

Influence of Illumination on Domain Switching and Photovoltaic Current in Poled $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$ Ferroelectric Ceramics

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The influence of photoexcited nonequilibrium carriers on domain switching and photovoltaic current was investigated in two kinds of poled La-modified PbTiO_3 ferroelectric ceramics, $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$ and $(\text{Pb}_{0.76}\text{La}_{0.24})\text{TiO}_3$, under illumination in the absence of external electric field. Both photovoltaic current and cumulative AE event counts increased with illumination time. The observed nonsteady-state photovoltaic current could be explained on the basis of the cycles of a series of physical events consisting the establishment of space charge field by photoexcited carriers trapped at the grain boundaries, the photoinduced domain switching, and the increase in the remanent polarization. An analysis of energy distribution of the observed AE signals also revealed that the space charge field in $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$ allowed both 180° and 90° domains to be switched during illumination.

Key words: Photoinduced domain switching, Photovoltaic effect, Space charge field, Acoustic emission, $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$ ceramics

I. Introduction

Over the past a few decades there have been many reports of unusual photoeffect in ferroelectrics.¹⁻⁸⁾ It is known that photoinduced domain switching, one of the photoferroelectric effect, in ferroelectric single crystals such as SbSI , BaTiO_3 , and PbTiO_3 is associated with the influence of nonequilibrium carriers on the screening of spontaneous polarization.²⁻⁴⁾ Nonequilibrium carriers excited under illumination are redistributed under an internal depolarization field and change the screening energy of the spontaneous polarization, and thereby result in the nucleation and growth of antiparallel domains or the lateral motion of the domain walls.²⁻⁴⁾ In contrast, in ferroelectric polycrystalline ceramics, it has been reported that nonequilibrium carriers are trapped at the grain boundaries and establish a space charge field, E_{sc} , which modulated the applied field, E_A , and assisted the domain switching process.⁷⁻⁹⁾ This phenomenon is defined as photoassisted domain switching. According to this mechanism, even under illumination in the absence of external electric field, the space charge field induces domain switching so that photovoltaic current which is driven by the bulk photovoltaic effect⁶⁻⁸⁾ will be nonsteady-state since the photoinduced domain switching may result in the change of remanent polarization. However, little is known about the influence of nonequilibrium carriers excited during illumination on domain switching and photovoltaic current in ferroelectric ceramics.

Acoustic Emission (AE) in ferroelectric materials has been examined on several systems, such as BaTiO_3 ,¹⁰⁾ TGS,¹⁰⁻¹¹⁾ $\text{Pb}_3\text{Ge}_3\text{O}_{11}$ ¹¹⁾ crystals, PZT-like,¹²⁻¹³⁾ and PLZT ceramics¹⁴⁻¹⁵⁾

under an electric field driving. It is reported that AE signals in ferroelectric materials are associated with the stress wave generated during the event of elastic energy release due to the domain switching. It has been suggested that AE observation has a potential applicability for in-situ monitoring of domain dynamics and ferroelectric fatigue.¹⁰⁻¹⁵⁾ It is thus expected that AE technique can be a useful tool to study the photoinduced domain switching.

In this study, the variations of both photovoltaic current and AE event count were observed as a function of illumination time for two kinds of poled La-modified PbTiO_3 ceramics under illumination in the absence of external electric field. On the basis of the observed experimental results, the influence of the nonequilibrium carriers on the domain switching and the photovoltaic current was discussed. Also, from the analysis of AE energy distribution, it was confirmed whether 180° or 90° domain switching occurred during the illumination.

II. Experimental Procedure

$(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$ (PLT15) and $(\text{Pb}_{0.76}\text{La}_{0.24})\text{TiO}_3$ (PLT24) ferroelectric ceramics were fabricated by a conventional sintering process. Both samples were prepared to have a grain size of around 7 μm by controlling sintering condition. Their relative densities were constant at around 96%. The tetragonality ratio (c/a ratio) values at the room temperature were determined to be 1.021 for PLT15 and 1.007 for PLT24, respectively. All the samples were shaped to be a diameter of 19 mm and a thickness of 4 mm and both sides of them were electroded with gold by sputtering technique.

At the same applied electric field of 1.5 kV/mm for 10 minutes, PLT15 sample was poled in silicone oil bath at 105°C and PLT24 sample at 40°C, respectively.

The measurement of both photovoltaic current and AE signals during illumination are made as follows. The detailed experimental set-up is illustrated in Ref. 16. Ceramic samples were coupled with silicone grease on an AE sensor with a resonant frequency of 175 kHz. This assembly was placed in a dark chamber. The ceramic samples were illuminated with the uniform light of a 300 W Xenon lamp through a waveguide and a focusing lens. AE signals from the AE sensor were filtered by a band pass filter with a range of 0.125-1 MHz. The overall gain was 70 dB and the threshold voltage was carefully chosen as 0.1 V. The detected AE signals were analysed with an AET 5500 system (Hartford Stream Boiler Inspection Technologies). The photovoltaic current was measured with a Keithley 486 Picoammeter, simultaneously with the AE measurement

III. Results and Discussion

The photovoltaic current of two samples with different c/a

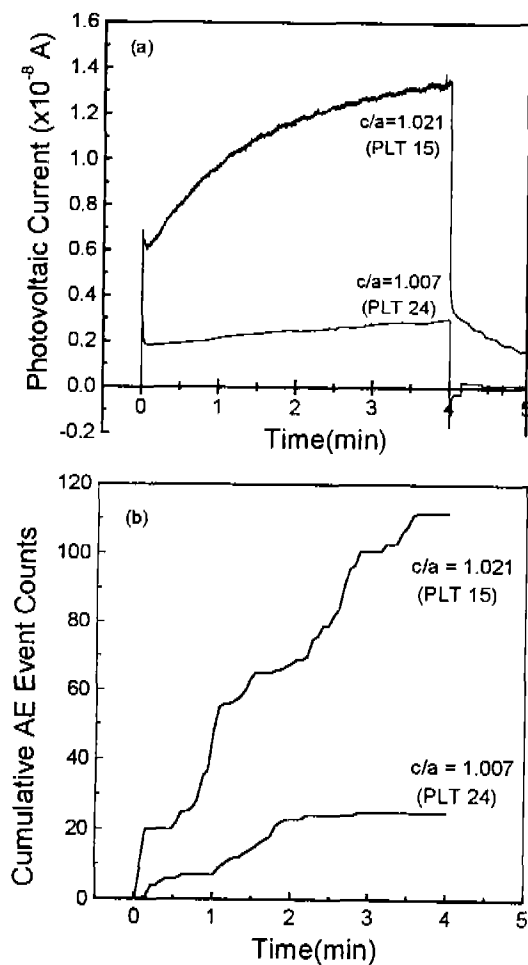


Fig. 1. Variations of photovoltaic current (a) and cumulative AE event counts (b) with illumination time for two samples with different tetragonality ratios.

ratios are shown in Fig. 1(a) as a function of illumination time. Both of the samples were preliminarily poled at 1.5 kV/mm and illuminated under the light intensity of 2.1 W/cm². The initial transient current just after the light is on is associated with the pyroelectric effect⁵⁾ since poled PLT ceramics are also pyroelectric. Interestingly, photovoltaic current tends to increase with illumination time. This experimental result is contradict to those of previous studies, generally reporting that photovoltaic current in single crystal is steady-state.^{1,5,9)} PLT15 sample with a high c/a ratio ($c/a=1.021$) shows higher absolute value of photovoltaic current and its total increment for 4 minutes than those of PLT24 sample with a low c/a ratio ($c/a=1.007$). Simultaneously observed cumulative AE event counts with illumination time are shown in Fig. 1(b). It is noticeable that the variations of cumulative AE event counts with illumination time show the same tendency as those of photovoltaic current in Fig. 1(a).

The observed nonsteady-state photovoltaic current behavior can be explained to be associated with the cycles of a series of the physical events that are caused by photoexcited nonequilibrium carriers, as systematically shown in Fig. 2. During poling process, domains are switched toward the direction of applied field and thereby the net remanent polarization is created in each grain (a). The nonequilibrium electrons are excited by the radiation of wavelength shorter

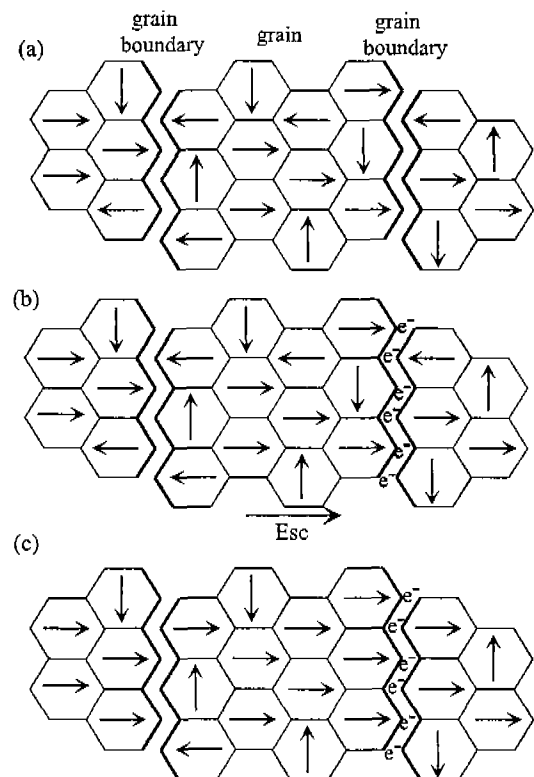


Fig. 2. Schematic diagram showing the mechanism of non-steady-state photovoltaic current: (a) before illumination, (b) establish a space charge field and (c) photoinduced domain switching.

than a bandgap and migrate toward the direction of the net remanent polarization. Then, they are trapped at the grain boundaries and establish space charge field which has the same direction as the average remanent polarazation (b), whereas the electrons remaining in the conduction band produce photovoltaic current.⁹⁾ The magnitude of space charge field across a grain is large enough to induce the domain switching^{8,17)} since the distance between the grain boundaries is sufficiently short. The AE signals observed in Fig. 1(b), in fact, reveal that photoinduced domain switching occurs during illumination (c). The photoinduced domain switching further increases the initial level of the remanent polarization provided by poling process. It is known that photovoltaic current increases with increasing the remanent polarization in ferroelectric ceramics.^{6,9)} Therefore, subsequent illumination makes more photoexcited electrons move toward the direction of the remanent polarization and thereby increases the initial level of photovoltaic current. Also, more electrons trapped at the grain boundaries increase the magnitude of space charge field so that the surrounding domains can be switched. A series of processes described above will be continuously repeated until the stored strain prevents the domains from being switched.

The AE signals observed in Fig. 1(b) were analysed with AE energy parameter, using the software provided by the AET 5500 system. AE energy was calculated as a function of both amplitude and duration time: energy=peak amplitude +10 log(duration time), where the peak amplitude is in dB above 0.1 mV at the preamplifier output, duration time in seconds, and energy in dB. The results are shown in Fig. 3. In PLT15 with a high *c/a* ratio (a), AE signals are clearly divided into two groups of energy distribution. One is a narrow distribution peak in the low energy region around 40dB. The other is a broad distribution peak in the high

energy region in the range of 50-70 dB. However, in the case of PLT24 whose *c/a* is 1.007 (b), only a narrow distribution peak remains in the small energy region around 40 dB. King and Goo¹⁸⁾ have reported that in compositions where *c/a* ratio is close to unity in (Pb_{1-x}Ca_x)TiO₃ ferroelectric ceramics, the lack of strain allows 90° domains to disappear. Authors¹⁹⁾ have also confirmed by TEM observation that Mn-doped PLT24 ceramics whose *c/a* ratio is 1.007 show almost no 90° domain. It can be seen in Fig. 3 that AE signals in PLT 24, only distributed around 40 dB, originate from 180° domain switching. Consequently, in PLT15, low energy AE signals are related to 180° domain switching and high energy AE signals are due to 90° domain switching.

It is known that the initial voltage out put from the AE sensor (V_o), is proportional to the square root of the energy release (E_g) during a given deformation process,¹⁴⁾

$$V_o = \Psi \sqrt{E_g} \tag{1}$$

where Ψ is a proportional factor, reflecting both the preamplifier characteristics and the attenuation in the body. In ferroelectric ceramics, it can be thought that the magnitude of the energy release associated with domain switching depends on the energy barrier for domain wall motions.¹⁶⁾ Fig. 4 is a schematic illustration of 180° (a) and 90° domain switching(b), considered in terms of only mechanical strain energy, in the tetragonal perovskite phase with a given *c/a* ratio. Note that the tetragon is a unit cell and black point in the unit cell, a Ti ion. The mechanism of 180° domain switching is associated with the small shift of Ti ion position within the unit cell. As shown in Fig. 4(a), Ti ion can reach the activated state by a small mechanical strain, i.e., small energy barrier ΔG_a^{180} . Although the following domain switching is continued, the magnitude of the strain in the activation state hardly changes since 180° domain switching is a pure ferroelectric. Thus, AE signals originated from the relaxation of the activation state have the small energy and

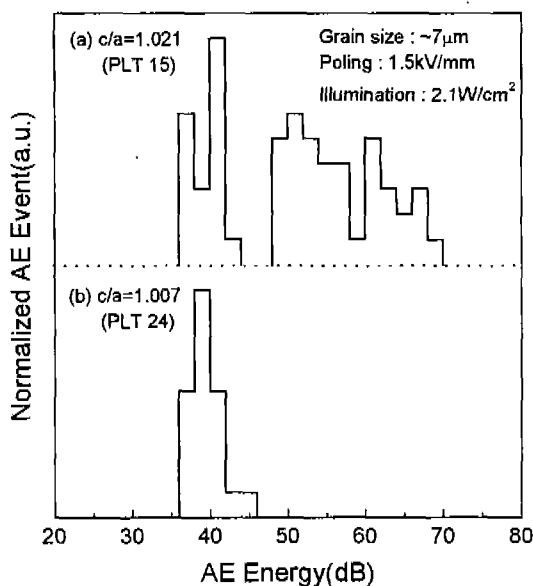


Fig. 3. Energy distributions of AE signals observed in Fig. 1(a) for a tetragonality ratio of 1.021(a) and 1.007(b)

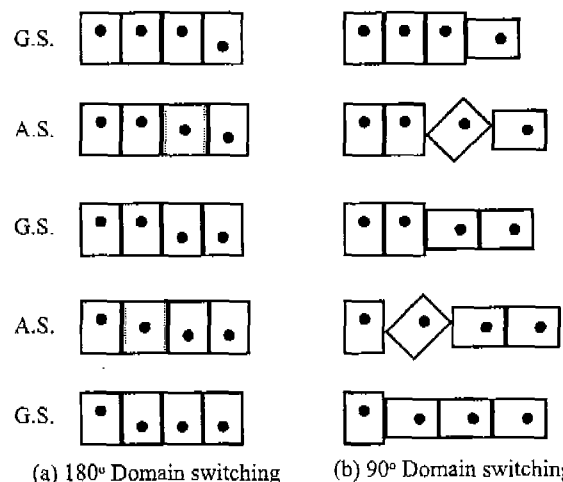


Fig. 4. Schematic illustration of 180° domain switching (a) and 90° domain switching (b): G. S. is ground state and A. S. activated state.

a narrow energy distribution as shown in Fig. 3(a) and (b). However, the unit cell itself has to be rearranged for 90° domain switching since it is associated with ferroelastic. Fig. 4(b) shows that a high activation state, ΔG_a^{90} is required to cause 90° domain switching, which results in a large dimensional change, comparing with that of 180° domain switching. ΔG_a^{90} is influenced by the strain energy state depending on the level of 90° domain switching.¹⁶⁾ Consequently, AE signals associated with 90° domain switching have a high energy and a broad energy distribution as shown in Fig. 3(b).

Fig. 1(a) obviously shows a marked difference in the absolute value of photovoltaic current between two samples with different *c/a* ratios. Generally, it is known that there is a quadratic relationship between the spontaneous deformation (*d*) and the spontaneous polarization (P_s) in perovskite ferroelectric materials²¹⁾:

$$d = k \cdot P_s^2 \quad (2)$$

where *k* is a constant depending on lattice structure. For the tetragonal case, *d* is roughly expressed as *c/a*-1 and *k* is $1 \times 10^7 \text{ cm}^4/\text{C}^2$. The value of spontaneous polarization is calculated to be $45.8 \mu\text{C}/\text{cm}^2$ for PLT15 (*c/a*=1.021) and $26.5 \mu\text{C}/\text{cm}^2$ for PLT24 (*c/a*=1.007), respectively. Micheron²⁰⁾ reported that photovoltaic current density is proportional to the magnitude of spontaneous polarization of material. According to Glass's model,¹⁾ high spontaneous polarization increases the possibility of electron transfer in the favorable direction and the displacement of the surrounding ions along polar axis. Consequently, it can be said that a difference in the spontaneous polarization between two samples is responsible for a marked difference in photovoltaic current value.

Another observation in Fig. 1 is the difference in total photovoltaic current increment and total AE event count for 4 minutes between two samples. It is believed that high spontaneous polarization in PLT15 leads to trap of more electrons at the grain boundaries, which results in higher space charge field compared with PLT24. It is clear that space charge field in PLT15 is more effective for domain switching. However, another noticeable thing is that in the case of PLT24 with mainly 180° domains, most 180° domains have been already switched during poling process since they require a small energy barrier, ΔG_a^{180} for switching. However, in PLT15 with both 180° and 90° domains, a large number of switchable domains, mainly including 90° domains, which remained unswitched after poling process can be switched by space charge field during illumination.

IV. Conclusions

In two kinds of poled La-modified PbTiO_3 ferroelectric ceramics, $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$ and $(\text{Pb}_{0.76}\text{La}_{0.24})\text{TiO}_3$, it was observed that both photovoltaic current and cumulative AE event counts increased with illumination time under no

external electric field. The observed nonsteady-state photovoltaic current could be explained to be associated with the increase in remanent polarization due to photoinduced domain switching resulting from space charge field established by photoexcited nonequilibrium electrons trapped at the grain boundaries. The detected AE signals revealed that the photoinduced domain switching occurred during illumination. From the analysis of energy distributions of AE signals, it was also confirmed that the space charge field in poled $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$ allowed both 180° and 90° domains to be switched.

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