreases dielectric constant value. Initially, the considerable increase in dielectric constant values may be mainly due to the reduction of grain size and the increase density as shown in Table1. This trend was observed atall frequencies.

The temperature dependences of the dielectric constant of all samples shownin Figure 5. All samples display (present) relaxor-live ferroelectric behavior. As the Sr^{2+} content increased (Past), a clear shift in the transition temperature to lower temperatures was observed. Inaddition, the dielectric constant maximum decreased as the Sr^{2+} content increased. Moreover, the dielectric constant peak became broader with increasing Sr^{2+} content.

The nature of the homogeneously polarized states is believed to be primarily controlled by the concentration of Sr^{2+}. Randall *et al*. (1993) and Xia and Yao (Xia *et al*. 2001) observed that excess PbO has a great influence on the electrical properties. In lead-based ferroelectric ceramics, liquidp hase sintering is present because of the low melting point of lead oxide. Thus, a small amount of excess PbO can be added to assist in the formation of the perovskite phase and for densification of the ceramic. However, an overabundance of PbO will result in PbO

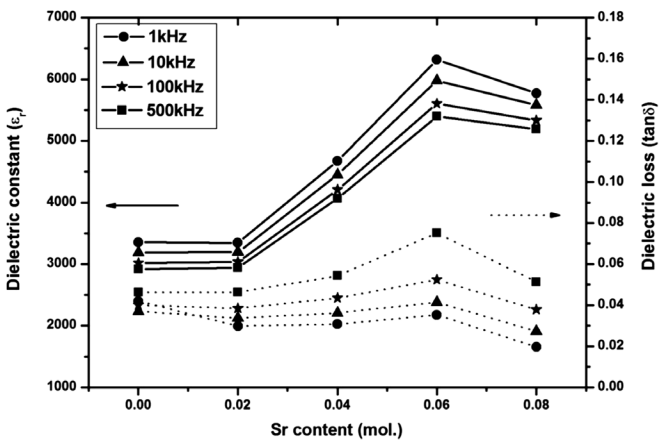

Figure 4. Dielectric constant (ε_r) and Dielectric loss (tanδ) measurements at room temperature

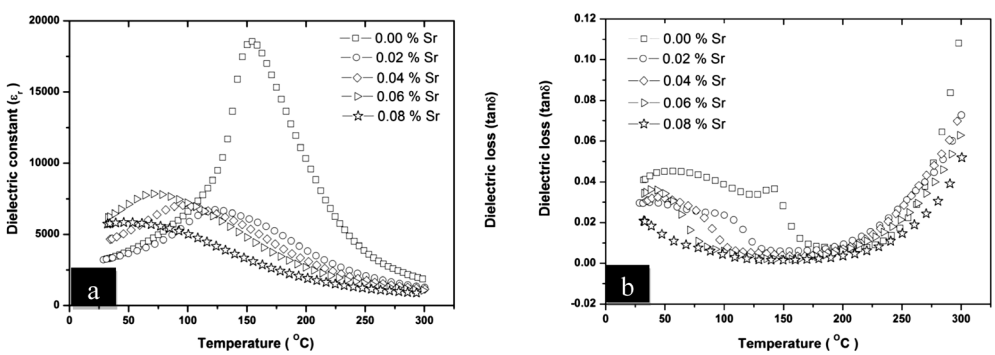

Figure 5. The temperature dependent of Dielectric constant (ε_r); a and Dielectric loss (tanδ); b of PSNN-PZT ceramics at frequency 1 kHz

enrichment of the grain boundary and the formation of a grain-boundary layer. Because this layer has a low dielectric constant (K∼ 20), the overall dielectric constant will be decreased due to the presence of the grain-boundary phase.

Although this behaviour was observed in all of compositions, the shift in the dielectric constant maximum and transition temperature was minimal at high concentrations of Sr. This is due to the fact that Sr substitution reduces the total amount of Pb wt% in the system. In this work, the temperature which maximum dielectric constant located (have after T_m) between 48.65°C and 153.85°C (No verb). The dielectric constant maximum and the transition temperature of the PSNN-PZT samples at 1 kHz are listed in Table 2. The maximum dielectric constants varied within the range of 5853–18536 for all Sr concentrations. As expected, Sr doping has been shown to produce a reduction in the transition temperature (T_m) with increasing Sr concentration. The relaxor ferroelectric can be described by a simple quadratic law. This arises from the fact that the total number of relaxors contributing to the permittivity response in the vicinity of the permittivity peak is temperature-dependent. The diffuseness of the phase transition can be determined from the modified Curie-Weiss law, which uses the following expression (Tang *et al*. 2004)

$$\frac{1}{\varepsilon_r} = \frac{1}{\varepsilon_{max}} + \frac{(T - T_m)^y}{2\varepsilon_{max}\delta^2}$$

Where ε_{max} is maximum dielectric constant, T_m is the phase transition temperature and ε_r is the dielectric constant of sample. For PSNN-PZT compositions, the diffusivity (γ) and diffuseness parameters (δ) can be assessed from the slope and intercept of the dielectric data displayed in Figure 6. The values of γ and δ are both material constants depending on the composition and structure of the materials. The parameter γ gives information on the character of the phase transition : for $\gamma = 1$, a normal Curie-Weiss law is obtained and $\gamma = 2$ describes a complete diffuse phase transition (Yao *et al*. 2003), while the parameter δ is used to measure the degree of diffuseness of the phase transition. The γ values of the prepared PSNN-PZT ceramics were found to vary between 1.92 and 2.11, which confirms the occurrence of the diffuse phase transition. The diffuseness parameter increased significantly with Sr doping. A similar trend was also observed for substitution with alkali-earth metals in lead-based perovskites (Ahn *et al*. 2000., Butcher *et al*. 1991). The parameter δ can be used to measure the degree of diffuseness of the phase transition in relaxor ferroelectric materials.

Figure 7 displays the hysteresis loops of

Table 2. The dielectric and ferroelectric properties of PSNN-PZT ceramics at frequency1 kHz

sample	T_m (°C)	Dielectric Properties				Ferroelectric Properties		
		ε_r^a	tanδ^a	ε_r^a max^b	tanδ^b	P_r (μC/cm^2)	E_C (kV/cm)	R_{sq}
X = 0.00	153.85	3355.04	0.0419	18536.44	0.0220	31.78	4.83	1.03
X = 0.02	123.07	3343.35	0.0298	6725.35	0.0110	12.22	8.14	0.69
X = 0.04	95.81	4674.18	0.0307	7034.55	0.0119	10.11	6.52	0.58
X = 0.06	71.65	6316.41	0.0353	7859.30	0.0158	5.26	4.08	0.34
X = 0.08	48.65	5771.42	0.0197	5853.38	0.0174	1.88	3.04	0.48

* a is the properties at room temperature. *b is properties at high temperature

the PSNN-PZT samples. As one can expect, the polarization decreased with increasing Sr concentrations. Ferroelectric property parameters (remanent polarization (Pr); coercive field (Ec) and squareness of hystersis loop (Rsq)) of the PSNN-PZT ceramics can be found in Table 2.

Haertling and Zimmer (1966) derived an empirical relationship between remanent polarization, saturation polarization and polarization at fields above the coercive field. This permits the quantification of changes in the hysteresis behavior for each sample by the following equation:

$$Rsq = \frac{P_r}{P_s} + \frac{P_{1.1Ec}}{P_r}$$

Where R_{sq} is the squareness of hysteresis loop, P_r is remanent polarization, P_s is saturation polarization and $P_{1.1Ec}$ is the polarization at an electric field equal to 1.1 times the coercive field (E_c). For an ideal hysteresis loop, the squareness parameter is equal to two (Pisitpipathsin *et al*. 2010). Normal square ferroelectric *P–E* loops were observed in PSNN-PZTsamples. The value of R_{sq} decreased from 1.03 to 0.34 with increasing Sr content. The remanent polarization (P_r) decreased with increasing Srconcentration from 31.78 to 1.88 μCcm^{-2}.

Conclusions

In this study, $Pb_{(1-x)}Sr_x(Ni_{0.33}Nb_{0.67})_{0.5}Ti_{0.35}Zr_{0.15}O_3$ compounds were successfully prepared by asolid-state mixed-oxide method, and the ceramics were fabricated by a conventional sintering process. With an increase in the Sr^{2+} content, the densification was improved, and grain growth was inhibited, which in turnresulted in the improvement of hardness value of the PSNN-PZT ceramics. An Sr content at 0.06 mole gave the highest value of fracture toughness. The transition temperature and the maximum dielectric constant decreased with increasing Sr^{2+} content. Inaddition, Sr doping caused the ferroelectric phase transition to become more diffuse.

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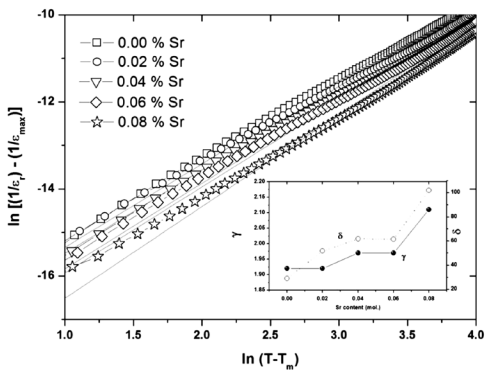

Figure 6. The Diffusivity (γ) and Diffuseness parameters (δ) of PSNN-PZT compositions

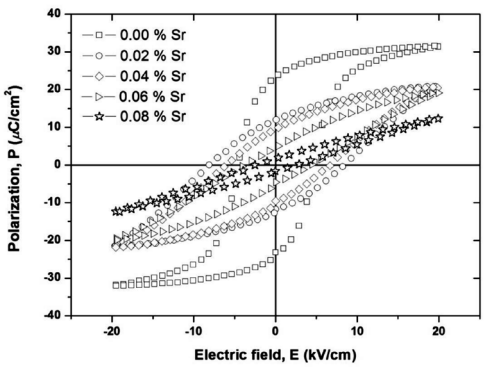

Figure 7. P-E loops for PSNN-PZT ceramics at room temperature at frequency 1 kHz

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