

Preparation and characterization of transparent PZN–PLZT ceramics

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Transparent $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (PZN–PLZT) ferroelectric ceramics have successfully been prepared by hot-pressed sintering in oxygen atmosphere. Uniform cylindrical samples with diameter as large as $\phi = 50$ mm can readily be obtained. X-ray analysis and scanning electron microscopy experiments showed a pure perovskite phase, thin grain boundaries, and uniform dense microstructures. Very good transparency was reached for wavelength from near ultraviolet to infrared. The dielectric constant was also measured as a function of temperature and frequency. Some novel phenomena such as good piezoelectric and electro-optical properties have been observed.

I. INTRODUCTION

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) single crystal exhibits outstanding dielectric and electrostrictive properties and also shows a very large electro-optic coefficient.^{1–3} However, there are still many technical challenges in making large-size crystals with uniform properties. PZN-based ceramics near the morphotropic phase boundary (MPB) have also been intensively investigated for many years due to their potential unique electromechanical properties.^{4–6} Unfortunately, it is very difficult to prepare PZN ceramics with a pure perovskite structure due to its inherently low tolerance factor and small absolute value of the bond valence sum of oxygen. The product is a mixture of perovskite and pyrochlore phase. It has been found that the pyrochlore phase in the PZN system can be eliminated by the addition of certain perovskite-type compounds with controlled calcinations and sintering conditions. Such PZN ceramics showed higher dielectric constants and a broad (diffuse) phase transition. However, the additions would reduce the dielectric and piezoelectric properties compared to those of PZN single crystal. For example, BaTiO_3 was considered to be an excellent addition for stabilizing the perovskite structure in PZN ceramics, but the substitution of Ba cation was

accompanied by lowering of the Curie temperature.⁷ Doped PZN systems show maximum dielectric constant much lower than that of PZN single crystal. In addition, such PZN ceramics, like many other ferroelectric materials, are optically opaque and cannot be used in optical devices.

Transparent $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (PLZT) ferroelectric ceramics were reported by Haertling in 1971.⁸ Since then, a great deal of research has been performed on this material due to its high optical transparency, large electro-optical effect, and other properties. It is easy to prepare uniform PLZT ceramics with a large size. In recent years, PLZT ceramics have received much attention for their pronounced advantages in optical communications. However, dielectric, piezoelectric, and electro-optical properties of PLZT are not as good as those of PZN single crystal, and the optical transmittance is limited to a wavelength of about 380 nm.

Our aim is to synthesize a solid solution of PZN and PLZT to form a new compound showing combined advantages of both materials, such as excellent piezoelectric and dielectric properties, high optical transmittance in a wide range of wavelength, and strong electro-optical effect. Such a material can be useful for designing new electric and optical devices.

II. EXPERIMENTAL

PZN and PLZT were synthesized using hot-pressed solid-state sintering method in an oxygen atmosphere. PbO , La_2O_3 , ZnO , Nb_2O_5 , ZrO_2 , and TiO_2 with purity of

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99.4–99.8% and micrometer particle size were used as starting materials. The stoichiometric mixture was ball-milled in a plastic container with zirconia grinding media in alcohol solution, then dried and ground. The ground mixture powders were pressed under 80 kg/cm^2 pressure into a cylindrical bar of 60 mm in diameter and 60 mm in height. During a sintering process, an oxygen flow of 3 L/min was passed through the oven. The sintering temperature was elevated to $950 \text{ }^\circ\text{C}$ at a rate of $200 \text{ }^\circ\text{C/h}$ and kept for $\frac{1}{2}$ h, then pressure was gradually applied to the sample until 480 kg/cm^2 while the oven temperature was increased to $1200 \text{ }^\circ\text{C}$ at the same time. The temperature and pressure were kept for 6 h before the pressure was released. Subsequently, the temperature was continuously increased to $1250 \text{ }^\circ\text{C}$ in $\frac{1}{2}$ h and kept for 10 h. After sintering, the oven was cooled down to $950 \text{ }^\circ\text{C}$ at a rate of $140 \text{ }^\circ\text{C/h}$ and then cooled naturally until room temperature. The sintered specimen was cut and polished to obtain the required size for different measurements. Gold electrodes were deposited on both surfaces of the PZN–PLZT samples to allow poling and to measure electrical properties. Interdigital electrodes were made for determining electro-optical properties. Microstructures of the PZN–PLZT transparent ceramics were investigated using scanning electron microscopy (SEM; JSM-6700 Field-Emission Scanning Electron Microscope) and the structural phase was identified by x-ray diffraction (XRD; D/MAX 2550V, Rigaku, Japan). The dielectric response as a function of frequency and temperature were carried out using an automated HP 4284 LRC meter from 100 to 10^6 Hz and in a temperature range of $30\text{--}260 \text{ }^\circ\text{C}$ on heating and subsequent cooling at a rate of $1.5 \text{ }^\circ\text{C/min}$ using a Delta 9023 oven. A piezoelectric coefficient d_{33} was measured by a Berlincourt meter. An optical transmittance of specimen was examined by a Perkin Elmer ultraviolet-Vis spectrometer in a range from 190 nm to 1100 nm and by Fourier-transform infrared spectroscopy (Perkin Elmer 2000) from 1100 nm to 12000 nm.

III. RESULTS AND DISCUSSION

Optical-quality PZN–PLZT ceramics with a pure perovskite structure have successfully been fabricated. Figure 1 shows x-ray diffraction patterns of $(\text{Pb}_{0.97}\text{La}_{0.03})(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.3}(\text{Zr}_{0.54}\text{Ti}_{0.46})_{0.7}\text{O}_3$. The XRD displays sharp peaks corresponding to perovskite structure and a preferred orientation in (110).

For stabilizing perovskite structure, the character of bonds must be taken into account. The percentage of ionic bonds in the compounds is proportional to the electronegativity difference between cations and oxygen. Therefore, the stability of perovskite structure can be improved by increasing electronegativity difference between cations and oxygen. The new composition PZN–PLZT reported in this paper can be considered as a

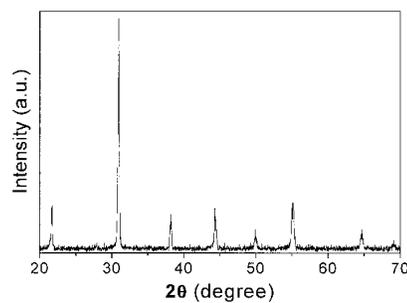


FIG. 1. X-ray diffraction patterns of PZN–PLZT transparent ceramics.

solid solution of PZN and PZT, while La substituted parts of Pb in both PZN and PZT. The electronegativity of La, Pb, and O are 1.1, 1.6, and 3.5, respectively. The electronegativity difference between La and O is larger than that between Pb and O

$$X_{\text{O}} - X_{\text{La}} = 3.5 - 1.1 = 2.4 > X_{\text{O}} - X_{\text{Pb}} = 3.5 - 1.6 = 1.9$$

A bond value parameter can be used to characterize the strength of bonds. The calculated⁹ bond value parameter of 2.172 for La–O is larger than 2.112 for Pb–O. Therefore, La and O can form stronger bonds than Pb and O. It is clear that part of Pb is replaced by La, which has smaller electronegativity, hence, is effective to stabilize the perovskite structure and suppress pyrochlore phase. In addition, PLZT itself is a perovskite-type ferroelectric and can be used for stabilizing perovskite structure in the PZN system.

Figure 2 is a SEM micrograph of a cross section of PZN–PLZT ceramic. The main features in the microstructures are high uniformity and tight contact between grains. No visible pores are observed, and grain boundaries are very sharp, even at the grain boundary triple points. Archimedes' density of PZN–PLZT ceramics was measured and reached to $8.03\text{--}8.04 \text{ g/cm}^3$, which is much higher than regular ceramics.

Lanthanum is capable of inhibiting grain growth and

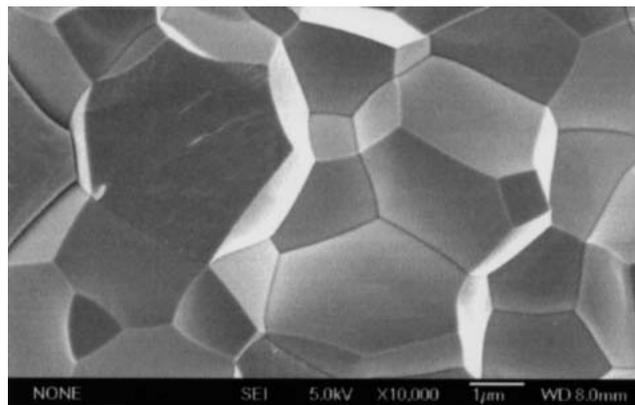


FIG. 2. SEM micrograph of a cross section of PZN–PLZT transparent ceramics.

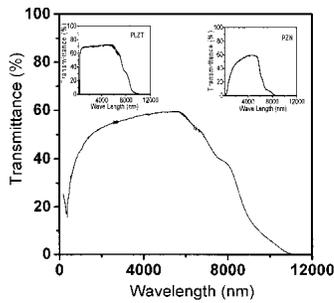


FIG. 3. Transmission spectrum of the PZN–PLZT ceramics from ultraviolet to infrared.

enhancing densification process by producing a significant number of lattice vacancies.¹⁰ It has been proven that a narrow range in grain size of 3–4 μm was found for all examined samples (Fig. 2), which are heat-treated at 1250 °C for various time from 8 to 96 h. It is observed that the La addition enhances densification and thus improves transparency.

A typical transmission curve from ultraviolet to infrared for the PZN–PLZT of 0.3 mm thickness is shown in Fig. 3, which covers the ranges of transmittance spectra of PZN single crystal and PLZT ceramics as shown in the inserts (the top-left is for PLZT ceramics of 0.3-mm thickness and the top-right is for PZN single crystal of 5-mm thickness). In other words, the transmittance of infrared wavelength extends as far as 11,000 nm, and the absorbing edge in the short wavelength shifts toward 190 nm in PZN–PLZT ceramics.

The transparent feature of our PZN–PLZT ceramics is demonstrated in Fig. 4. It appears that the transparency of the left sample {Pb_{0.97}La_{0.03} (Zn_{1/3}Nb_{2/3})_{0.3} (Zr_{0.54}Ti_{0.46})_{0.7} O₃} is better than that of the right one {Pb_{0.97}La_{0.03} (Zn_{1/3}Nb_{2/3})_{0.3} (Zr_{0.40}Ti_{0.60})_{0.7} O₃}. XRD patterns indicated that the two specimens of the same thickness of 0.3 mm with diameter of 50 mm show different lattice parameters ratio *a/c* (*a* = *b*). The *a/c* ratio of the left sample is 1.0010 and the right one is 1.0045. It means that higher structural symmetry (closer to cubic) leads to higher transparency.



FIG. 4. Demonstration of the transparencies of two PZN–PLZT ceramics with different compositions.

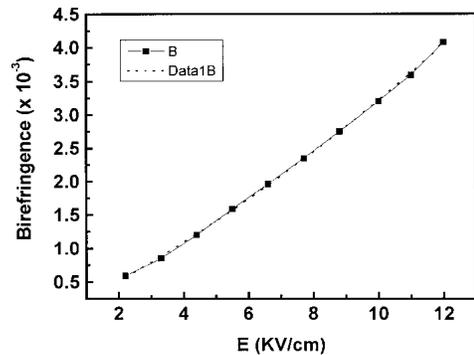


FIG. 5. Electro-optical effect of PZN–PLZT ceramics.

The birefringence Δn as a function of electric field E was measured for PZN–PLZT ceramics {Pb_{0.97}La_{0.03} (Zn_{1/3}Nb_{2/3})_{0.3} (Zr_{0.54}Ti_{0.46})_{0.7} O₃} and is shown in Fig. 5. The data are usually expressed in the form of polynomial regression

$$\Delta n = A + BE + CE^2 + DE^3 + \dots \quad (1)$$

where A is a constant, and B , C , and D are parameters related to linear, quadratic, and cubic electro-optical effects, respectively. In our case, $B = 2.8868E-8$, $C = 4.5567E-16$, $D = 1.1057E-20$ are obtained. It is obvious that B is much bigger than C and D , indicating a nearly linear electro-optical effect.

The polynomial fitted result is also shown in Fig. 5. A transverse effective linear electro-optic coefficient r can be used to define the linear electro-optical effect, which is determined by the following formula

$$\Delta n = 1/2 n^3 r E = BE \quad (2)$$

Here, $n = 2.569$ is the refractive index at the wavelength of 6328 Å measured by VASE (J.A. Wollamco. Inc., USA); E is an external applied field and the direction of E is perpendicular to the propagation direction of the light beam. From Eq. (2), $r = 3.4(10^{-10} \text{ m/v})$ has been calculated, which is much bigger than that of PLZT ceramics.¹¹

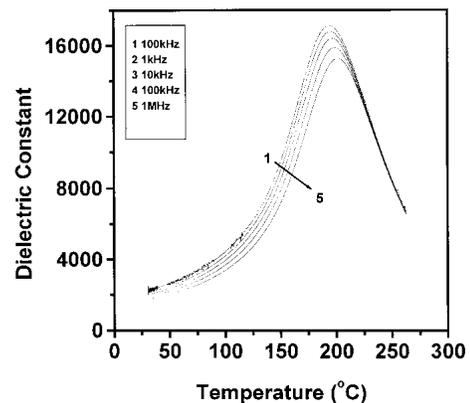


FIG. 6. Dielectric constant as a function of temperature and frequency for PZN–PLZT ceramics.

The piezoelectric constant d_{33} was measured for transparent PZN–PLZT ceramics and reached 780 pC/N. This value is comparable to that of soft PZT–5H ceramics. The variations of dielectric constant with temperature and frequency are shown in Fig. 6. One can see that the PZN–PLZT transparent ceramics exhibited typical relaxor characteristics with a diffuse phase transition and strong frequency dispersion of the dielectric maximum. The peak dielectric constants are in a range of 15,500 to 17,000. The T_{\max} (around 210 °C) is higher than that of PZN and PLZT, which is helpful for some device applications.

IV. CONCLUSIONS

Transparent PZN–PLZT ceramics with a pure perovskite structure have successfully been fabricated using hot-pressed sintering in oxygen atmosphere. The temperature dependence of the dielectric constant measured for PZN–PLZT ceramics shows a diffuse phase transition and strong dispersion. The optical transmittance spectrum of the PZN–PLZT is broader than both PLZT ceramics and PZN single crystals. An inspiring result is that PZN–PLZT ceramics possesses both outstanding piezoelectric properties and electro-optical properties. Although La is an excellent substitute for stabilizing perovskite structure due to the larger electronegativity difference and the bond strength between lanthanum ion

and oxygen ion, there is an upper limit for the La dopants that can be put into the structure to form a pure perovskite phase. In our experiments, La content is controlled between 2.8% and 5%.

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