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Ceramics International 29 (2003) 35–39

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Dielectric and piezoelectric properties of $PbZrO_3$–$PbTiO_3$–$Pb(Ni_{1/3}, Sb_{2/3})O_3$ ferroelectric ceramic system

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Received 23 January 2002; received in revised form 25 February 2002; accepted 15 May 2002

Abstract

Perovskite PZT variants were synthesized from stoichiometric oxide ratios of Pb, Zr, Ti, Ni and Sb. The oxide powders were mixed mechanically and calcinated, and then sintered to form the desired perovskite phase. The multi-component ceramic system consisting of the $PbZrO_3$–$PbTiO_3$–$Pb(Ni_{1/3}, Sb_{2/3})O_3$ (PZT-PNS) ternary system near the rhombohedral/tetragonal morphotropic phase boundary (MPB) was investigated by X-ray diffraction and dielectric properties. The MPB traces an almost linear region between the two MPB compositions of PZT-PNS 46/44/10 and PZT-PNS 41/49/10. The piezoelectric properties of PZT-PNS were analyzed using the resonant frequency method. The maximum electromechanical coupling factor $kp = 0.69$ was found at PZT-PNS 46/44/10, where dielectric constant $\varepsilon = 3100$ and $Tc = 278$ °C were obtained.

Keywords: C. Dielectric properties, C. Piezoelectric properties; D. Perovskites; $Pb(Zr, Ti)O_3$–$Pb(Ni_{1/3}, Sb_{2/3})O_3$ solid solution; Diffuse phase transition

1. Introduction

$Pb(Zr_x, Ti_{1-x})O_3$ (generally known as PZT), a solid solution of perovskite ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$ in different Zr/Ti ratios has been considered an important material for a wide range of piezoelectric, pyroelectric and ferroelectric device applications such as transducers, computer memory and display and pyorelectric sensors [1,2]. Since the discovery of relaxor behavior in $Pb(Mg_{1/3}, Nb_{2/3})O_3$ [3], $Pb(Zn_{1/3}, Nb_{2/3})O_3$ [4], and $Pb(Ni_{1/3}, Nb_{2/3})O_3$ [5], the studies of relaxor ferroelectrics with $Pb(B'_{1/3}, B''_{2/3})O_3$-type perovskites have attracted much attention because of their excellent dielectric and electromechanical properties. $PbTiO_3$, $PbZrO_3$ and $Pb(Zr_x, Ti_{1-x})O_3$ belong to the perovskite structural family with general formula ABO_3 (A = mono or divalent ions, B = tri- to pentavalent cations). It is well established that the physical properties or device parameters of PZT can be tailored by synthesizing the material with improved processing techniques and making suitable substitutions at A and/or B-sites. The electrical properties of relaxor ferroeleectics are greatly influenced by the manner in which the B-site cations (B′ and B″ ions) are distributed and ordered on the the B-site sublattice. The Zr/Ti ratio is known to strongly influence properties, such as the elastic constant, the piezoelectric constant, the permittivity, the coupling factor, etc. Near the morphotropic phase boundary (MPB), all these properties take extreme values when x corresponds to the composition of the morphotropic phase boundary (MPB) which separates the tetragonal (T) and rhombohedral (R) phases towards Ti-rich and Zr-rich sides, respectively.

The MPB has believed to be a sharp transition, but in practice the MPB has a finite range of compositions over which the tetragonal and rhombohedral phases coexist in ceramics. The width of the MPB has been investigated by many authors and found to be related to the heterogeneous distribution of Zr^{4+} and Ti^{4+} cations on the B-site of the perovskite lattice [6,7]. Investigations of the $Pb(Zr_x, Ti_{1-x})O_3$ system have shown the existence of an almost temperature independent morphotropic phase boundary at $x = 0.52$–0.53, which separates a rhombohedral phase from a tetragonal one. By means of X-ray diffraction, the co-existence of the two phases over a range of compositions around the

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0272-8842/02/$22.00
PII: S0272-8842(02)00086-X

MPB was demonstrated [8–18]. Many authors have shown that the co-existence of the two phases at the MPB is due to the frozen-in compositional fluctuations at the Zr/Ti site because of the diffusional limitations of the conventional solid state processing route.

Many factors have been found to influence the non-uniformity of composition of PZT near the MPB, such as the raw powder particle size, surface area and purity. More important however are process variables such as calcination temperature and the method employed to minimize PbO loss. The volatility of the PbO component of PZT at high temperatures makes the stoichiometry difficult to control. Either an excess or a deficiency of PbO can degrade the intrinsic electromechanical properties. Excess PbO is usually added to compensate for loss of PbO during calcing and sintering, by reducing the concentrations of lead and oxygen vacancies.

The objective of the present work is to describe the ceramic, dielectric and piezoelectric properties of xPb ZrO_3–(90-x)$PbTiO_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 ternary system by X-ray diffractometry (XRD). Another purpose of this work is to show a structural transformation boundary in the ternary system.

2. Experimental procedure

The raw materials were commercially available powders, in oxide form, of high purity: Pb_3O_4 (99.9%), TiO_2 (99.56%), ZrO_2 (99.9%) with average particle sizes of less than 10 μm. PZT was doped with 10 wt.% of selected metal oxides NiO (99.9%) and Sb_2O_3 (99.9%) to alter the properties of the ceramic. The general chemical formula for the investigated composition is: xPbZrO_3–(90-x)$PbTiO_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 near the rhombohedral–tetragonal morphotropic phase boundary, were prepared from mixed oxides. This chemical formula is abbreviated in the text as PZT-PNS. Table 1 shows the atomic properties of the starting constituents. For doping, Ni2+ and Sb5+ ions were used to occupy the B sites of the structure.

2.1. Sample preparation for crystallographic structure

Lead zirconate titanate ceramics near the morphotropic phase boundary composition were prepared following a previously described procedure of the mixed oxide calcinations route [14]. The selected composition was: xPb ZrO_3–(90-x)$PbTiO_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3, where $39 < x < 47$. Powders were sintered from 850 to 1200 °C for 2 h. To prevent PbO loss or vaporization during the high temperature sintering, an equilibrium PbO vapor pressure was established with $PbZrO_3$ powder. The powder samples were examined by XRD using a Siemens D500-X-ray diffractometer. The voltage and currents ratings used were 40 kV, 30 mA respectively, and $Cu_{K\alpha}$ radiation was used. The diffraction data were collected from 43 to 46° with an X-ray scan speed of 0.1° min^{-1}.

Table 1
Atomic properties of PZT-PNS

Material	Ions	Ionic radius	Atomic weight
PbO (Pb_3O_4)	Pb^{2+}	1.32	207.20
TiO_2	Ti^{4+}	0.64	47.90
ZrO_2	Zr^{4+}	0.87	91.22
Sb_2O_3	Sb^{5+}	0.90	121.75
NiO	Ni^{2+}	0.62	58.71

2.2. Sample preparation for electrical measurements

For electrical and piezoelectric measurements, the samples were prepared by the usual ceramic technique. The oxides were mixed mechanically during 10 h in batches about 80 g and pressed at 1200 kg/cm^2 into pellets about 15–20 mm high and 13 mm diameter. After mixing, pre-firing of the powders took place at 800 °C for 2 h, followed by dry ball-milling for 30 h. The calcined powders were ground thoroughly, and specimen discs were made with a diameter of 12 mm and a thickness of 0.8 mm, were pressed at 14,000 kg/cm^2. After binder burnout, the samples were sintered at a temperature of 1050–1200 °C in the Al_2O_3 crucible. It was verified after each sintering run that there was no weight loss in the pellets due to the possible escape of PbO at high temperatures.

After sintering, silver paste was fired onto the faces of ceramics at 750 °C for 30 min. The specimens were immersed in silicone oil and poled in a 20–35 kV cm^{-1} DC field. The electrical field was applied at a temperature of 110 °C for 30 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 by a method similar to that of the IRE standard resonance method. The resonance and antiresonance frequencies were obtained using the maximum and minimum of admittance spectra.

3. Results and discussion

Sintered powders were examined by X-ray diffractometry to ensure phase purity and to identify the phases and lattice constants of the materials. The phases of the samples were detected using XRD (at room temperature) of the peak (200) in the $x$$PbZrO_3$–(90-$x$) $PbTiO_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 for several compositions given in Table 2. Most of the samples did show the splitting of peaks into triplets indicating tetragonal and rhombohedral phases. Thus, the samples were perovskite structure, a condition critical for the piezoelectric effect. A transition from rhombohedral to tetragonal phase is

Table 2
Series of compositions and crystal structure

Compositions $x/y/z$	Crystallographic structure					
	850 °C	950 °C	1050 °C	1150 °C	1180 °C	1200 °C
48/42/10	R	R	R	R	R	R
47/43/10	T+R	T+R	T+R	T+R	R	R
46/44/10	T+R	T+R	T+R	T+R	R	R
45/45/10	T+R	T+R	T+R	T+R	T+R	T+R
44/46/10	T+R	T+R	T+R	T+R	T+R	T+R
43/47/10	T+R	T+R	T+R	T+R	T+R	T+R
41/49/10	T+R	T+R	T+R	T+R	T	T
39/51/10	T+R	T+R	T+R	T+R		
37/53/10	T	T	T	T		

T = tetragonal; R = rhombohedral; T + R = mixture of tetragonal and rhombohedral phases.

observed as the concentration of $PbTiO_3$ increases. The transition zone is a region where both phases exist simultaneously. Fired PZT-PNS 46/44/10 indicates a rhombohedral phase, while PZT-PNS 41/49/10 has a tetragonal phase. However, compositions from PZT-PNS 45/45/10 to PZT-PNS 43/47/10 exhibit three different peaks, representing a mixture of the rhombohedral and tetragonal (R + T) phases. The co-existence region is therefore quite narrow ($\Delta x = 0.05$) and extends between x_T and x_R. The coexistence of tetragonal and rhombohedral phases has, therefore, to be attributed to the first order nature of the MBP, this is marked contrast to the proposition of Kakegawa et al. [17,18] that the coexistence is invariably due to compositional fluctuations. The intrinsic range of composition for this coexistence is, however, very narrow and is easily distinguishable from the extrinsic, wide range of coexistence region in compositionally inhomogeneous samples prepared by the conventional dry route.

The dielectric constant (ε) and the electromechanical coupling factor (kp) were measured for specimens of various compositions sintered at 1180 °C. Fig. 1 shows dielectric properties of the xPbZrO$_3$–(90-x)PbTiO$_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 ceramics. The composition PZT-PNS shows a large dielectric constant maximum of around 3100. 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. 2, The Curie temperature varies from 250 to 305 °C as a function of $PbTiO_3$ in the xPbZrO$_3$–(90-x)PbTiO$_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 system.

The evaluation results of the electromechanical coupling factor kp are shown in the xPbZrO$_3$–(90-x)PbTiO$_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 system in Fig. 3. PZT-PNS exhibits very large kp values around the MPB. The largest value of PZT-PNS 44/46/10 which is near the MPB region. Many parameters affect the final piezoelectric properties of ceramics including composition, impurities, phase purity, fired density, grain size, Tc, electrode material, poling condition and measurement procedure.

$PbTiO_3$, $PbZrO_3$ and Pb(Zr_x, Ti_{1-x})O_3 belong to the perovskite structural family with general formula ABO_3 (A = mono or divalent ions, B = tri-to pentavalent cations). It is well established that the physical properties or device parameters of PZT can be tailored by synthesizing the material with improved processing techniques and making suitable substitutions at A and/or B-sites. Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 is a typical Pb($B_{1/3}$, $B'_{2/3}$)O_3-type relaxor with rhombohedral symmetry at room temperature, while $PbTiO_3$ is a normal ferroelectric tetragonal

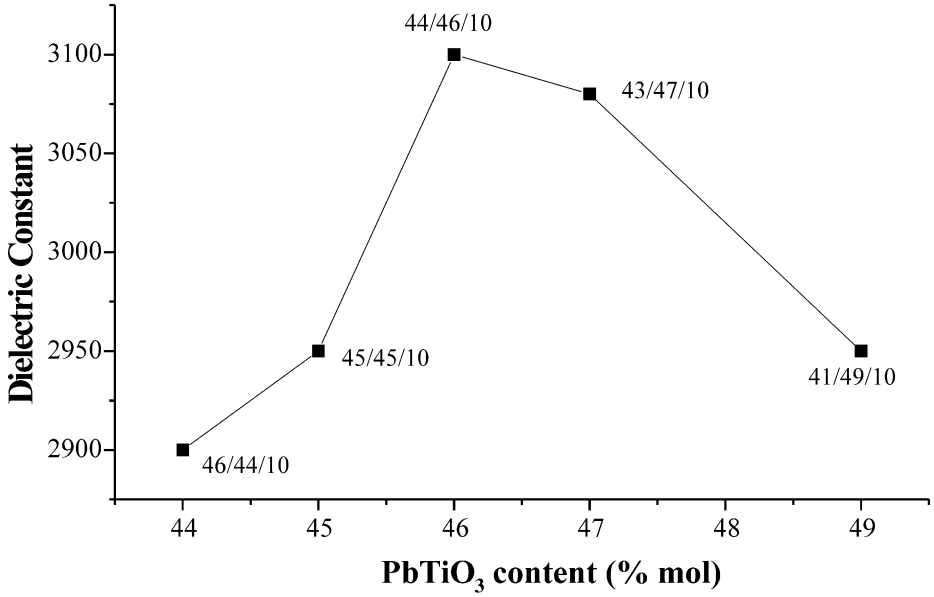

Fig. 1. The dielectric constant ϵ for xPbZrO$_3$–(0.9-x)PbTiO$_3$–0.1Pb($Ni_{1/3}$, $Sb_{2/3}$)O_3 system.

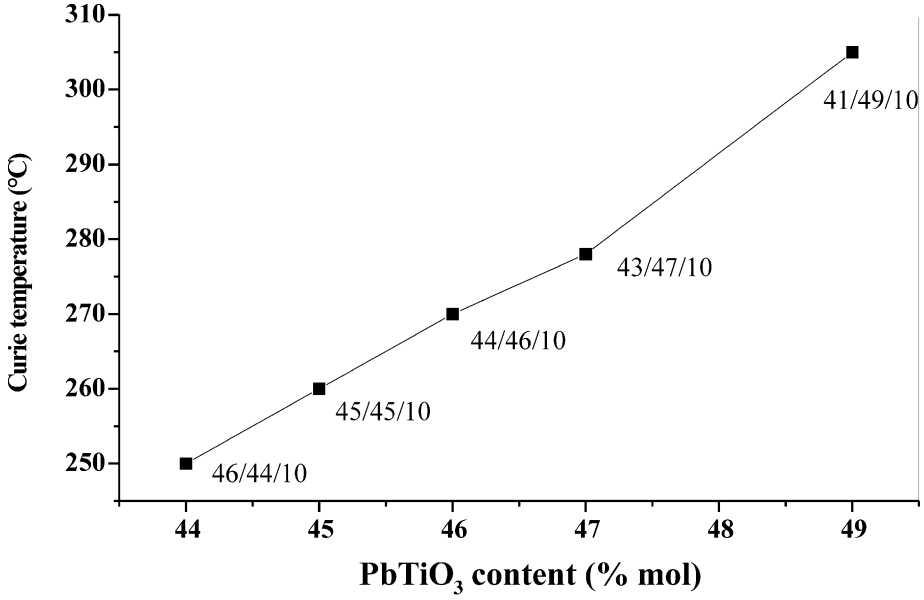

Fig. 2. Dependence of Curie temperature on $PbTiO_3$ content in the xPbZrO$_3$–(0.9-x)PbTiO$_3$–0.1Pb($Ni_{1/3}$, $Sb_{2/3}$)O$_3$ system.

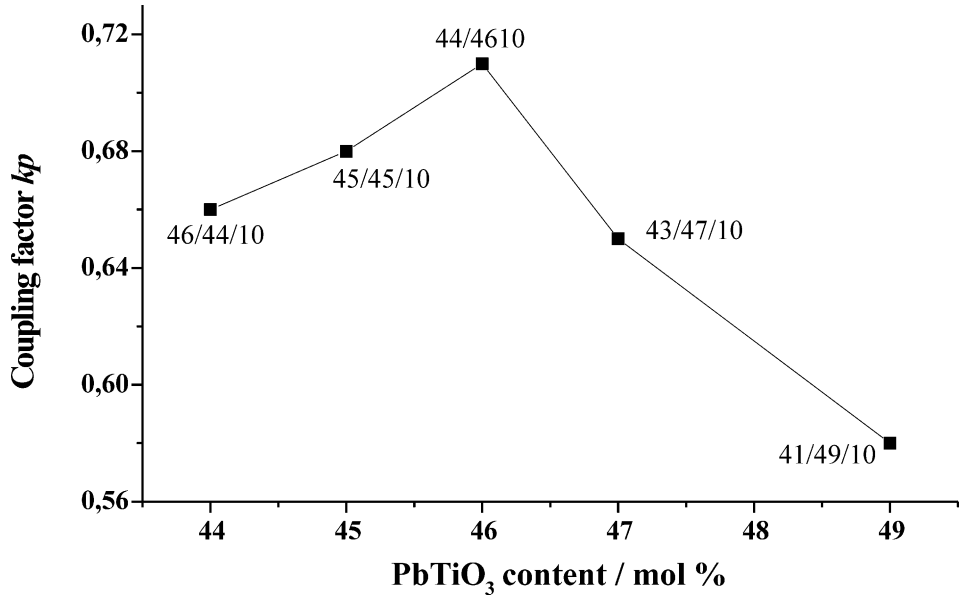

Fig. 3. The electromechanical coupling factor kp for xPbZrO$_3$–(0.9-x)PbTiO$_3$–0.1Pb($Ni_{1/3}$, $Sb_{2/3}$)O$_3$ system.

symmetry. The content of $PbTiO_3$ is over 39% our in xPbZrO$_3$–(90-x)PbTiO$_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O$_3$ ternary system. If there were no $PbZrO_3$ in the system, the system would be a normal ferroelectric with tetragonal symmetry. However, as stated above, the increase of Zr/Ti ratio in the xPbZrO$_3$–(90-x)PbTiO$_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O$_3$ ternary system increases the fraction of rhombohedral phase and enhances the extent of dielectric dispersion and diffuse phase transition around dielectric permitivity peak. The enhanced diffuse phase transition in Pb($B_{1/3}$, $B'_{2/3}$)O$_3$-type perovskites suggests that more 1:1 short-range ordered micro-domains formed [4]. Since the average Ni:Sb ratio in the xPbZrO$_3$–(90–x)PbTiO$_3$–10Pb($Ni_{1/3}$, $Sb_{2/3}$)O$_3$ system is 1:2 (as different from 1:1 for the ordered micro-domains), the enhanced 1:1 short-range ordering of Ni:Sb in the presence of $PbZrO_3$ thus expedites the B-site compositional fluctuation occurring on a nanometer scale. This further illustrates that micro-compositional inhomogeneity is responsible for the diffuse phase transition behavior in Pb($B_{1/3}$, $B'_{2/3}$)O$_3$-types perovskites. For this type of ordering, because the Ni:Sb ratio is 1:1 within the nanometer-sized ordered domains,

strong charge effects will result, where the ordered (Ni-rich) micro-domains will have a net negative charge with respect to the disordered (Sb-rich) matrix.

From considerations of ionic radii it is highly probable that Zr^{4+} ions occupy the B sites of perovskite structure. A possible substitution of Zr^{4+} ions for Sb^{5+} ions would lead to a Ni:Zr order. However, consideration of the possible 1:1 ordering of Ni^{2+} and Zr^{4+} ions in a xPbZrO$_3$–(90-x)PbTiO$_3$–10Pb(Ni$_{1/3}$, Sb$_{2/3}$)O$_3$ solid solution yields the local B-site valency of +3 and is therefore electrostaticaly less favorable than Sb:Zr order, which is an expected 1:1 order when Zr^{4+} ions substitute for Ni^{2+} ions in the B sites of perovskite structure. Because of the coulombic effect, the substitution of Zr^{4+} is a more possible substitution for Ni^{2+} is more probable than the substitution for Sb^{5+} ions. In addition, Zr^{4+} is a more possible substitution for Ni^{2+} because the radii of Zr^{4+}. Since Zr is tetravalent and Ni is divalent, the Zr behaves as a donor dopant. Therefore, the donor doping with Zr^{4+} ions would be expected to compensate the charge imbalance effect resulting from the 1:1 ordering of Ni:Sb. This charge compensation in turn stabilizes the ordered micro-domains, and hence favors an increasing degree of short range ordering. On the other hand, it is believed that Ti^{4+} ions are not closely involved with the short-range ordering in the Pb(B$_{1/3}$, B′$_{2/3}$)O$_3$-types perovskites [4]. Consideration of the possible 1:1 ordering of Ni^{2+} and Ti^{4+} ions yields the local B-site vacancy of +3 and is electrostaticaly less favorable than Ni:Sb order. Sb:Ti ordering is also unlikely since this type of 1:1 ordering involves the substitution of small-sized Ti^{4+} ion for relatively large-sized Ni^{2+} ion which requires larger strain energy than Ni:Sb ordering. Therefore, the degree of the short-range B-site order is expected to decrease with increasing $PbTiO_3$ content. This prediction is consistent with the observation that the degree of diffuse phase transition and dielectric dispersion decreases with increasing $PbTiO_3$ content across the morphotropic phase boundary.

4. Conclusions

The dielectric and electrical properties of xPbZrO$_3$–(90-x)PbTiO$_3$–10Pb(Ni$_{1/3}$, Sb$_{2/3}$)O$_3$ ternary ceramic materials near the morphotropic phase boundary (MPB) were investigated. Samples were prepared by a conventional ceramic procedure, sintered at 1180 °C for 2 h. The MPB traces an almost linear region between the two MPB compositions of PZT-PNS 46/44/10 and PZT-PNS 41/49/10. The electromechanical coupling factor (kp) and the dielectric constant reach their maximum at the new MPB. This material system offers high electromechanical coupling factors ($kp > 0.58$) with Curie temperature ranging from 250 to 305 °C.

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