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The influence of domain structure on the optical and electrical properties of transparent $(Pb,La)(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ceramics

Jiangtao Zeng*, Guorong Li, Wei Ruan, Liaoying Zheng, Huarong Zeng, Aili Ding, Qingrui Yin

Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences,1295 Dingxi Road, Shanghai 200050, PR China

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Abstract

Transparent $(Pb,La)(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PLMNT) ceramics were prepared by two stage sintering method. Two different domain structures were formed in PLMNT transparent ceramics with the same composition by changing the cooling rate. Large strip-like domain structure was formed in rapidly-cooled samples, while fine fingerprint-type domain structure was formed in slowly-cooled samples. The large domain structure in transparent PLMNT ceramics caused light scattering and decreased the transmittance. The cut-off wavelength was also red-shifted for PLMNT ceramics with large domain structure, which was attributed to the inner stress in the ceramics. PLMNT ceramics with different domain structures showed different electrical properties: Compared with PLMNT ceramics with large domain structure, PLMNT ceramics with fine domain structure had smaller coercive field, larger electric field induced strain and lower freezing temperature (T_{VF}).

Keywords: C. Dielectric properties; C. Ferroelectric properties; C. Optical properties

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) ferroelectrics show excellent piezoelectric, pyroelectric and electro-optic (E-O) properties [1–5], and they have been intensively studied during the past decade. For example, E-O coefficient of transparent PMNT ceramics is several times larger than that of $(Pb,La)(Zr,Ti)O_3$ (PLZT) ceramics [4], which makes them potential candidates for high speed electro-optic switch and other E-O devices.

Properties of ferroelectrics are greatly influenced by their domain structures. It is well known that domain engineered ferroelectric single crystals have enhanced piezoelectric properties [6]. Our preliminary results also showed that a fine domain structure of PMNT transparent ceramics could result in a larger E-O coefficient [4]. The domain structures of PMNT are strongly dependent on the composition: from low $PbTiO_3$ (PT) content to high PT content, the domain structure of PMNT changes from nano domain to small fingerprint-type domain, and then to large strip-like domain [7–9]. For PMNT ferroelectrics with a certain composition, some researchers also found that the electric field or stress state could change the domain structures [10–12], but the influence of domain structure on properties of ferroelectric with the same composition has rarely been reported. In this study, we showed two different domain structures in transparent PMNT ceramics with the same composition and the influence of different domain structures on their optical and electrical properties was also discussed.

2. Experimental

Transparent ceramics $0.75(Pb_{0.97}La_{0.03})(Mg_{1/3}Nb_{2/3})_{0.9925}O_3$–$0.25PbTiO_3$ (PLMNT) were prepared by two stage sintering method from conventional starting materials. During cooling, the furnace was partially opened in order to get different cooling speed. After sintering, the sample was cut and polished to mirror face. Optical transmittance spectra were measured with HITACHI U-4100 spectrophotometer. The domain structure of PLMNT ceramics was observed by

*Corresponding author. Tel.: +86 21 52412034; fax: +86 21 52413122.
E-mail address: zjt@mail.sic.ac.cn (J. Zeng).

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piezoresponse force microscopy (PFM) (SPA 400, SPI3800N, Seiko Inc. Japan). Before measuring electrical properties, Ag electrode was fired on both sides. The temperature dependence of dielectric constant was measured by a broad band dielectric spectrometer (Novocontrol Concept 40). The polarization–hysteresis loops and field induced strain of PLMNT sample was measured by the Aixacct TF-2000E analyzer.

3. Results and discussion

PLMNT ceramics prepared by two stage sintering method had good transparency, while they showed different colors with different cooling rates. Slowly cooled PLMNT ceramics (PLMNT-SC) is light yellowish while rapidly cooled sample (PLMNT-RC) is dark yellowish (shown as Fig. 1). Fig. 2 shows the PFM images of the two kinds of ceramics. Surprisingly, it was found that the domain structures of these two ceramics were very different even though they had the same composition. The slowly cooled PLMNT ceramics have very fine and discontinuous domain structure, while rapidly cooled PLMNT ceramics have large strip-like domain structure. From previous results, it can be known that the large strip-like domain structure can only be seen in PMN-PT system with high PT content (PT $\geq$ 35%) [9]. In our samples, the PT content is only 25%, and La doping further decreased the Curie temperature, so the large strip-like domain structure was very peculiar in the PLMNT ceramics. There must be some other reasons for the phenomena, which will be discussed below. The results also suggest that the domain structure of PMNT ceramics could be tailored by adjusting the cooling rate.

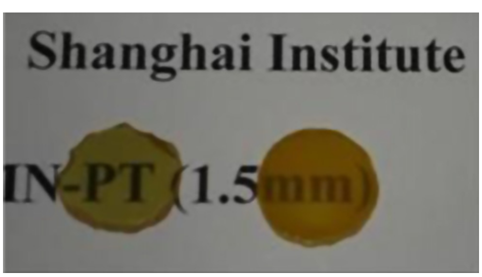

Fig. 1. Photograph of two PLMNT ceramics with the same composition but different cooling rates.

Fig. 3 shows the optical transmittance of the two PLMNT ceramics. It can be seen that slowly cooled PLMNT ceramics also shows much higher transparency than that of rapidly cooled one. The difference in transparency is more obvious when the wavelength is below 900 nm. It is reasonable that large domain in rapidly cooled PLMNT ceramics cause the light scattering effect, thus decrease the transmittance. It should be noted that the cut-off wavelength for rapidly cooled PLMNT ceramics is slightly larger than that of slowly cooled ceramics, indicating the energy band gap was changed slightly.

These two PLMNT ceramics with different domain structures also have different dielectric properties (Fig. 4) though both ceramics show typical relaxor feature. The room temperature dielectric constant of PLMNT-SC ceramics (ε_r=16900 at 1 kHz) is much higher than that of PLMNT-RC ceramics (ε_r=6500 at 1 kHz) because PLMNT-SC ceramics has fine domain structure and domain wall density is much higher than that of PLMNT-RC ceramics. The T_m (temperature with the maximum dielectric constant) of PLMNT-RC is slightly higher than that of PLMNT-SC. Because the two ceramics have the same composition, the change of T_m may be caused by the inner stress. The similar phenomena could also be found in other ceramics [13].

Dielectric relaxation in two PLMNT ceramics was found to follow the Vogel–Fulcher Law (shown as Fig. 5) [14], which is given as:

$$f = f_0 \exp\left(-\frac{E_a}{k_B(T-T_{VF})}\right) \quad (1)$$

where E_a is the activation energy, T_{VF} is the freezing temperature of polarization fluctuations, and f_0 is the pre-exponential factor. The values of E_a, T_{VF}, and f_0 obtained

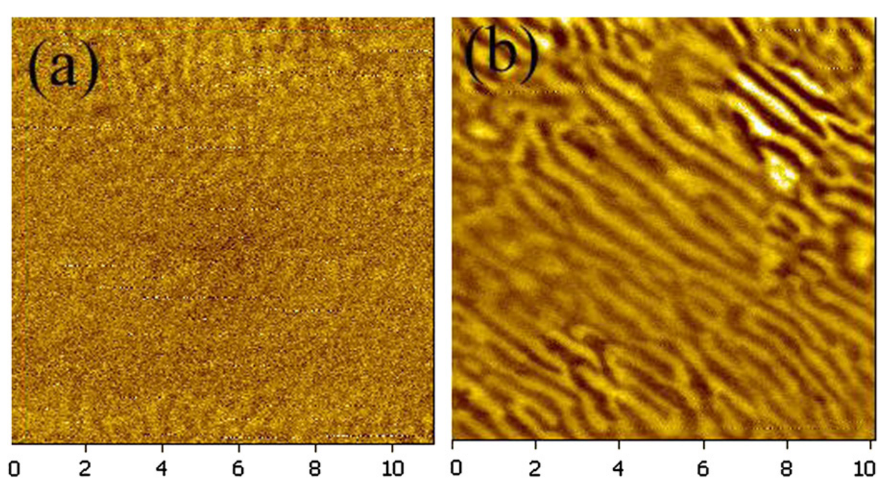

Fig. 2. PFM images of the two kinds of PLMNT ceramics: (a) Slowly cooled PLMNT ceramics (PLMNT-SC) with high transparency and (b) rapidly cooled PLMNT ceramics (PLMNT-RC) with low transparency.

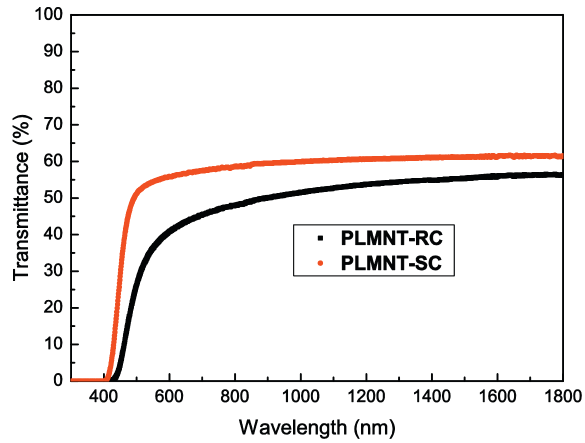

Fig. 3. Optical transmittance of PLMNT ceramics prepared by hot press method with different cooling rates.

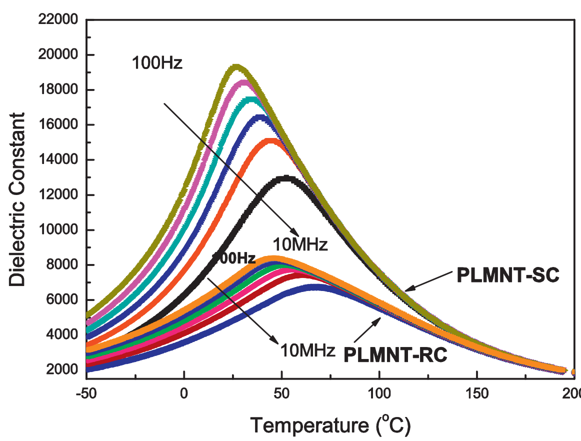

Fig. 4. Temperature dependence of dielectric constant of PLMNT-SC and PLMNT-RC ceramics.

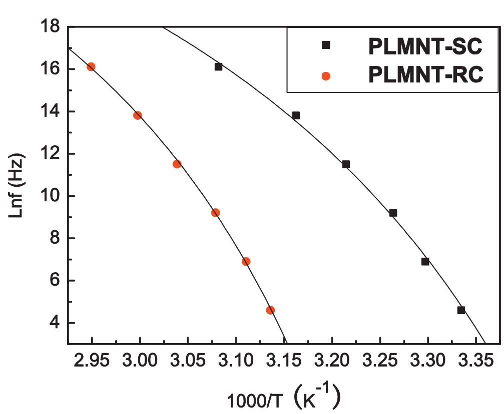

Fig. 5. *Lnf* vs. $1/Tm$ curve for PLMNT-SC and PLMNT-RC ceramics; solid lines represent the fits to the Vogel–Fulcher law.

for PLMNT-SC were 0.1105 eV, 258.4 K, and 3.25×10^{15} Hz, respectively; while the values of Ea, T_{VF}, and f_0 obtained for PLMNT-RC were 0.095 eV, 283.6 K, and 4.0×10^{15} Hz. T_{VF} of PLMNT-SC is much lower than that of PLMNT-RC, which indicates that polarization fluctuation

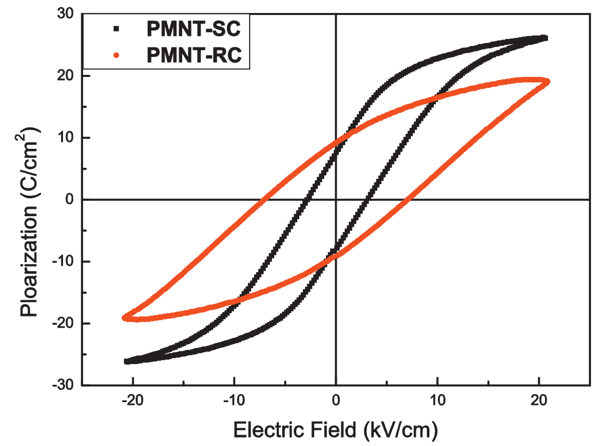

Fig. 6. Polarization–electric field (P–E) loops for PLMNT-SC and PLMNT-RC ceramics.

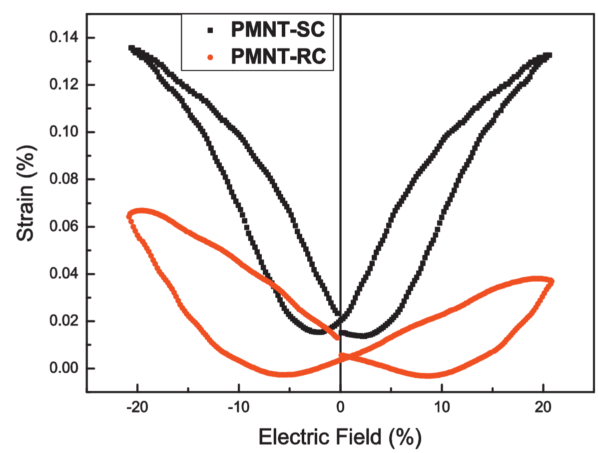

Fig. 7. Bipolar electric field induced strain for PLMNT-SC and PLMNT-RC ceramics measured at room temperature.

in PLMNT ceramics with fine domain structure is easier to freeze.

Fig. 6 shows the polarization–electric field (P–E) loops for two ceramics. PLMNT-SC ceramics have a slim loop like other E-O ceramics (PLZT 9/65/35). PLMNT-RC ceramics have the similar remnant polarization as PLMNT-SC, but its coercive field is much higher than that of PLMNT-RC (5 kV/cm vs. 2 kV/cm). It is reasonable when considering the large domain structure in PLMNT-RC ceramics which was difficult to reverse under the electric field.

Fig. 7 shows the bipolar electric field induced strain for two PLMNT ceramics measured at room temperature. It can be seen that the PLMNT-SC ceramics have much larger strain than that of PLMNT-RC ceramics. The electric field induced strain d_{33} in the ferroelectrics can be expressed via the following equation:

$$d_{33}=2Q_{\mathrm{eff}}\varepsilon_0\varepsilon_r Ps \quad (2)$$

where Q_{eff} is the effective electrostriction coefficient, ε_0 and ε_r are the dielectric constant of free space and relative dielectric constant. Since the dielectric constant of PLMNT-SC ceramics is much higher than that of PLMNT-RC ceramics, the strain for PLMNT-SC ceramics is also much larger than that of PLMNT-RC ceramics.

It should also be noted that PLMNT-RC ceramics has more pronounced hysteresis than that of PLMNT-SC ceramics because large domains are more difficult to reverse under electric field than small domains. The butterfly loops of PLMNT-RC is unsymmetrical while it is symmetrical for PLMNT-SC. Usually there are some reasons for the unsymmetrical butterfly loops, such as inner electric field and inner stress etc. From Fig. 6, the P–E loop is quite symmetrical, so the inner electric field can be excluded. In this study, the fast cooling of PLMNT ceramics induced the inner stress, and thus caused the unsymmetrical of butterfly loops. The inner stress in PLMNT-RC ceramics also induced the large domain structure and the red shift of the cut-off wavelength.

4. Conclusion

In summary, we reported two kinds of PLMNT transparent ceramics with the same composition, but different optical and electrical properties. The changes of the properties can be attributed to the inner stress which formed in rapidly cooled PLMNT ceramics. The inner stress caused the red-shift of cut-off wavelength and induced peculiar large domain structure in PLMNT ceramics. The large domain structure in transparent PLMNT ceramics caused light scattering and decreased the transmittance. Compared with PLMNT ceramics with large domain structure, PLMNT ceramics with fine domain structure had smaller coercive field, larger electric field induced strain and lower T_{VF}. The results of this study also indicate that control of the inner stress and domain structure is very important for transparent ferroelectric E-O ceramics.

Acknowledgments

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