

## Effects of Grain Boundaries on Photovoltaic Current and Photoinduced Domain Switching in Ferroelectric Ceramics

Sung-Ryul Kim, Dong-Gu Choi and Si-Kyung Choi

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taejeon, 305-701, Korea  
(Received September 23, 1998)

We investigated the effect of the grain size on the photovoltaic current in  $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$  ceramics, and the photoinduced domain switching in  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$  and  $\text{BaTiO}_3$  ceramics. These behaviors in ferroelectric ceramics were attributed to the grain boundary at which photoexcited electrons were trapped. As the charged grain boundary acted as an electro-potential barrier which impeded the movement of electrons, the photovoltaic current showed a peak at a critical grain size. The space charge field built by the electrons trapped at the grain boundaries was accounted for the photoinduced domain switching, and AE experimental results support well this account.

**Key words:** Photovoltaic current, Grain boundary, Space charge field, Photoinduced domain switching, Electro-potential barrier

### I. Introduction

It is well known that ferroelectric crystals possess the photovoltaic effect that produces greater steady-state voltage than a band gap under illumination in the absence of an external field.<sup>1,2)</sup> The first explanation of this effect on ferroelectric crystal was proposed by Chen<sup>3)</sup> on the assumption that there was an internal field in the direction from the positive end of the spontaneous polarization of the crystal to the negative end under illumination. This internal field made photoexcited electrons drift toward the positive end of the spontaneous polarization. Later, this was explained by Glass et al. in terms of the local asymmetry of the pyroelectric host.<sup>4)</sup> Since ionic distances in the direction of the spontaneous polarization were different, the probabilities of intervalence charge transfer differed. This structural asymmetry induced higher momentum of photoexcited electrons in the direction of the spontaneous polarization. Even if no internal field existed in the ferroelectric crystals, Chens model was convenient for considering the photovoltaic effect and had no drawbacks. Therefore, it was conceivable that the photovoltaic effect was induced by an imaginary internal field that was created in ferroelectric ceramics during illumination.

As promising applications of the photovoltaic effect, several novel devices have been proposed such as optical storage,<sup>5)</sup> photostrictor,<sup>6)</sup> and power conversion.<sup>7)</sup> These studies have been mostly carried out in single crystals. But the photovoltaic effect has also been observed in ferroelectric ceramics,<sup>8,9)</sup> which have many merits for practical use. Since the principal difference between crystals and ceramics is the presence of grain boundaries in the latter, extensive

studies have been conducted to explain the effect of the grain size on the photovoltaic properties of ferroelectric ceramics.<sup>10,11)</sup> It has been reported that the photovoltaic voltage was inversely related to the grain size, and was interpreted using a multi-junction effect.<sup>10)</sup> The smaller-than-bandgap photovoltages generated across individual grains were additive so that the accumulated voltage across an entire specimen greatly exceeded the band gap. It has also been reported that the photovoltaic current had a peak at about in 1.5 kV/mm in lead lanthanum zirconate titanate (PLZT) ceramics,<sup>11)</sup> but the reason for this is not yet known.

The screen mechanism was introduced to account for the change of the domain structure under illumination in single crystals.<sup>12)</sup> Since the illumination of single-domained crystals increased the free carrier concentration, and thereby decreased the screen length, a single domain state was energetically unfavorable, which caused the acceleration of poly-domainization. The space charge field established by trapped carriers also contributed to the photodomain effect.<sup>9)</sup> When an external field was applied with illumination, the space charge field aided the domain switching process. It was defined as the photo-assisted domain switching, since the space charge field only modulated an external field.<sup>13)</sup> However, if the space charge field was very strong, the domain switching was possible without an external electric field. This condition should be defined as the photoinduced domain switching to discriminate from the photo-assisted domain switching.

Acoustic emission (AE) is defined as the high-frequency stress waves generated by the rapid release of energy that occurs within a material during crack growth, plastic deformation, or phase transformation.<sup>14,15)</sup> Because this energy

may have originated from the stored elastic energy as in domain realignment or from the stored chemical free energy as in a phase transition, the AE technique is used on the domain switching,<sup>16)</sup> the paraelectric-to-ferroelectric phase transition,<sup>17)</sup> and microcracking<sup>17)</sup> in ferroelectrics.

In this study, we investigated the effect of the grain size on the photovoltaic current in  $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$  ceramics, on the basis of the electro-potential barrier built by the electrons trapped at the grain boundaries. We also explored the photoinduced domain switching in  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$  and  $\text{BaTiO}_3$  ceramics. The space charge field built by the electrons trapped at the grain boundaries was accounted for the photoinduced domain switching, and AE experimental results support well this account.

## II. Experimental Procedure

The experiments on the photovoltaic current were carried out at room temperature for  $(\text{Pb}_{1-x}\text{La}_x)\text{TiO}_3$  (PLTx) ceramics and  $\text{BaTiO}_3$  (BT) ceramics. PLTx ceramics with  $x=0.1, 0.15,$  and  $0.2$  were sintered at  $1250^\circ\text{C}$  for differing times to create variations in the grain size. The relative densities of PLTx ceramics were all approximately 97%. However we could not obtain dense BT ceramics by a conventional solid state sintering, thus the BT ceramics were prepared by a hot isostatic press (HIP) after pre-sintering, so that the relative density was about 99%. After cutting to the size of  $2 \times 4 \times 5 \text{ mm}^3$  both ceramics were electroded with silver paste on  $2 \times 5 \text{ mm}^2$  or  $4 \times 5 \text{ mm}^2$  faces, and electrically poled. Then they were homogeneously illuminated by a 300 W xenon lamp. The photoinduced current under the lamp on and off was measured by using a Keithly 486 picoammeter.

AE signals were also measured for PLTx ceramics coupled with silicone grease on an AE sensor with a resonant frequency of 175 kHz. These assemblies were placed in the dark chamber and samples were illuminated with a xenon lamp. The 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 70dB and the threshold voltage was chosen as 0.1 V. The detected AE signals were analyzed by an AET-5500 system (Hartford Stream Boiler Inspection Technologies).

## III. Results and Discussion

### 1. Effect of Grain Size

The photovoltaic current ( $J_{pv}$ ) can be divided into two components:

$$J_{pv} = J_e + J_i \quad (1)$$

where  $J_e$  is the photovoltaic current due to electrons, and  $J_i$  due to ions. This relies on previous study of Glass *et al.*,<sup>4)</sup> who introduced a directional electronic transfer based on the asymmetry of the lattice and Frank-Condon relaxation of ions. Thus both of electrons and ions may contribute respectively to the photovoltaic current. In ferroelectric cera-

mics, photoexcited electrons move toward the spontaneous polarization and are easily trapped at the grain boundary. Although the thickness of the grain boundary is very small compared to that of the grain, electrons trapped at the grain boundary may build an electro-potential barrier which impedes the movement of following electrons. If so  $J_e$  is a probability function of an electro-potential barrier ( $F$ ) and an imaginary internal field ( $E$ ), because the latter acts as the driving force for the movement of photo-excited electrons while the former impedes this movement. As  $F$  is proportional to the area of the grain boundary and  $E$  is unrelated to the grain size, the probability function can be expressed as  $\exp(-\gamma d^2)$ , where  $d$  is the grain size and  $\gamma \propto 1/E_1$ . In ceramics, the average number of grains is inversely proportional to their average volume ( $d^3$ ). However, since, only the grain boundaries perpendicular to the direction of the spontaneous polarization act as electro-potential barriers, the average number of grains is inversely proportional to the grain size ( $d$ ). Then, the photovoltaic current ( $J_{pv}$ ) as a function of the grain size in ceramics can be expressed as follows,

$$J_{pv} = \beta d \exp(-\gamma d^2) + J_i \quad (2)$$

where  $\beta$  is the modified constant from  $J_e$ , since in the single crystal the grain size goes infinite, and equation (2) is invalid.

Fig. 1 shows the simulated photovoltaic current as a function of the grain size. The dependence of the photovoltaic current on the grain size are divided into three regions: with increasing the grain size, the photovoltaic current increases (region 1); decreases after a peak (region 2); and is finally constant (region 3). In region 1, the number of electro-potential barriers decreases with increasing the grain size, so that the photovoltaic current increases. In regions 2 and 3, the height of electro-potential barriers act more effectively that less electrons flow across the grain boundary, and only  $J_i$  is observed in region 3.

Fig. 2 shows the experimental results of the photovoltaic current as a function of the grain size in PLTx ceramics poled under an electric field of  $4 \text{ kV/mm}^2$ . Three prominent

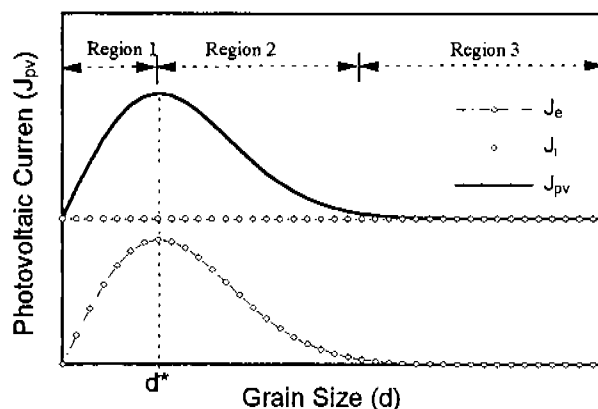


Fig. 1. Simulated photovoltaic current as a function of grain size.

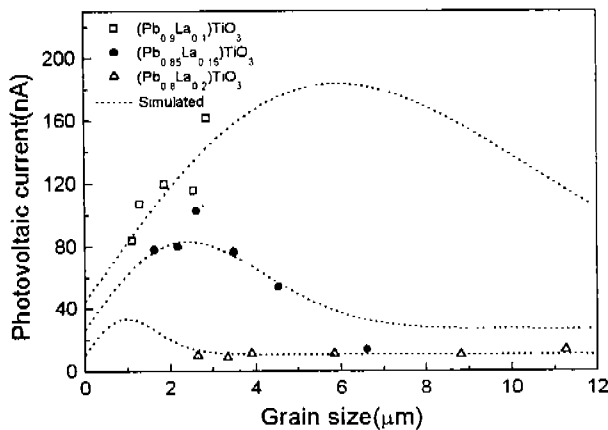


Fig. 2. Photovoltaic current as a function of grain size in  $(\text{Pb}_{0.9}\text{La}_{0.1})\text{TiO}_3$  ceramics ( $\square$ ),  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$  ceramics ( $\bullet$ ),  $(\text{Pb}_{0.8}\text{La}_{0.2})\text{TiO}_3$  ceramics ( $\triangle$ ) and simulated photovoltaic current (dashed line).

dependences are observed with the different lanthanum concentration in PLTx ceramics. In  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$  (PLT15) ceramics, after a plateau at about 2.2 kV/mm, the photovoltaic current decreases with increasing the grain size. However, the photovoltaic current is linearly proportional to the grain size in  $(\text{Pb}_{0.9}\text{La}_{0.1})\text{TiO}_3$  (PLT10) ceramics, but independent of the grain size in  $(\text{Pb}_{0.8}\text{La}_{0.2})\text{TiO}_3$  (PLT20) ceramics. In order to explain above experimental results, we introduce a critical grain size at which the photovoltaic current shows a peak. This critical grain size can be obtained by requiring the photovoltaic current to have maximum;

$$d^* = (1/2\gamma)^{1/2} \propto (E_i)^{1/2} \quad (3)$$

where  $d^*$  is a critical grain size. A critical grain size increases with increasing the strength of the imaginary internal field, or the spontaneous polarization. A critical grain size is smallest in PLT20 ceramics, and largest in PLT10 ceramics. Therefore the grain sizes investigated in PLT10 ceramics correspond to region 1, in PLT15 ceramics region 2, and in PLT20 ceramics region 3. These results allow us to conclude that the photovoltaic current has a peak in all the PLTx ceramics respectively as shown in Fig. 1, even if it was necessary to investigate the photovoltaic current at another region of the grain size.

## 2. Photoinduced Domain Switching

In the ferroelectric crystals, it is well known that the curves of current flow vs. illumination time show the transient pyroelectric current and steady state photovoltaic current. However, during illumination of the polycrystalline ceramics poled at an intermediate electric field (1.5 kV/mm), non-steady state photovoltaic current is observed as shown in Fig. 3. The photovoltaic current, after the pyroelectric current which decays in a few seconds, increases as the illumination time goes on. It is also noticeable that after the light is off, the pyroelectric current on cooling is not observed. It is possible to think that the change of the sam-

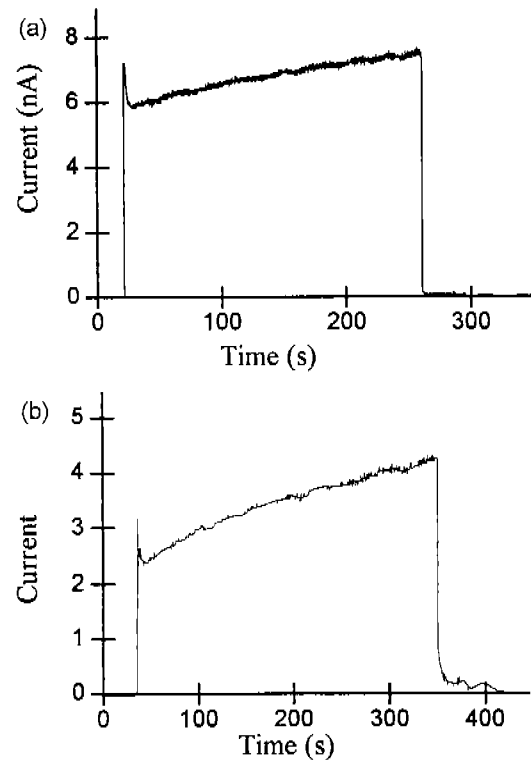


Fig. 3. Non-steady state photovoltaic current under illumination in (a)  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$  and (b)  $\text{BaTiO}_3$  ceramics.

ple temperature is so little that the pyrocurrent current on cooling may not be detected. However the pyroelectric current on cooling is observed with a few seconds of illumination, it is obvious that the temperature of the sample is changed.

Under homogeneous illumination, the photoexcited electrons move toward the positive end of the spontaneous polarization, which is caused by the photovoltaic effect.<sup>18)</sup> Some of them are trapped at the grain boundary and the rest remain in the conduction state. Then the trap sites become charged by the trapped electrons, and the space charge field is created between the charged trap sites at the grain boundary and the positive ionized centers in the grain and has the same direction of the remanent polarization.<sup>3)</sup> On the other hand, the electrons remaining in the conduction state contribute to the photovoltaic current in the short circuit. The strength of the space charge field is a primary function of the density of trapped electrons and the active region where the space charge affects, i.e.

$$\begin{aligned} (\text{the strength of space charge field}) &= (\text{voltage})/(\text{distance}) \\ &\propto (\text{density of trapped electrons})/(\text{the active region}) \end{aligned}$$

In the ferroelectric ceramics, since there are many defect sites at the grain boundary, the density of electrons trapped at the grain boundary is very high. Moreover, the active region is about the size of a grain (the grain size is about 0.003 mm for PLT15 ceramics and about 0.025 mm for BT ceramics). Therefore, the origin of the non-steady state of

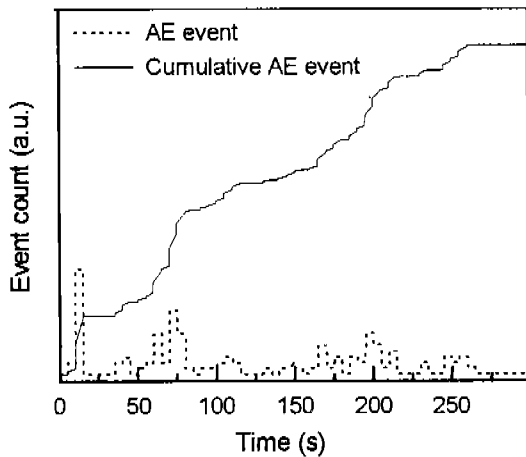


Fig. 4. AE events and cumulative AE counts in  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$  ceramics as a function of illumination time.

the photovoltaic current is due to the increase of both of the spontaneous and the remanent polarization during illumination. Since the space charge field is strong and has the same direction of the remanent polarization in the ferroelectric ceramics, it increases the spontaneous polarization and switches domains where the polarization has the opposite direction of the remanent polarization. The increase of the remanent polarization makes the photovoltaic current increase, because the photovoltaic current is proportional to the remanent polarization.<sup>8)</sup>

Fig. 4 shows the AE event count and the cumulative AE event count as a function of illumination time for the PLT15 ceramics which was poled at 1.5 kV/mm. The AE event is continuously detected and the cumulated AE event gradually increases during illumination. Since an external electric field or mechanical force was not applied, and the threshold voltage was carefully chosen as 0.1 eV to avoid other effects during illumination, the release of energy is due to the photoinduced realignment of the domains. Fig. 4 is decisive evidence that the domain switching can occur only by illumination in the ferroelectric ceramics.

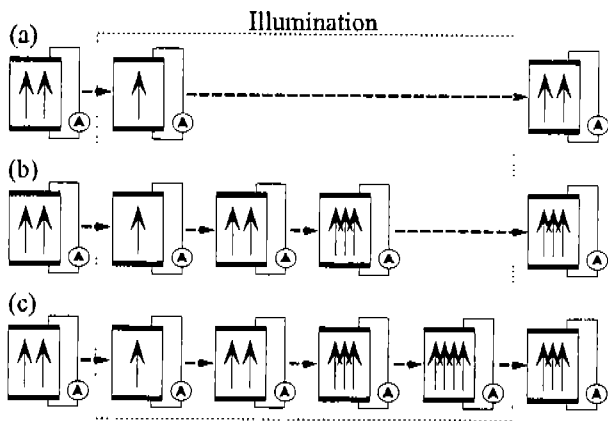


Fig. 5. Schematic diagram illustrating change of polarization with illumination.

If the ferroelectric crystal with the positive pyroelectric coefficient is cooled, the spontaneous polarization increased and then the pyroelectric current flows.<sup>19)</sup> On the other hand, the space charge field induces the increase of the spontaneous polarization during illumination. Therefore when the increment of the polarization due to the space charge field (photo-induced increment) exceeds the increment of the polarization due to the cooling (pyro-induced increment), no pyroelectric current on cooling can be obtained after the light is off. Fig. 5, where the number of arrows means the amount of both of the spontaneous and the remanent polarization, illuminates this situation. If the photoinduced domain switching does not occur as shown in Fig. 5(a), the polarization increases just after the light is off. Conversely, when the photoinduced increment is so large that it exceeds the pyro-induced increment as shown in Fig. 5(c), the polarization does not increase, but decreases on cooling after the light is off. In this situation, the current is also observed since the polarization is changed, but it is not the pyroelectric current. The decrease of the polarization induces this current (we define this current as the relaxation current), which has the opposite sign of the pyroelectric current on cooling. If the photoinduced increment and the pyro-induced increment have the same value as shown in Fig. 5(b), the polarization does not change after the light is off, so any current on cooling cannot be obtained.

Fig. 6 shows the variations of the relaxation current and the pyroelectric current on cooling. The experiments were

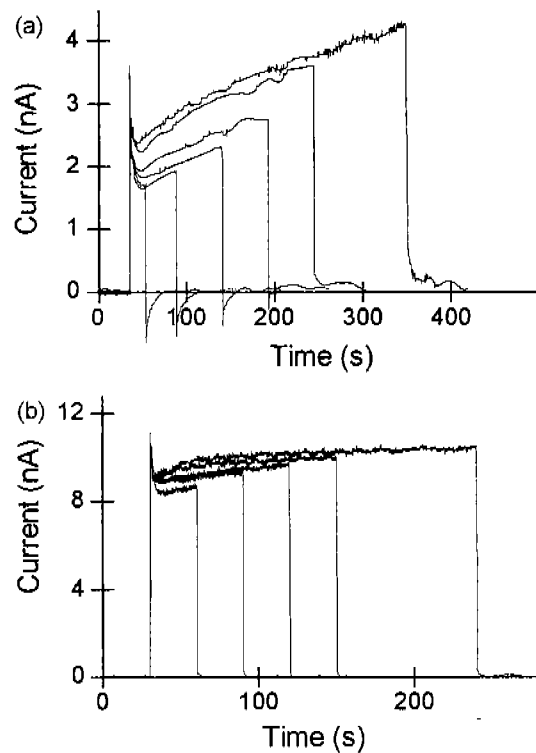


Fig. 6. Pyroelectric currents and relaxation currents as a function of illumination time in (a)  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$ , and (b)  $\text{BaTiO}_3$  ceramics.

repeatedly performed with varying the illumination time from 10 seconds to 300 seconds to control the amount of the photoinduced domain switching for both of the PLT15 and BT ceramics. The pyroelectric current is observed with short illumination time in BT ceramics. But, as the illumination time goes longer, the pyroelectric current diminishes, and finally only the relaxation current is observed in BT ceramics. As expected in Fig. 5, the more the photoinduced domain switching occurred, the more the relaxation current was obtained.

#### IV. Conclusions

We investigated the effect of the grain size on the photovoltaic current in PLTx ceramics and elucidated the experimental results. The photovoltaic current had a peak at a critical grain size which increased with increasing the spontaneous polarization. This effect was contributed to an electro-potential barrier which was built by photoexcited electrons trapped at the grain boundary. Since an electro-potential barrier impeded the movement of the following photoexcited electrons, the maximum photovoltaic current could be obtained at a critical grain size, where an electro-potential barrier plays a minimum role.

We have also investigated the photoinduced domain switching in ferroelectric ceramics poled under an intermediate electric field. Non-steady state photovoltaic current in  $(\text{Pb}_{0.85}\text{La}_{0.15})\text{TiO}_3$  and  $\text{BaTiO}_3$  ceramics was due to the space charge field built by electrons trapped at the grain boundary, and this was strong enough to cause the photoinduced domain switching without an external field. This was proven by the acoustic emission signal originating from the stored energy in the domain realignment. No pyroelectric current on cooling was another evidence for the photoinduced domain switching. Due to the domain switching under illumination, not pyroelectric current on cooling but relaxation current was observed.

#### Reference

1. V. M. Fridkin, I. I. Groshik, V. A. Lakhovizkaya, M. P. Mikhailov and V. N. Nosov, "Current Saturation and Photoferroelectric Effect in SbSI," *Appl. Phys. Lett.*, **15**, 354-356 (1967).
2. H. Heyszenau, "Electron Transport in the Bulk Photovoltaic Effect," *Phys. Rev.*, **B18**, 1586-1592 (1978).
3. F. S. Chen, "Optically Induced Change of Refractive Indices in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ ," *J. Appl. Phys.*, **40**, 3389-3396 (1969).
4. G. Chanussot and A. M. Glass, "A Bulk Photovoltaic Effect due to Electron-Photon Coupling in Polar Crystals," *Phys. Lett.*, **59A**, 405-407 (1976).
5. J. J. Amodei, "Electron Diffusion Effects During Hologram Recording in Crystals," *Appl. Phys. Lett.*, **18**, 22-24 (1971).
6. K. Uchino, *Piezoelectric Actuators and Ultrasonic Motors* (Kluwer Academic Publishers Boston Dordrecht London 1997).
7. A. M. Glass, D. von der Linde, D. H. Auston and T. J. Negrann, "Excited State Polarization, Bulk Photovoltaic Effect and the Photorefractive Effect in Electrically Polarized Media," *J. Electronic Materials*, **4**, 915-943 (1975).
8. C. E. Land and P. S. Peercy, "Photorefractive Effects in PLZT Ceramics," *Ferroelectrics*, **22**, 677-679 (1978).
9. W. L. Warren and D. Dimons, "Photoinduced Hysteresis Changes and Charge Trapping in  $\text{BaTiO}_3$  dielectrics," *Appl. Phys. Lett.*, **64**, 866-868 (1994).
10. P. S. Brody, "High Voltage Photovoltaic Effect in Barium Titanate and Lead Titanate-Lead Zirconate Ceramics," *J. Solid State Chemistry*, **12**, 193-200 (1975).
11. T. Sada, M. Inoue and K. Uchino, "Photostriction in PLZT Ceramics," *J. Ceram. Soc. Jpn. Inter. Ed.*, **95**, 499-504 (1987).
12. V. M. Fridkin, "Photodomain Effect in  $\text{BaTiO}_3$ ," *Ferroelectrics* **4**, 169-175 (1972).
13. F. Micheron, C. Mayeux and J. C. Trotier, "Electrical Control in Photoferroelectric Materials for Optical Storage," *Appl. Opt.*, **13**, 784-797 (1974).
14. P. Buchman, "On Acoustic Emission from Ferroelectric Crystals," *Solid-State Electron.*, **15**, 142-144 (1972).
15. H. Iwasaki and M. Izumi, "Acoustic Emission and Piezoelectricity During Poling in PZT-like Ferroelectric Ceramics," *Ferroelectrics*, **37**, 563-566 (1981).
16. D. G. Choi and S. K. Choi, "Dynamic Behaviour of Domains During Poling by Acoustic Emission Measurements in Lammodified  $\text{PbTiO}_3$  Ferroelectric Ceramics," *J. Mater. Sci. in Electron.*, **32**, 421-425 (1997).
17. L. J. Graham and G. A. Alter, *AD 745000, Final Report*, (Naval Air Systems Command, Contract No. N00019-17-C-0334, 1972).
18. A. M. Glass, D. von der Linder and T. J. Negrann, "High Voltage Bulk Photovoltaic Effect and the Photorefractive Process in  $\text{LiNbO}_3$ ," *Appl. Phys. Lett.*, **25**, 233-253 (1974).
19. A. S. Zheluev, *Physics of Crystalline Dielectrics*, (Plenum Press, New York, 1971).