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Short communication

Effect of composition on the electromechanical properties of $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ ceramics

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Abstract

The effect of composition on the structure and piezoelectric properties of $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ sintered samples, with $0.40 \leq x \leq 0.49$, was investigated. The samples structure was determined by X-ray diffractometry and the piezoelectric properties by the resonance–antiresonance method. A morphotropic phase boundary (MPB) with optimum piezoelectric properties was found around $x = 0.45$. The maximum electromechanical coupling factor was $k_p = 0.64$.

Keywords: C. Dielectric properties; C. Piezoelectric properties; D. PZT; Morphotropic phase boundary

1. Introduction

Piezoelectric lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT) ceramics have been widely investigated owing to their several possible applicational fields [1]. The crystal structure is the perovskite one (ABO_3) with a pronounced maximum in dielectric and piezoelectric constant near the morphotropic transformation at Zr/Ti between 0.52 and 0.55. Additive modified with PZT has been widely studied in order to improve its properties. However, the modifications generally lead to the creation of undesirable defects due to a lack of compensation in some of the components.

Many works have been reported on the piezoelectric properties of PZT solid solution using various techniques [2–5]. The Zr/Ti ratio is known to strongly influence properties, such as elastic constant, piezoelectric constant, permittivity, coupling factor, etc. All these properties take extreme values near the morphotropic phase boundary (MPB) when x corresponds to the MPB composition [6–14]. PZT is normally sintered at temperatures between 1150 and 1300 °C. The MPB is an almost temperature-independent boundary that separates two ferroelectric phases: a tetragonal crystal structure and a rhombohedral structure. The co-existence of the two phases (tetragonal–rhombohedral) over a range of compositions around MPB was demonstrated [15–19]. Compositional fluctuations are believed to be responsible for the co-existence of tetragonal and rhombohedral phases for compositions near the MPB. Due to this inhomogeneity, several novel preparatory techniques have been investigated in order to obtain PZT with minimal compositional variation near the MPB.

The aim of the present contribution was to evaluate properties of different compositions of $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ ceramics. X-ray diffractometry (XRD), in conjunction with the evaluation of dielectric and piezoelectric properties, was used to determine the exact composition of the MPB.

2. Experimental

A perovskite solid solution of the stoichiometric composition $Pb[Zr_xTi_{(0.9-x)}(Cr_{0.2}, Zn_{0.2}, Sb_{0.6})_{0.1}]O_3$ where $0.40\ x \leq 0.49$, was chosen as the basis of the investigation. Reagent grade 99% pure Pb_3O_4, TiO_2, ZrO_2, Sb_2O_3, ZnO, and Cr_2O_3 were used as starting materials. Mixed oxides, after milling, were calcined at 800 °C for 2 h at heating and cooling rates of 2 °C/min. After calcination, the ground and milled powders were pressed into disks 13 mm in diameter and about 1 mm in thickness. Pressed disks of $3PbO + 2ZrO_2$ placed in a capped crucible to prevent PbO evaporation during sintering were sintered at 1180 °C for 2 h in PbO atmosphere. After sintering, silver paste was fired on to the faces of ceramics at 750 °C for 30 min.

X-ray diffraction (XRD, Simens D500) was used to determine the crystalline phases present in the powder. The

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compositions of the PZT phases were identified by analysis of the peaks [(0 0 2)T, (2 0 0)R, (2 0 0)T] in the 2θ range 43°–6.5°. The tetragonal (T), rhombohedral (R) and tetragonal–rhombohedral phases were characterized and their lattice parameters were calculated. The rhombohedral lattice parameter was calculated on the assumption that the rhombohedral distortion was constant (unit cell angle $\alpha_R = 89.9°$) [9,10]. In order to ensure an accurate determination of the lattice parameters, the X-ray peaks were recorded gradually with 0.01° steps.

Measurements were made of the dielectric constant and dissipation factor at least 24 h after the specimens were silvered. Before measuring the piezoelectric properties, the specimens were poled in silicone oil at 110 °C by applying a d.c. field of 2.6 kV/mm for 45 min. Twenty-four hours after poling, the piezoelectric properties (electromechanical planar coupling factor k_p, piezoelectric constant (d_{31}, g_{31}) and Young's modulus (Y) were measured by a method similar to that of the IRE standard. The resonance and the antiresonance frequencies were obtained using the maximum and the minimum of admittance spectra

3. Results and discussion

Sintered powders were examined by X-ray diffractometry to ensure phase purity and to identify the crystal structure. The co-existence of tetragonal and rhombohedral phases near the morphotropic phase boundary implies the existence of compositional fluctuations which can be determined from the width of the X-ray diffraction peaks. However, determination of the compositional fluctuation for samples near the morphotropic phase boundary is difficult. XRD patterns of PZT powders were analyzed for detecting the characteristic rhombohedral and tetragonal splittings. The 2 0 0 reflections form a doublet in the tetragonal phase while 1 1 1 is a singlet. For the rhombohedral phase, 1 1 1 is a doublet while the 2 0 0 is a singlet.

The powder X-ray patterns of $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ ceramics with different x values are shown in Fig. 1. For x in the range of 0.44–0.47, the diagram indicates that a mixture of phases should be present, which is illustrated by the (0 0 2) and (2 0 0) tetragonal doublet enclosing the (2 0 0) rhombohedral line. For x in the range of 0.40–0.42 there is a little evidence of the (2 0 0) R peak, indicating a virtually single-phase tetragonal structure. X-ray powder diffraction patterns from $x = 0.48$ to $x = 0.49$ indicated the presence of single-phase pérovskite structure illustrated by the (2 0 0) line. It is evident from Fig. 1 that as the Zr content increases, the rhombohedral phase becomes more prominent whereas the tetragonal decreases.

Fig. 2 shows the lattice constant at room temperature as function of x. It can be seen that the tetragonal lattice parameter a_T increases linearly with increasing x, while the c_T parameter decreases linearly to a smaller extent. In all the composition range where the tetragonal phase is present, c_T and a_T are closing to gather a_T when Zr content decreases, particularly inside the co-existence region, meaning that the structure is approaching the cubic geometry. The rhombohedral lattice parameter a_R appears to oscillate between 4.07 and 4.052 Å. It can be seen that tetragonality (c_T/a_T ratio) decreases with x and becomes close to unity near $x = 0.47$.

The room temperature dielectric constant, ε, measured at 1 kHz for $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ for x in the range of 0.4–0.49 is shown in Fig. 3a. ε value increases with an increase of x and reaches a peak at $x = 0.45$, then decreases. The dielectric properties of the MPB compositions which show a first-order phase transition have a very weak frequency dispersion of dielectric constant. Fig. 3b is a plot of the dissipation factor (at room temperature, 1 kHz) versus composition. All the samples within the investigated compositional range ($x = 0.40$–0.49) have dissipation factors of <5%.

Fig. 4 shows the piezoelectric properties. The electromechanical coupling factor k_p increases with an increases of x, reaches a peak value at $x = 0.45$ and then decreases. The maximum of k_p coincides with the maxima of the dielectric constant and piezoelectric constant (d_{31}, g_{31}). The composition $Pb[Zr_{0.45}Ti_{0.45}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ shows a k_p value of 64%. The value of Y decreases as the x increases, and Y attains a minimum value at $x = 0.45$. Thus, from the trend of the variation of electromechanical properties and their optimum values, it is obvious that the MPB lies approximately at $x = 0.45$

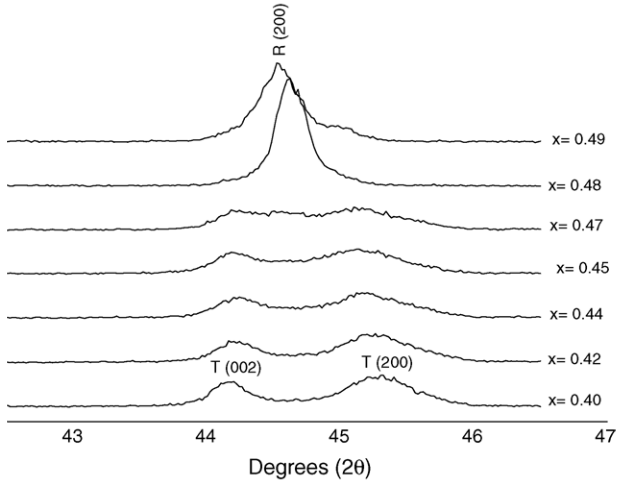

Fig. 1. X-ray diffraction patterns of $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ ceramics sintered at 1180 °C for 2 h.

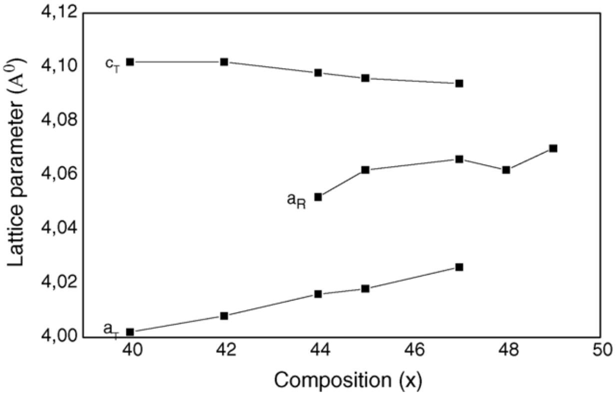

Fig. 2. Variation of the unit cell dimensions as a function of composition.

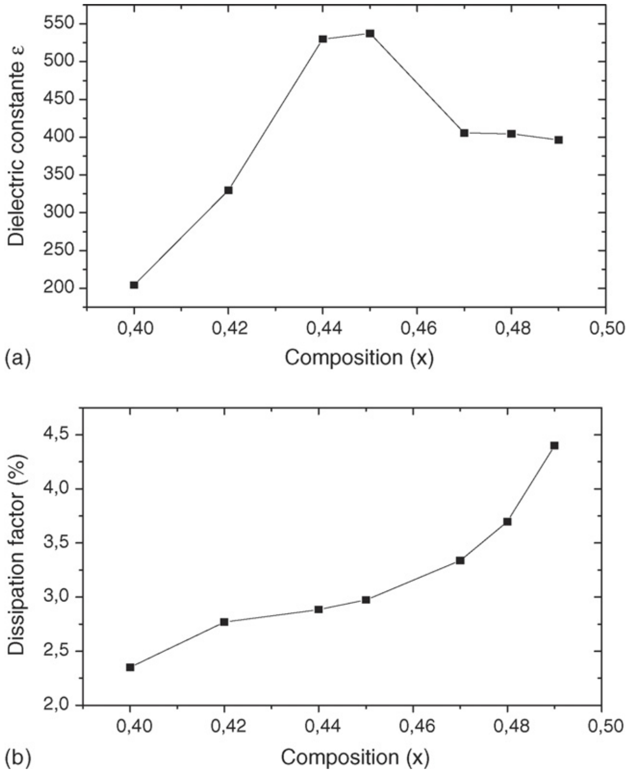

Fig. 3. Variation of (a) the dielectric constant ε, (b) the dissipation factor (at room temperature, 1 kHz) vs. function of composition.

in $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$. The composition with $x = 0.45$ contains both tetragonal and rhombohedral phases in equal quantities and favours strong piezoelectric effect due to the increased ease of reorientation during poling by transformation of a number of 180° domains into 90° ones. Therefore, it appears that the MBP zone of the solid solutions investigated is situated around the composition with $x = 0.45$. 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.

The co-existence of the tetragonal and rhombohedral phases was due to frozen compositional fluctuations at the Zr/Ti site because of the diffusional limitations of the conventional solid-state route. This can be explained by microscopic compositional fluctuations occurring in these perovskite materials, which cannot provide a real homogeneity in the solid solutions, and also by the different stresses induced in the ceramic grains, which determined the co-existence of tetragonal–rhombohedral phases. The increase of sintering temperature and firing time enhanced the diffusion effects within these regions and led to a relative homogenization of the local composition in the material. The transition from tetragonal to rhombohedral phase as a function of composition can be assumed to occur by two processes. (1) The tetragonal and rhombohedral distortions decrease continuously as one approaches the MPB composition from either side. (2) If the tetragonal to rhombohedral transition is of first order, one would expect the two phases to co-exist over some range of x around the MPB composition. Within this co-existence range, the d-spacings of the two phases will be the same as that of the pure phases just outside the MPB range.

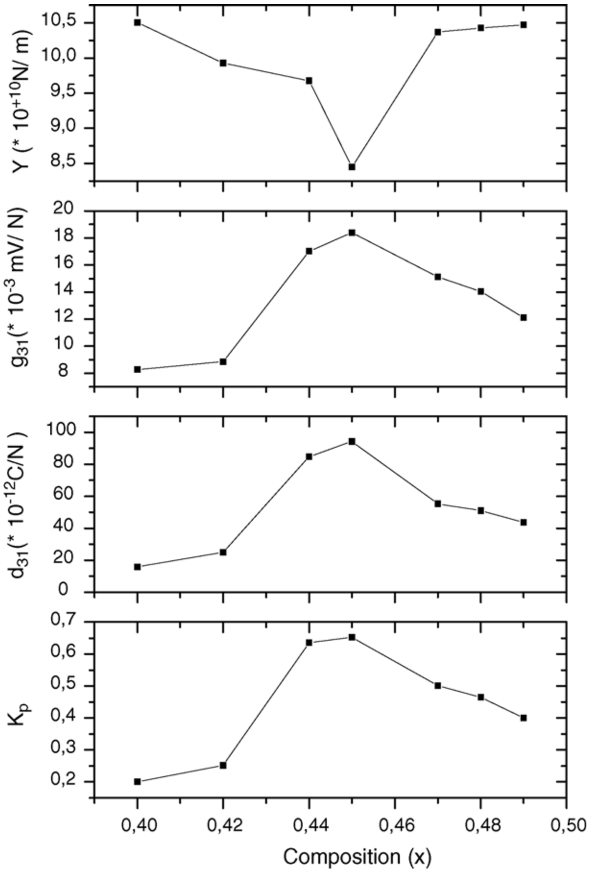

Fig. 4. Piezoelectric properties of $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ ceramics as a function of composition.

4. Conclusions

The co-existence region was investigated by X-ray diffraction. The study of the morphotropic phase boundary has established that the phase transition from tetragonal to rhombohedral symmetry in $Pb[Zr_xTi_{(0.9-x)}(Cr_{1/5}, Zn_{1/5}, Sb_{3/5})_{0.1}]O_3$ takes place at $x = 0.45$ and the width of the phase boundary has been found to be in the range of $0.44 < x < 0.47$ at 1180 °C. The lattice parameters a_T and c_T of the tetragonal structure and a_R of the rhombohedral structure were found to change with composition. The electromechanical coupling factor (k_p) and the dielectric constant reach their maximum at the new MPB. This material system offers high electromechanical coupling factors ($k_p > 0.64$).

The existence of a phase boundary between the antiferroelectric and ferroelectric phases suggests that PZT-PFNS solid solution is an attractive material for applications in piezoelectric, electrostrictive and pyroelectric devices.

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