

Electrically induced light scattering performances of lanthanum-modified lead zirconate titanate transparent ceramics

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Abstract A series of lanthanum-modified lead zirconate titanate (PLZT) ceramics of Zr/Ti (70/30) with different La concentration (La=7.6, 7.8, 8.0 mole %) were prepared by a hot pressing process. The performances of electrically induced light scattering for PLZT (X/70/30) ceramics were investigated and analyzed systematically. All samples are crystallized into a single perovskite phase. The PLZT (7.6/70/30) sample exhibits a ferroelectric behavior while both PLZT (7.8/70/30) and PLZT (8.0/70/30) samples show an antiferroelectric behavior. The phase transition temperature (T_c) of the PLZT (X/70/30) ceramics shifts slightly from ~ 86 °C to ~ 89 °C with the increasing of La concentration at 1 kHz. All three ceramic samples exhibit a high transmittance, i.e., greater than 60 %, with a thickness of 0.4 mm over a wide range of wavelength band, from visible to near IR. The PLZT (X/70/30) ceramics exhibit three different types of light scattering behavior depending on the La concentration (examined at $\lambda=632.8$ nm). Among them, PLZT (8.0/70/30) presents a unique applicable auto-switchable property with a low threshold value of electric field and high transmittance. Noticeably, the contrast ratio increases correspondingly with the thickness of the sample, and the contrast ratio aroused by the transverse electric field is about twice as big as that aroused by the longitudinal one. The light scattering properties of the PLZT (8.0/70/30) ceramic may represent a creative application in optical modulators.

Keywords PLZT · Light scattering · Domain · Ferroelectricity

1 Introduction

Nowadays lanthanum-modified lead zirconate titanate (PLZT) ceramics are receiving increasing attention for their unique electrically induced light scattering performances. Such performances promise the potential applications in optical modulators and optical shutters, et al., to meet the urgent demand for developing laser technology [1–3]. Compared with the conventional light scattering liquid crystal materials [4, 5], the PLZT ceramics exhibit several important advantages, such as fast response speed, good temperature stability, high optical damage threshold, and relatively low electric field, which make them more applicable to the modern laser technology [6, 7]. To satisfy the applications for memory and display devices [1, 8, 9], many investigations had been carried out on the PLZT (X/65/35) light scattering ceramics in the past decades. However, those PLZT ceramics must be poled first which greatly lowered their transmittances. As a result of the low transmittance, the PLZT material has a large insert dissipation, and thus severely limiting their application in the optical modulating system.

PLZT (X/70/30) ceramic is another series of light scattering material. Kumada [7] first reported the results on the PLZT (X/70/30) ceramic. Both antiferroelectric (AFE) phase and ferroelectric (FE) phase coexisted in PLZT (7.6/70/30), and the phase transition from AFE to FE could be initiated by a low electric field to induce the light scattering. PLZT (7.9/70/30) also presents a reversible light scattering performance without poling in advance [10]. When an appropriate strength of electric field is applied, an AFE to FE

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phase transition will take place, accompanied with the occurrence of light scattering. When the applied electric field is removed, the light scattering phenomenon automatically disappears and its transparency recovers simultaneously. This material presents a high transmittance when no electric field is applied on it. All these merits make such PLZT ceramic quite available to the electrically controlled optical modulators. But to date, there is less systematic work devoted to the PLZT (X/70/30) ceramics except several reports in the early time [11–14]. Almost no more significant development has been reported in the latest time to meet the increasing demands for the developing laser technology.

In this paper, a series of high transparent PLZT (X/70/30) ceramics with different La concentrations (La=7.6, 7.8, 8.0 mole %) were prepared by a hot pressing process. Various properties, i.e., phase structure, microstructure, dielectric properties and ferroelectric hysteresis loops of the PLZT ceramics, were examined and analyzed. Especially the influences of La concentration, the way of electric field applied and the sample thickness on the performances of light scattering were further investigated and discussed.

2 Experimental procedure

The PLZT (X/70/30) (La=7.6, 7.8, 8.0 mole %) transparent ceramics were prepared by a hot pressing process using PbO (99 %), ZrO₂ (99 %), TiO₂ (99 %), La₂O₃ (99 %) as raw materials in stoichiometric proportions. An excess of 10 % PbO by weight was used so as to compensate for the evaporation loss of lead at about 880 °C during the sintering process [15]. The raw materials were ball milled in the ethanol medium for 24 h, and then dried and calcinated at 900 °C for 2 h. The powder was cold pressed into pellets. Finally, all pellets were sintered at 1220 °C for 12 h in an O₂ atmosphere.

The phase structures of the sintered samples were examined by X-ray diffraction (XRD, D/MAX-2550 V, Rigaku, Tokyo, Japan). The scanning electron micrographs (SEM) of the polished and thermally etched ceramic surfaces were obtained using a Hitachi S-4800 (Tokyo, Japan). The dielectric properties were measured at different frequencies (100 Hz to 1 MHz) as a function of temperature using a Hewlett Packard LCR meter. The polarization versus electric field (*P-E*) hysteresis loops were measured on a Work-Station equipment (Radiant Technologies, U.S.A.) at room temperature in a silicone oil bath. The chromium and gold electrodes were evaporated on both sides of the major surfaces. The transmittance was measured by a U2800 spectrophotometer (Hitachi, Tokyo, Japan) on the polished wafers with a thickness of 0.4 mm. The performances of electrically induced light scattering were studied by investigating into the transmittance of the samples under a variable electric

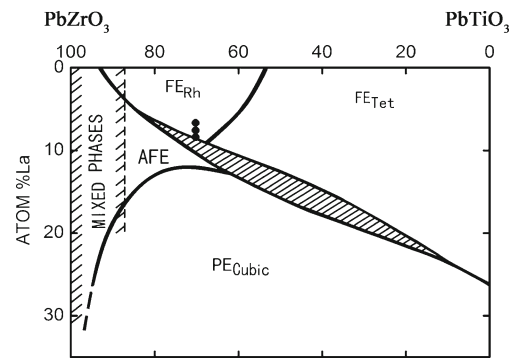


Fig. 1 The phase diagram of PLZT system at room temperature

field (examined at $\lambda=632.8$ nm). The tin doped indium oxide (ITO) transparent electrodes were deposited on both sides of the polished surfaces. The way of electric field applied to the sample was normal and parallel to the polished surface, namely longitudinal and transverse electric field, respectively.

3 Results and discussion

Figure 1 shows the phase diagram of PLZT system at room temperature [16]. The selected compositions 7.6/70/30 and 7.8/70/30 are located in the rhombohedral phase region, while the composition of 8.0/70/30 is at the boundary between the complex phase region (cross-hatched area) and rhombohedral phase.

The XRD patterns of the PLZT ceramic samples with three different compositions, i.e., 7.6/70/30, 7.8/70/30 and 8.0/70/30, are shown in Fig. 2. All PLZT ceramic samples are crystallized into a single perovskite phase. The SEM images of the polished and thermally etched ceramic surfaces for PLZT (X/70/30) ceramic samples are shown in Fig. 3. It is to be noticed that all samples exhibit fully dense, uniform microstructures with well developed grains, and the grain size increases with the

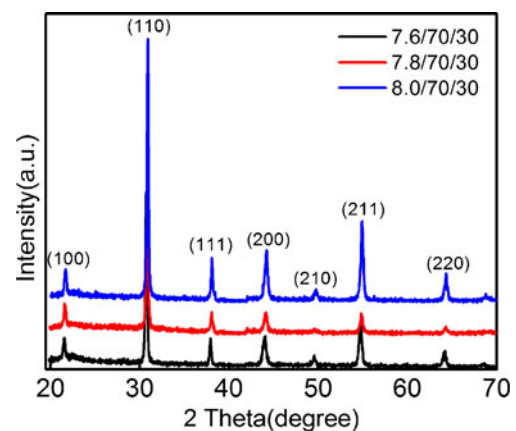
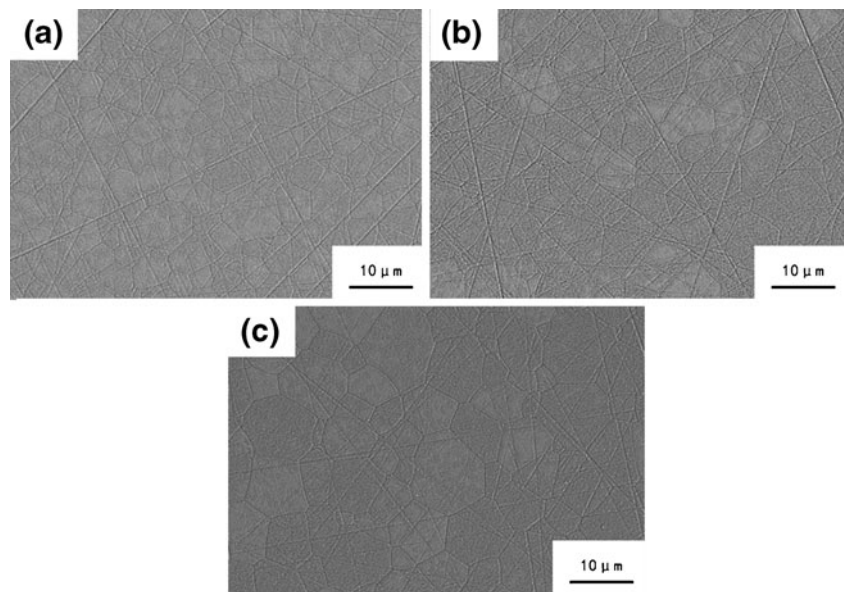


Fig. 2 The XRD patterns of the PLZT ceramics

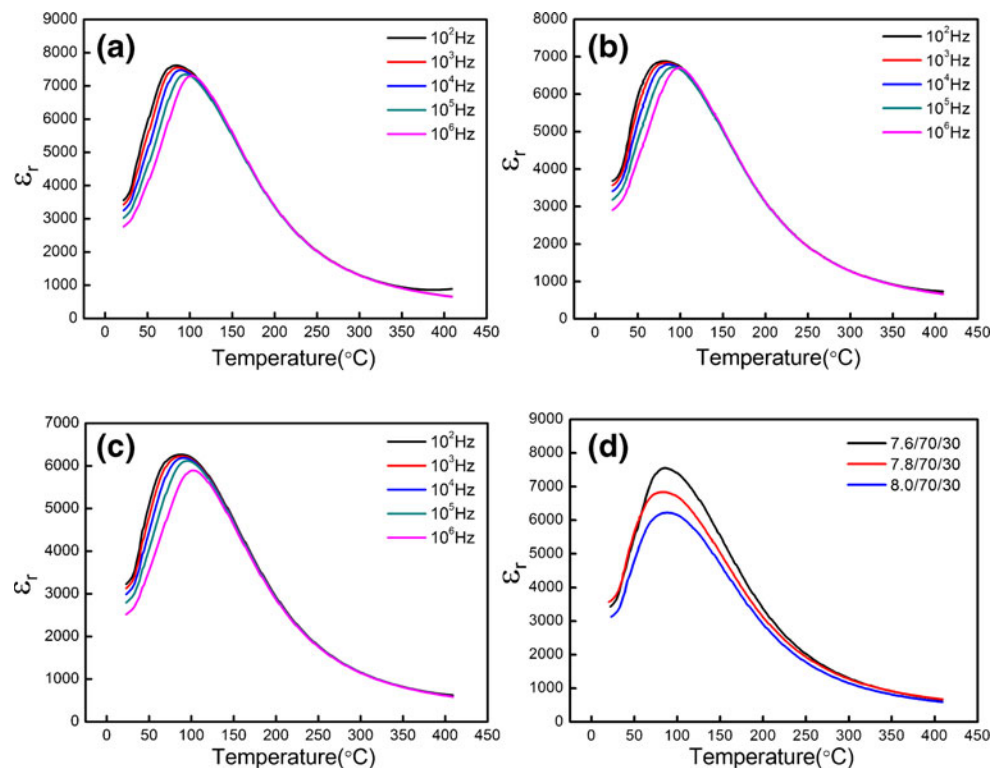
Fig. 3 The SEM images of the polished and thermally etched ceramic surfaces for PLZT (X/70/30) ceramics, (a) 7.6/70/30, (b) 7.8/70/30, (c) 8.0/70/30



increasing of La concentration [17]. It is taken into account that the sintering process leads to the ion diffusion which promotes the grain growth of PLZT (X/70/30) ceramics. Compared with Pb^{2+} (1.2 Å) ion, La^{3+} (1.06 Å) ion possesses a smaller ionic radius, thus accelerating the ion diffusion. With the increasing of La concentration, the vacancy of B-site in the material will increase accordingly. As a result of the higher La concentration in the sample, the ion diffusion is faster during sintering, which makes the grain grow bigger.

The dielectric constants (ϵ_r) were measured as a function of temperature at different frequencies for the ceramic samples with three different compositions, and the results are, shown in Fig. 4(a)–(c). A broad and diffused phase transition is observed, and the temperature at which ϵ_r exhibits the maximum value ϵ_{max} is found to increase with the increasing of frequency; however, the magnitude of ϵ_{max} decreases with the increasing of frequency. It is also to be noticed that as shown in Fig. 4(d), the La concentration exerts slight

Fig. 4 (a)–(c) Temperature-dependent of dielectric constant (ϵ_r) for PLZT ceramics at different frequencies, (a) 7.6/70/30, (b) 7.8/70/30, (c) 8.0/70/30; (d) Temperature-dependent of dielectric constant (ϵ_r) for PLZT ceramics with different compositions at 1 kHz



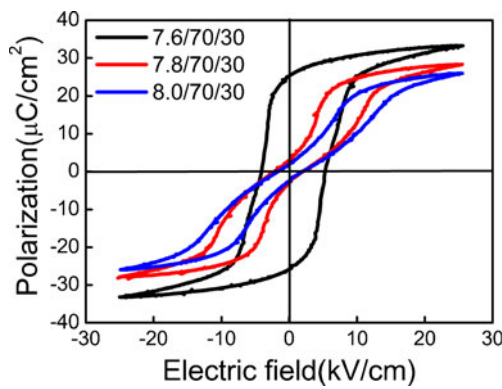


Fig. 5 The *P-E* hysteresis loops of PLZT ceramics with different compositions at room temperature

influences on the phase transition temperature (T_c) of PLZT (X/70/30) ceramics which shifts from $\sim 86^\circ\text{C}$ to $\sim 89^\circ\text{C}$ at 1 kHz.

The *P-E* hysteresis loops of PLZT ceramics are presented in Fig. 5. The PLZT (7.6/70/30) shows a square-shaped hysteresis loop of ferroelectric phase, while the PLZT (7.8/70/30) and PLZT (8.0/70/30) samples show double hysteresis loops which are due to the AFE phase property. It is also found that the remanent polarization (P_R) of PLZT (X/70/30) ceramic sample decreases sharply as the La concentration increases. As a result, once an electric field is removed, it is easier for the PLZT ceramic samples of 7.8/70/30 and 8.0/70/30 compositions to return to the original state.

Figure 6 shows the transmittance spectra of PLZT ceramics as a function of wavelength with a thickness of 0.4 mm. Since the material has a high refractive index (n) of about 2.4–2.5 in the range from visible to near IR wavelength, a large reflection loss (R) exists at the air/ceramic interfaces. The R can be calculated from the refractive index and the incidence angle with the Fresnel equation. When the direction of the

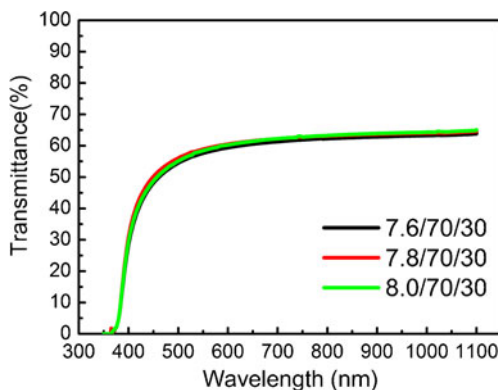


Fig. 6 The transmittance spectra versus wavelength curves of PLZT ceramics with a thickness of 0.4 mm

incidence light is normal to the medium surface, the equation for R is as below.

$$R = \frac{(n_1 - n)^2}{(n_1 + n)^2} \tag{1}$$

Where,

$n_1 = 1$ in air

$n = 2.48$ at 632.8 nm for PLZT ceramics in air,

The R is estimated to be about 30.22 % when it is calculated up to three-grade [18]. All PLZT ceramic samples with different compositions in this study exhibit high

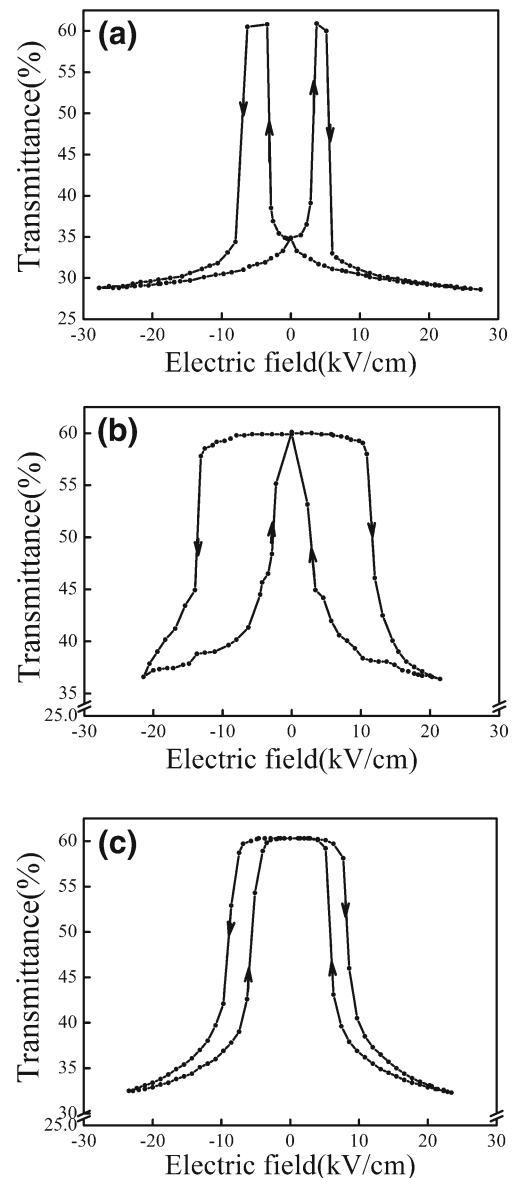
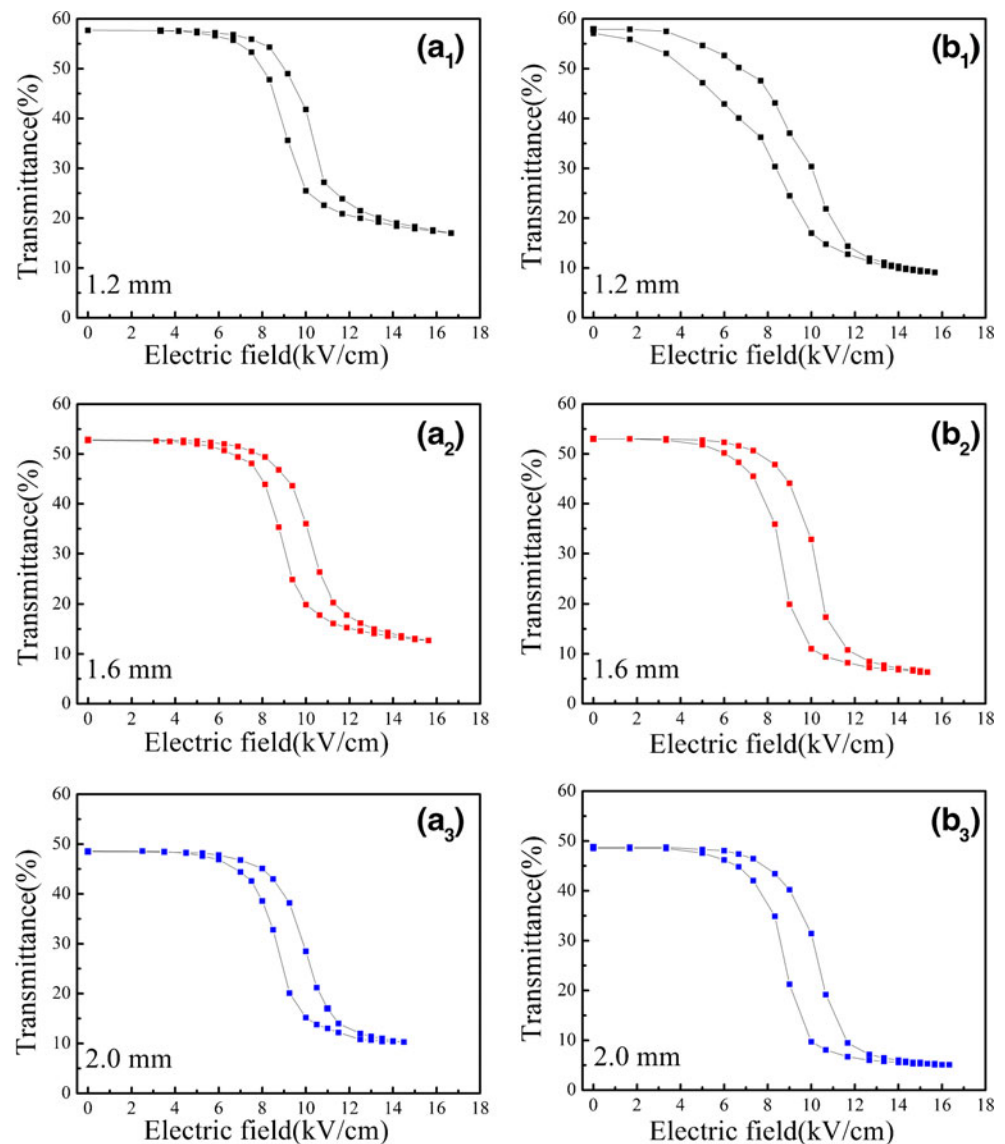


Fig. 7 The transmittance versus electric field curves of PLZT ceramics with different compositions ($\lambda = 632.8$ nm), (a) 7.6/70/30, (b) 7.8/70/30, (c) 8.0/70/30

Fig. 8 The transmittance versus electric field curves of PLZT ceramics with different thicknesses and ways of electric field applied ($\lambda=632.8$ nm), (a₁)-(a₃): longitudinal electric field; (b₁)-(b₃): transverse electric field



transmittances, greater than 60 % over a wide wavelength range. i.e., visible to near IR [19–21].

It was proposed that the scattering centers in the PLZT ceramics were refractive index discontinuities at the domain walls [22]. When an electric field is applied, the inner domains will grow and switch, leading to the light scattering and consequently the decreasing of transmittance. Therefore, the electrically induced light scattering performances of the PLZT ceramics were studied by investigating into the variation of transmittance of the samples under a variable electric field. Firstly, a longitudinal electric field with a direction in parallel to the light propagating, was selected to act on the PLZT samples (a thickness of 0.4 mm). The electric field applied is in the range from 0 to about 20–30 kV/cm. After one electric field cycle experience, the PLZT (7.6/70/30) was found to be opaque. It showed a relatively high contrast ratio, but its transmittance could not return to the original value until a suitable reverse

electric field was applied, see Fig. 7(a). Its transmittance reached the maximum at about the coercive electric field (E_c). This result is agreed with that reported by Kumada et al. [7]. The curves of transmittance v.s. electric field for PLZT (7.8/70/30) and PLZT (8.0/70/30) samples are shown in Fig. 7(b) and (c), respectively. Both samples with the corresponding composition could recover to its original state with high transmittances when the electric field was removed. In particular, compared with the PLZT (7.8/70/30)

Table 1 The contrast ratios for the transverse and longitudinal electric field (15 kV/cm) with different thicknesses of PLZT (8.0/70/30)

| Thickness/mm | Transverse electric field | Longitudinal electric field |
|--------------|---------------------------|-----------------------------|
| 1.2 | 6.22:1 | 3.22:1 |
| 1.6 | 8.37:1 | 4.02:1 |
| 2.0 | 9.17:1 | 4.70:1 |

sample, the PLZT (8.0/70/30) sample displayed a smaller threshold value of electric field (at this electric field, the transmittance decreases sharply) and a smaller hysteresis while the electric field drawn back. The great differences of light scattering behavior among the three compositions are due to the different component of phase structure. All three composition ceramics are located near the boundary between the complex phase and rhombohedral phase, see Fig. 1. With the increasing of La concentration, the content of antiferroelectric phase increases consequently, and the hysteresis loop evolves from a square-shaped loop with a large P_R to a double hysteresis loop with a small P_R . The lower the P_R value is, the easier the domain can grow and switch. This is thought to be the main reason for PLZT (8.0/70/30) to present an auto-switchable light scattering behavior with a low threshold value.

The influences of the way of electric field applied and the sample thickness on the light scattering property for the PLZT (8.0/70/30) sample is shown in Fig. 8. An electric field of 15 kV/cm was applied normal (longitudinal) and parallel (transverse) to the polished ceramic surface, respectively. With the increasing of the sample thickness, the contrast ratio increases accordingly whatever the way of electric field applied is either longitudinal or transverse. The thicker the sample is, the more the inner domains will be formed. Thus, more domain walls resulted from the inner domains arouse more serious light scattering which further decreases the transmittance. Noticeably, the contrast ratio caused by the transverse electric field is about twice as big as that of the longitudinal one (see Table 1). It is well known that the inner domains are always polarized along the direction of electric field [1, 23]. When the light propagates normal to the direction of electric field, it will be scattered intensively by the large amounts of vertical domain walls aroused by the transverse electric field, and then the transmittance will reduce sharply. So a transverse electric field is more beneficial to obtain a high efficient light scattering.

4 Conclusion

PLZT (X/70/30) (La=7.6, 7.8, 8.0 mole %) ceramics with a pure perovskite phase and dense microstructure were obtained by a hot pressing process. PLZT (7.6/70/30) exhibits a ferroelectric behavior, while PLZT (7.8/70/30) and PLZT (8.0/70/30) show an antiferroelectric behavior. The La concentration also exerts slight influences on phase transition temperature (T_c) of PLZT (X/70/30) ceramics which slightly shifts from ~86 °C to ~89 °C at 1 kHz. All three composition ceramics exhibit a high transmittance greater than 60 % over a wide range of wavelength band, from visible to near IR. Electrically induced light scattering

performances of PLZT (X/70/30) ceramics were investigated comprehensively. Dependent on the La concentration, PLZT (X/70/30) ceramics exhibit three different kinds of light scattering behaviors: (i) PLZT (7.6/70/30) presents a unique transmittance variation loop with a high contrast ratio, but the sample's transparency can't recover to its original state until a coercive reverse electric field is applied; (ii) PLZT (7.8/70/30) exhibits an auto-switchable electrically induced light scattering behavior, but unfortunately its threshold value of electric field is relatively high and the hysteresis is serious; (iii) PLZT (8.0/70/30) demonstrates a desirable auto-switchable light scattering behavior under an electric field, accompanied with a high transmittance and low threshold value which may be attributed to its low P_R . The contrast ratio of PLZT ceramics increases as the sample thickness increases. Moreover, because of the different orientation of domain walls, the contrast ratio caused by the transverse electric field is about twice as big as that of the longitudinal one. The PLZT (8.0/70/30) sample, as a light scattering ceramic may represent promising and desirable device for potential application as special optical modulators, such as optical shutters and variable optical attenuators.

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