JOURNAL OF SOLID STATE CHEMISTRY 12, 186–192 (1975)

Memory and Display Applications for PLZT Ceramics*†

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Received July 3, 1974

The useful electrooptic effects in lead lanthanum zirconate titanate (PLZT) ceramics divide into three general classes: variable birefringence, light scattering, and surface deformation. These effects are related to electrical switching of ferroelectric domains and electrically induced changes in the lattice distortion. Certain compositions exhibit memory properties due to remanent polarization of the domains, while some nonremanent compositions offer an electrostatic memory capability.

A number of memory and display devices use longitudinal electrooptic effects. All three classes of electrooptic effects have been utilized in ferroelectric–photoconductor devices for information storage and display. Longitudinal light depolarization scattering is useful in alpha-numeric displays as is a fringe-field effect. The three classes of electrooptic effects in PLZT ceramics are also under evaluation for use as optical data input devices for optical memory systems.

Introduction

Over the past few years the list of potential electrooptic applications for lead lanthanum zirconate titanate (PLZT) ceramics has continued to grow. Modulators, shutters, color filters, image storage and display devices, alpha-numeric displays, holographic storage media, and data input devices for optic memory systems are some of the device applications. Some of these devices have progressed to essentially final development, while others hold promise for achieving a use status in a few years. Several of these applications use the conventional transverse electrooptic birefringence effects. However, many of these devices have resulted from the discovery of new electrooptic effects which are controllable in the longitudinal mode; i.e., the electric field is applied through the plate thickness parallel to the incident light.

The electrooptic effects in PLZT ceramics are separable into the three general classes of variable birefringence, variable light scattering and variable surface deformation. The properties within each class are primarily dependent on the composition and the grain size of the ceramic. The electrooptic effects are related to electrically induced changes in the orientation of ferroelectric domains and in the lattice distortion of domains. Certain compositions exhibit memory properties due to the remanent polarization of domains while some nonremanent compositions offer an electrostatic memory capability.

One category of longitudinal electrooptic devices consists of ferroelectric–photoconductor (FE–PC) structures which permit selective storage and erasure of information. All three classes of electrooptic effects are useful in FE–PC devices for information storage and display. Another category of longitudinal mode devices to be described later uses a light depolarization scattering effect and a fringe-field birefringence effect to display alpha-numeric information. A third category of longitudinal mode devices with applications in optical memory systems is the matrix-

* This work supported by the U.S. Atomic Energy Commission.

† Invited paper.

addressed data input device which may use any of the three classes of electrooptic effects.

Properties of PLZT Ceramics

The transparent PLZT ceramics are obtained by replacing some lead with lanthanum in the lead zirconate titanate—$Pb(Zr,Ti)O_3$—solid solution system (*1–4*). Modification of the PZT system with five or more atom%La significantly increases the transparency of the PLZT materials in the visible and near ir (0.4–6 μm). It also tends to lower the Curie temperature and the electric field needed to realign the ferroelectric domains.

The phase diagram for the PLZT ceramics is quite complex (*1*). At room temperature there are rhombohedral and tetragonal ferroelectric phases as well as a paraelectric phase among the compositions of general interest. The electrooptic properties of the PLZT materials are a sensitive function of the composition.

For longitudinal-mode device applications, only two compositions need to be discussed since the effects to be treated seem to be optimized in one or the other composition. This is due in part to their proximity to phase boundaries (*1*). The compositions are the 7/65/35 and 9/65/35 PLZT where the first number denotes the La content in atom% and the latter numbers denote the lead zirconate–lead titanate ratio. The 7/65/35 composition is a rhombohedral phase material. It exhibits a hysteresis loop with a maximum remanent polarization P_R which is about 90% of the saturation polarization obtained with an electric field. It has a continuum of stable remanent polarization states P_r obtainable by applying and removing an electric field slightly larger than the coercive field. The electrooptic effects observed in this composition have their entire electrically controllable range between P_R and the electrically depoled state $P_r = 0$. The longitudinal strain-biased birefringence effect (*5*, *6*), the longitudinal P_r-dependent light scattering effect (*6*, *7*), and the surface deformation effect (*8*) are all obtainable in the 7/65/35 composition.

The magnitude of all these effects is closely tied to a recent discovery (*9*) that the volume of a thermally annealed 7/65/35 sample decreases for all remanent polarization states after the first few switching cycles around the hysteresis loop as illustrated in Fig. 1. The maximum decrease in volume occurs near $P_r = 0$. This decrease is due to an electrically induced phase change in some domains to a unit cell symmetry of lower volume (*9*). The effect occurs in both coarse (>3 μm) and fine (<3 μm) grain size materials. The volumetric decrease relates strongly to the degree of domain alignment in the strain-biased (*5*) and self strain-biased (*10*) longitudinal birefringence effects in fine-grained material. The longitudinal P_r-dependent light scattering effect is principally due to the electrically controllable mixture of the two crystallographic phases in coarse-grained material (*9–11*). The surface deformation effect is achieved by selectively switching portions of a ceramic plate. While reorientation of the domains contributes to the effect, the volumetric decrease is the dominant mechanism for the effect.

The 9/65/35 composition is a slim-loop

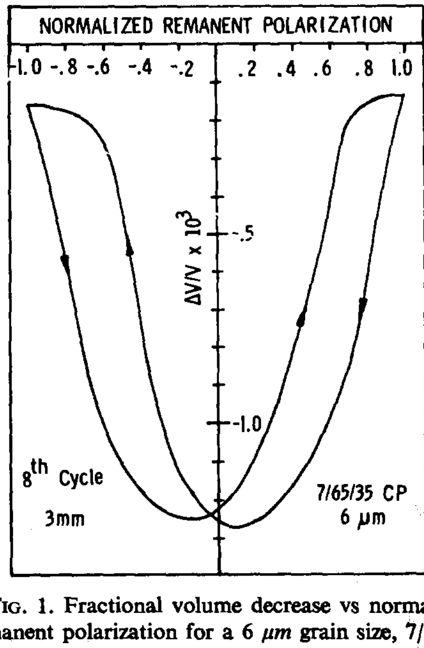

FIG. 1. Fractional volume decrease vs normalized remanent polarization for a 6 μm grain size, 7/65/35 PLZT ceramic bar with 3 mm-square cross section. Measurement is relative to the thermally annealed volume.

ferroelectric, i.e., there is little remanent polarization, and the material appears optically isotropic in the absence of an electric field. In fact, if the electric field is always applied with the same polarity to a thermally annealed sample there is no polarization in the absence of the field. (Apparently, some charge becomes trapped at the ceramic–electrode interface upon the initial reversal of the voltage polarity.) The zero-field isotropy gives an excellent off-state for any device placed between a crossed polarizer and analyzer.

The application of an electric field actually causes a distortion of the unit cell from a pseudocubic symmetry. The material becomes ferroelectric with the domains aligned as closely to the field direction as allowed by symmetry considerations. In addition to important applications in transverse, quadratic electrooptic devices, the 9/65/35 composition exhibits two longitudinal electrooptic effects which are useful in alpha-numeric displays. One effect is a longitudinal depolarization scattering phenomenon (*7*, *12*) in coarse-grained samples which is probably due to an admixture of crystallographic phases in the field-enforced ferroelectric state. The resulting refractive index discontinuities at domain and grain boundaries, while small, cause a depolarization of the incident light and scattering into a cone with 90% of the light in a 4° cone. In the second effect birefringence is obtainable at the edge of a sharply defined electrode due to the transverse component in the fringing of the longitudinally applied field (*13*).

Ferroelectric–Photoconductor Devices

A FE–PC device is a layered structure consisting of a thin ferroelectric plate that is first coated on one or both major surfaces with a photoconductive film and then covered with electrodes of which at least one must be transparent. The use of a photoconductive layer on the ferroelectric plate allows selective addressing with a light beam to obtain a spatial variation in the remanent polarization. This result is achievable principally because the resistance of the photoconductor limits the current transporting the polarization charge through the photoconductive layer for a given applied voltage and illumination level. For a photoconductor with a high resistivity, the time for switching in the dark may be hours. With an illumination pattern, such as a photographic image, there is a different effective *RC* time constant for each intensity level. After the remanent polarization of the maximally illuminated areas is switched the desired amount, the stored pattern of remanent polarization will replicate the image if the voltage is removed. Selective erasure and the storage of new information are possible by illuminating only the area to be changed.

This property of an FE–PC structure is useful for information storage and display devices employing one or more of the three classes of longitudinal electrooptic effects of remanent materials like 7/65/35 PLZT. In fact, the most promising of these FE–PC devices utilizes both the surface deformation and the P_r-dependent light scattering effect.

Variable Birefringence FE–PC Device

A clever strain-biased device structure exists for achieving a transverse electrooptic birefringence with a longitudinal electric field in PLZT ceramics (*5*). After transparent electrodes are deposited on the major surfaces of a 7/65/35 PLZT plate, it is bonded with a transparent epoxy resin to a Plexiglas substrate. By flexing the substrate to achieve either tensile or compressive stress, the ferroelectric domains are aligned predominantly along the axis of tensile stress which creates an optic axis. Application of an electric field between the electrodes provides a method of varying the number of domains aligned along this axis. A half wavelength of retardation change is achievable in a plate only 75 μm thick by varying P_r from P_R to 0. If a FE–PC structure is bonded to the Plexiglas substrate, the resultant device, called a FERPIC, stores images as a spatial variation of the birefringence. The FERPIC is capable of an image resolution of 40 line pairs/mm and a contrast ratio of 15 dB. The device requires about 100 V for its operation with a ceramic plate of 75 μm thickness.

The strain-biased concept has several limitations with the most severe being the epoxy bond. It must be extremely uniform optically and must withstand strains of at least 2×10^{-3}. Also, the strain-biased device is bulky due to the fixture needed to flex the Plexiglas. There are critical tolerances on the polishing of the ceramic and on the polarization switching in order to obtain optimum contrast and grey scale. Optical restrictions include a 3 dB insertion loss due to the polarizer and analyzer and the necessity of a nearly monochromatic light source for viewing the image. Finally, an anisotropy is present in the image resolution (*5*).

Variable Surface Deformation FE–PC Device

As illustrated in Fig. 2a, the surface deformation FE–PC device, called the FERICON, is a five-layer structure with a reflective metal electrode. Two photoconductive layers are used to produce deformations on both surfaces of the ceramic plate. This minimizes those strains which tend to distort the structure from its planar configuration. The deformations on the ceramic surface are replicated by the photoconductor and electrode until the lateral dimension of the area being selectively switched approaches the thickness of the photoconductive layer, typically 4 μm. Surface deformations with a resolution of 57 lp/mm were observed on a 7/65/35 ceramic plate of 0.25 mm thickness. For resolutions (spatial frequencies) of 4 lp/mm or less the surface deformation was measured to be 0.13 μm for storage between $P_n = P_r/P_R = 1$ and $P_n = 0$. However, this deformation decreases at higher spatial frequencies.

One method for storing information in the FERICON is with the entire ceramic plate initially at $P_n = 1$. A light intensity pattern is focused on the transparent electrode side until the maximally illuminated areas are switched to near $P_n = 0$. In Fig. 2b an optical Ronchi ruling is used to superimpose a modulation on low spatial frequency elements (<16 lp/mm). Without this modulation only the edges of the bars would be observable in the displayed image. The deformation pattern of a stored image causes some incident collimated light to be diffracted into the first and higher orders. The diffracted light can be reimaged with a Schlieren optical network to achieve a projected image. If a Ronchi ruling is used to store the image, the maximum resolution in the projected image is about one-half the number of lp/mm of the ruling (*14*).

The advantages of the FERICON are the separation of the writing or information storage optics from the reading optics and possibly a low insertion loss since the light is reflected and diffracted from a reflective surface. However, information storage in the

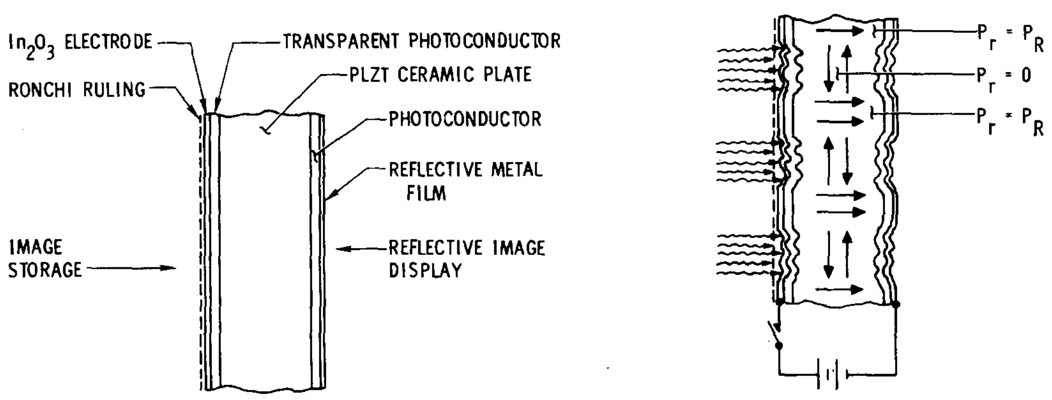

FIG. 2. (a) Illustration of the FERICON structure for image storage and display (b) Illustration of the surface deformations resulting from a bar pattern stored through the Ronchi ruling.

current devices slightly distorts the device from its planar configuration and limits the contrast ratio to about 5–7 dB for an image projected with a white-light source. Another constraint in the use of the device is that the reflecting surface must be free of defects, such as scratches, down to the dimension of the smallest resolution element.

Variable Light Scattering FE–PC Device

If the reflective metal electrode of the FERICON is replaced with a transparent electrode, the surface deformation effect is also useful in a transmission-mode FERICON which uses fine-grained PLZT ceramics. The contrast is again low, but the resolution is still high. If a coarse-grained 7/65/35 PLZT ceramic is used, the P_r-dependent longitudinal scattering effect is also present. These two effects combine to create a FE–PC device with a resolution of 35–40 lp/mm resolution and a contrast ratio of 17–20 dB in a projected image The CERAMPIC, as this device is referred to, seems to have optimal image quality for 6 μm grain size, 7/65/35 PLZT plates of 0.25–0.30 mm thickness.

With both effects present each effect compensates for the other's weakness. The bulk scattering effect is limited to resolutions of 16–20 lp/mm, by fringing of the electric field in the ceramic plate but it permits contrast ratios of 20 dB for low spatial frequencies The surface deformations have the previously stated high resolution capability and lower contrast ratio. In combination the effects produce a device for which the contrast ratio remains high for resolutions up to 20 lp/mm and then steadily declines until the 40 lp/mm resolution limit is reached.

The magnitude of the P_r-dependent scattering effect is large as evidenced by the data in Fig. 3 (*4*). This is a plot of insertion loss vs P_n for a 6 μm grain size, 7/65/35 PLZT plate of 275 μm thickness with transparent electrodes on the major surfaces. The data were obtained by monitoring the transmitted 6328 Å light with a detector of 1° angular aperture as P_r was varied from the thermally annealed state (point A) to $P_R(B)$, $P_r = 0(D)$, and $-P_R(B')$. An image stored in a CERAMPIC is viewed with a modified Schlieren optical network similar to that used to obtain this data. The projection system includes a collimated white light source, the CERAMPIC, a lens, a variable aperture in one focal plane of the lens, and a screen. The variable aperture controls the angular acceptance for scattered light at the viewing screen. With about a 2° aperture angle CERAMPIC images of photographic quality are obtained as Fig. 4 demonstrates.

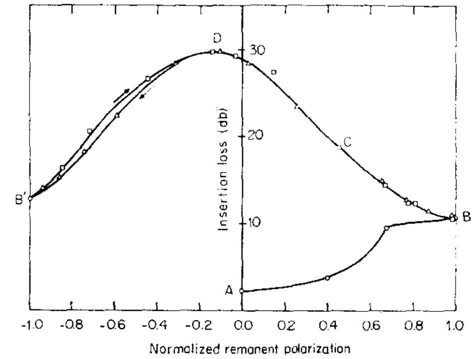

FIG. 3. Insertion loss (dB) vs normalized remanent polarization (P_r/P_R) for the longitudinal electrooptic scattering effect in a 275 μm thick 7/65/35 ceramic plate. (Average grain size is 4.5 μm.)

The most promising application areas for the CERAMPIC or the other two FE–PC devices is for storage of analog data transmitted digitally from a remote location and used to modulate the intensity of a laser beam which scans the device. The principal concern in the use of the CERAMPIC is whether it will survive millions of storage–erasure cycles. Tests at Bell Laboratories (*15*) indicate that cycling between $P_n = +1$ and $P_n = 0$ is possible for at least 2×10^4 times with no sign of degradation in a CERAMPIC with CdZnS photoconductive films.

Alpha-Numeric Display Devices

Of the two longitudinal-mode effects in 9/65/35 PLZT ceramics that are useful in alpha-numeric displays, the fringe-field effect appears to have better use potential than the depolarization scattering effect. The fringe-field device configuration consists of metal mesh electrode deposited on one side of the

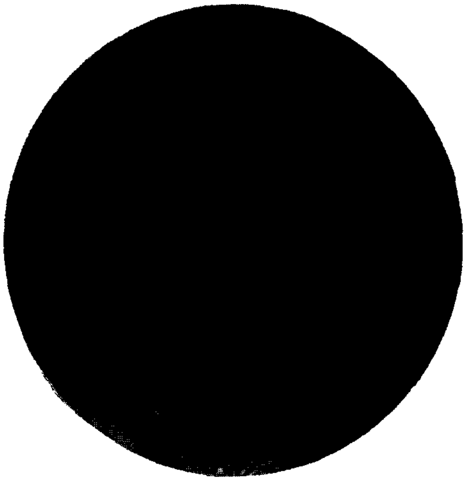

FIG. 4. Photograph made by projection of an image stored in a scattering-mode FE–PC device. The device configuration is a circular disc, 3.25 cm diam × 0.31 mm thick.

ceramic plate. Prototype devices use 2–4 μm grain size PLZT plates of 125 μm thickness with a mesh electrode having a line width and gap width of 250 μm.

For a transmission-mode device a transparent electrode is deposited on the other ceramic surface. With crossed polarizers oriented at 45° to the mesh electrode line directions, the behavior of the device as a function of electric field is shown in Fig. 5. Contrast ratios of 20:1 are obtained for applied voltage of 30 V. In reflection-mode devices a reflective metal is deposited on the back surface and a polarizer and quarter wave plate are placed in front with the polarizer aligned at 45° to one direction of

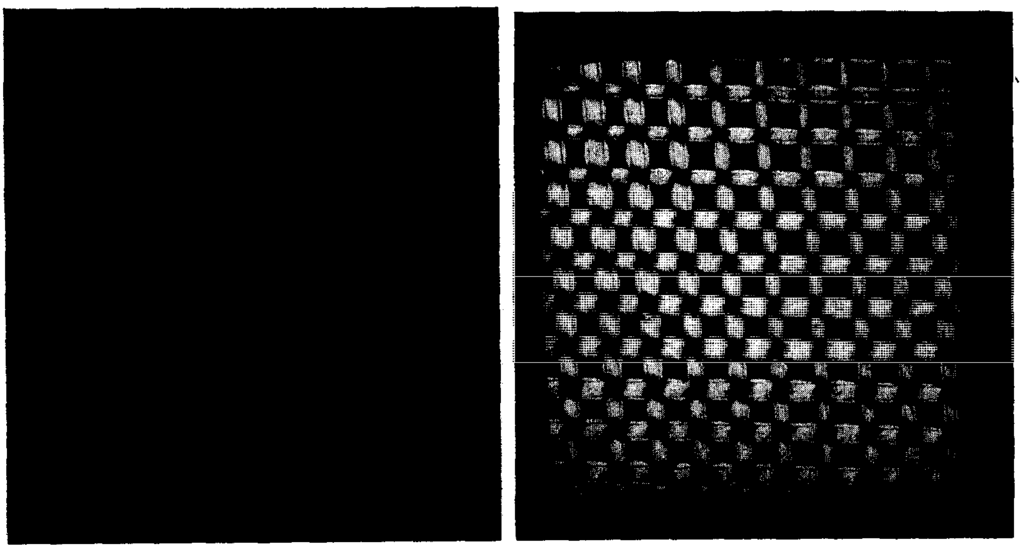

FIG. 5. Illustrations of the fringe-field effect in a 9/65/35 PLZT ceramic plate (a) no applied field; (b) 4kV/cm applied.

electrode lines in the mesh pattern. In this mode the optical effect of an applied voltage is easily visible over a large angular range under ambient lighting, because there is always a transverse component of electric field for any viewing angle. Numeric displays are made with the front mesh electrode deposited in a seven-segment array to form the number 8.

The longitudinal depolarization scattering effect is used in prototype transmission- or reflection-mode alpha-numeric displays in coarse-grained 9/65/35 PLZT plates with a transparent front surface electrode. In the transmission mode, the back electrode is segmented and transparent. For a 250 μm thick plate placed between a crossed polarizer and analyzer, contrast ratios of about 20 dB are obtained with a narrow aperture detector, such as the human eye, for an applied voltage of 400 V.

Both of these longitudinal mode effects are under evaluation for applications. One or both may prove suitable for ambient light displays, such as watch faces, in a reflective mode. The resistivity of the 9/65/35 materials is greater than 10^{14} Ω-cm so that capacitive storage of displayed information is also possible. In a hermetically sealed environment, information has remained stored for days with only minor degradation. Shorting the electrodes immediately turns off the display.

Matrix-Addressed Data Input Devices

Another design configuration for longitudinal-mode electrooptic devices is a matrix-addressing scheme. Row electrode strips are placed on one ceramic plate surface and orthogonal, column electrodes are deposited on the other surface. Recent studies (*16*) have evaluated matrix-addressed devices using the strain-biased, the P_r-scattering, and the fringe- or edge-field effects in 7/65/35 PLZT for application as block data composers. These composers serve as digital data input devices for coherent optical memories and processors. The strain-biased device suffers from many of the previously mentioned limitations. The other two effects provide marginal contrast ratios for optical system use. A fourth effect called a differential phase mode (*16*) holds promise for future use in optical data memory systems. The effect uses the surface deformation effect (*8*, *9*) and a change in the index of refraction to create a difference in optical path length of $\lambda/2$ to distinguish a "0" and a "1" state. Part of the change in refractive index may also be tied to the electrically controlled mixture of crystallographic phases (*9*). To record data with this phase modulator, a double exposure hologram is obtained with first all 0's and then with the pattern of 0's and 1's. Contrast ratios of 35:1 are expected in future devices.

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