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Bilateral switching of the modulated electrooptic contrast in PLZTN ceramics

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Abstract

Spatial distribution of ferroelectric polarization in $Pb(Zr,Ti)O_3$ ceramics doped with lanthanum and niobium has been investigated using scanning electrooptic confocal microscopy. Measurement of the modulated electrooptic signal in presence of a sinusoidal electric field reveals ferroelectric domains at microscopic scale not accessible to conventional polarized optical imaging. Both electrooptic images and local electrooptic loops have been observed after applying a bias electric field to the ceramic samples, being initially non-ferroelectric macroscopically. Bilateral reversal of the electrooptic contrast during the poling cycle has been detected and explained taking into account non-180° switching processes in ferroelectric grains of arbitrary orientation.

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Technologically important properties of modern ferroelectric materials are mainly due to the inhomogeneous spatial distribution of the spontaneous polarization. Microscopic domains in single crystals, grains in ceramics and thin films, isolated polar clusters in relaxors, and local built-in electric fields at structural defects cause the macroscopically measured parameters to be a complex statistical mean value of the local properties added with essential extrinsic contribution due to the motion of domain walls. Complete understanding of the physical mechanisms, imposed by the domain structure, requires reliable spatially resolved experimental data. Meanwhile, most of the information on ferroelectrics and relaxors still comes from macroscopic dielectric, optical, and X-ray measurements.

The last decade is marked with fast development of scanning piezoelectric force microscopy (PFM) becoming one of the principal sources of information about domains and their kinetics during the ferroelectric polarization reversal [1]. Adding the modulation principle to classical atomic force microscopy (AFM), it provides not only maps of ferroelectric polarization, but it also allows to probe dielectric and piezoelectric properties of the material with nanoscopic resolution. Optical microscopy, being for a long time the tool of choice to study the ferroelectric domain structure, needs innovations to overcome two important obstacles, namely, the limited spatial resolution and the lack of distinct optical contrast between antiparallel domains in many basic configurations [2]. Similar to the AFM case, the latter problem can be resolved by use of modulation of the optical properties by an external sinusoidal electric field. The resulting technique is scanning electrooptic microscopy (SEOM) [3–6].

The SEOM contrast between domains with different directions of ferroelectric polarization is caused by the dependence of the linear electrooptic response on mutual orientation of ferroelectric polarization, probe electric field, and polarization of incident light [4]. The analysis is simple enough in case of single crystals with small number of possible domain orientations. The probing of in-plane and out-of-plane polarization in thin films can be made by additional

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measurements in presence of a Dc bias field as shown in Ref. [6]. However, the situation can be more complicated in case of ferroelectric ceramics or materials with extremely fine domain structure (like relaxors) where a wide variety of both direction and absolute value of the local ferroelectric polarization can be expected.

In this paper, we obtain and analyze the SEOM images of $Pb(Zr,Ti)O_3$ (PZT) ceramics doped with lanthanum and niobium (PLZTN). The PZT system is one of the most studied ferroelectric materials due to excellent dielectric and piezoelectric properties [7] promising also for non-volatile ferroelectric memory [8]. Doping with lanthanum and niobium allows reduction of electric conductivity as well as improvement of optical properties [9,10]. The features of the phase diagram like morphotropic phase boundary and relaxor state [7,11] allow numerous domain orientations useful for investigation of the specific features of SEOM imaging of non-crystalline ferroelectrics.

The ceramic samples of the composition $(Pb,La)(Zr,Ti)O_3$ doped with 0.4% niobium and with La/Zr/Ti = 7/60/40 were prepared using a conventional solid-state reaction process. Stoichiometric amounts of oxide precursors were wet balls milled for 48 h and calcined at 850 °C for 4 h. The reacted powders were uniaxially (75 MPa) and isostatically (150 MPa) pressed in thin disks (thickness 2 mm, diameter 30 mm), sintered at 1250 °C for 2 h, and isostatically hot pressed at 950 °C for 2 h at pressure of 100 MPa with Ar working gas. The samples with typical sizes $8\times3\times3\ \mathrm{mm}^3$ were polished with 1 μm diamond powder. The pairs of stripe electrodes have been painted on the surface with silver paste with typical spacing of 0.2–0.3 mm to provide application of both Ac and Dc electric fields for the electrooptic probing and the polarization reversal.

The scanning confocal microscope is similar to the setup described in Ref. [4]. A high-numerical aperture (NA = 0.8) objective (Nikon CFI LU EPI P 50×) is filled by 633 nm laser light passed through a spatial filter and a beam expander. The raster scanning is produced by a 90° pair of galvanometrically controlled metallic mirrors placed before the objective. The light reflected from the crystal surface passes back through the objective and spatial filter to be registered by a high-frequency photodetector (Nirvana, New Focus). The map of intensity of the reflected light corresponds to the conventional confocal optical image. The linear electrooptic image is formed by point-to-point measurement of the in-phase signal from a lock-in amplifier at the frequency of the Ac electric field applied to the crystal. Both optical and electrooptic pictures are acquired simultaneously during the same scanning cycle.

Fig. 1(a) shows the optical image of the ceramic surface (map of the Dc component of the reflected light intensity). Surface imperfections, grain structure, traces of polishing, and interference patterns can be seen in this picture. The optical image remains unchanged during all variations of the electric field used in the experiments. This means that most of the optical features observed in this image have no direct relation to the ferroelectric domain structure.

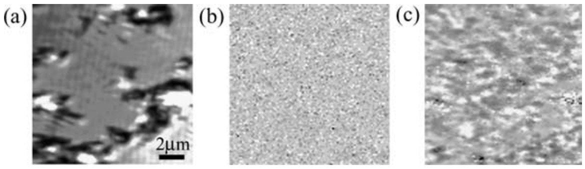

Fig. 1. Optical (a) and electrooptic (b,c) images of the PLZNT ceramics before (b) and after (c) application of the Dc bias voltage of −50 V.

The Ac image, corresponding to spatial distribution of the linear electrooptic response, shows no macroscopic domain structure for virgin samples before application of strong electric fields (Fig. 1(b)). The electrooptic signal is null everywhere except usual temporal fluctuations. This coincides with earlier observations provided by piezoelectric and optical microscopy for PLZT samples in a pseudocubic 'α-phase' [12] corresponding to the chemical composition 7/60/40 of our sample.

We have found, however, that numerous electrooptically active regions arise irreversibly throughout the sample between the painted silver electrodes after application for a certain time of a moderate Dc bias voltage (50–100 V). An example of such electrooptic pattern is presented in Fig. 1(c). Microscopic domains of different value and sign of the Ac component of the modulated electrooptic signal can be seen. Bright areas correspond to the positive Ac response (in phase with the field) while electrooptic signal in dark areas is 180° shifted. The spatial resolution of the electrooptic picture is about 0.5 μm, close to the resolution obtained for the optical image. This means that the real size of the ferroelectrically ordered regions (expected to be of rhombohedral symmetry or 'β-phase' [12,13]) is probably much smaller, but the signal is averaged at the spatial scale of the order of the wavelength (633 nm) which is typical for diffraction-limited confocal microscopy. Practically all ferroelectric domains, well resolved in the electrooptic mode of observation, have no corresponding features in the optical Dc picture (Fig. 1(a)).

Extrinsic properties of the PLZTN ceramics are governed by kinetics of the domain structure in an applied electric field. Typical evolution of the electrooptic picture during variation of the Dc bias voltage from −100 to +100 V and back is shown in Fig. 2. It was found that most of the spatial regions change

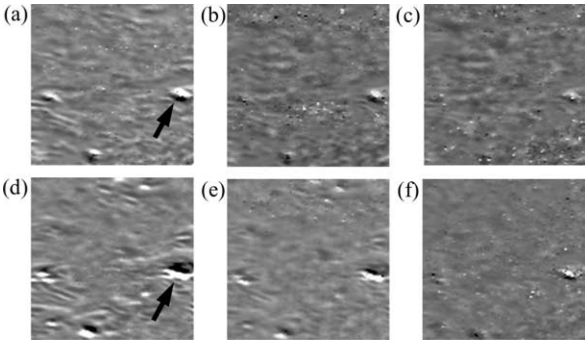

Fig. 2. Evolution of the domain structure in PLZTN ceramics during application and variation of the Dc bias voltage: (a) −100 V, (b) 0 V, (c) +35 V, (d) +100 V, (e) 0 V, (f) −70 V.

the sign of electrooptic response at the highest absolute values of the applied voltage (Fig. 2(a) and (d)), while intermediate stages of the switching process (corresponding to lower voltage) are characterized by reduced electrooptic contrast (Fig. 2(b) and (e)). This is another indirect confirmation of the fine intermediate structure of the real domains below the threshold of optical resolution.

An interesting feature of electrooptic images of PLZTN ceramics is a bilateral change of the sign of the response induced by the Dc bias field. If, for example, the field is switched from negative to positive (Fig. 2(a)–(d)), some regions change their color from dark to bright while other ones, inversely, from bright to dark. This is easy to see following the high-contrast domain pairs like that one indicated by arrows in Fig. 2. Such behavior is not typical for more conventional imaging techniques where the output signal tends to be homogeneous in high field (either dark or bright) depending on the field sign. This feature was not present also in previous SEOM studies of ferroelectric single crystals [4].

Origin of this unusual contrast as well as other features revealed by SEOM can be understood from the analysis of the electrooptic equation. For normal reflection from a crystallite of rhombohedral $3m$ symmetry the electrooptic response is proportional to

$$\Delta(1/n^2) = r_{ijk}E_k = r_{13}E\cos\theta\sin^2\varphi + r_{33}E\cos\theta\cos^2\varphi + 2r_{51}E\sin\theta\sin\varphi\cos\varphi,$$

where r_{ijk}, electrooptic tensor; n, optical index; E, applied sinusoidal electric probe field and the angles θ and φ describe deviation of the electric field and of the light polarization direction, respectively, from the ferroelectric c-axis component in the plane of the surface [4]. Reversal of the ferroelectric polarization results in shift of both angles θ and φ by 180°, and the Ac signal changes its sign but keeps the same absolute value. However, the chaotic angular distribution of crystallographic axes, typical for ceramics, combined with continuous distribution of angles between field and local ferroelectric polarization, make non-180° switching possible and even likely. The phase of the electrooptic response is not longer symmetric with respect to switching, as readily seen, for example, from Fig. 4(b) of Ref. [4]. Even small variations of the angle θ can induce reversal of the electrooptic contrast, and both dark-to-bright and bright-to-dark signal changes can coexist at the same geometrical conditions. It is interesting to note that, for example, tetragonal barium titanate shows no such variety of possible electrooptic response (Fig. 6(b) of Ref. [4]) due to the fact that, for this material, one component of the electrooptic tensor is much higher than the other ones. It means that, first, effect of the bilateral switching of the electrooptic contrast should not be observed in $BaTiO_3$ ceramics, and second, the SEOM images of a ceramic material allow one to draw some conclusions about features of its electrooptic tensor even without any quantitative measurements.

Another information supplied by SEOM in addition to the imaging of ferroelectric polarization is contained in local electrooptic loops measured at separate points of the sample [3,5]. They are similar to usual macroscopic ferroelectric loops but reveal local ferroelectric properties with microscopic spatial resolution. The SEOM loops measured on our PLZTN ceramics (Fig. 3) show relatively soft ferroelectric behavior with low width and high repeatability. The small asymmetry of the loops is likely due to inhomogeneous internal built-in electric fields arising during initial development of the microscopic ferroelectric domain structure from the virgin relaxor state induced by the symmetry-breaking electric bias field. However, this effect in PLZTN ceramics is much less pronounced comparing for instance to relaxor PMN-PT single crystals [14].

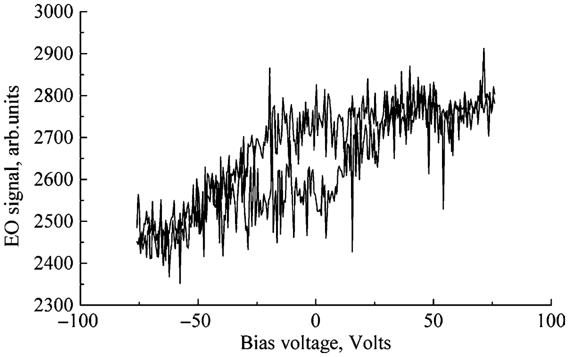

Fig. 3. Local electrooptic loop in PLZNT ceramics.

In brief, we have applied scanning electrooptic confocal microscopy to investigate the ferroelectric domain structure of the PLZTN ceramics with composition 7/60/40. No electrooptic response has been found at microscopic scale in the virgin relaxor state, but ferroelectric domains have arosen irreversibly after application of a bias electric field. Evolution of the domain structure during the switching cycle shows an interesting phenomenon not observed in single crystals—bilateral reversal of the electrooptic contrast in different grains. Such effect can be explained by the analysis of the rhombohedral electrooptic tensor taking into account non-180° switching processes and continuous angular distribution of crystallographic axis in ceramic samples.

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References

[1] O. Kolosov, A. Gruverman, J. Hatano, K. Takahashi, H. Tokumoto, Phys. Rev. Lett. 74 (1995) 4309.
[2] J. Levy, O. Tikhomirov, in: M. Alexe, A. Gruverman (Eds.), Nanoscale Characterisation of Ferroelectric Materials: Scanning Probe Microscopy Approach, Springer, Berlin, 2004, p. 115.
[3] C. Hubert, J. Levy, A.C. Carter, W. Chang, S.W. Kiechoever, J.S. Horwitz, D.B. Chrisey, Appl. Phys. Lett. 71 (1997) 3353.
[4] O. Tikhomirov, B. Red'kin, A. Trivelli, J. Levy, J. Appl. Phys. 87 (2000) 1932.
[5] O. Tikhomirov, H. Jiang, J. Levy, Appl. Phys. Lett. 77 (2000) 2048.

[6] O. Tikhomirov, H. Jiang, J. Levy, Phys. Rev. Lett. 89 (2002) 147601.
[7] E. Sawaguchi, J. Phys. Soc. Jpn. 8 (1953) 615.
[8] J.F. Scott, Ferroelectr. Rev. 1 (1998) 1.
[9] D. Goldring, Z. Zalevsky, E. Goldenberg, A. Shemer, D. Mendlovic, Appl. Opt. 65 (2003) 6536.
[10] R. Gerson, J. Appl. Phys. 31 (1960) 188.
[11] D. Viehland, J.F. Li, S.J. Jang, L.E. Cross, M. Wuttig, Phys. Rev. B 46 (1992) 8013.
[12] E.T. Keve, K.L. Bye, J. Appl. Phys. 46 (1975) 810.
[13] V.V. Shvartsman, A.L. Kholkin, A. Orlova, D. Kiselev, A.A. Bogomolov, A. Sternberg, Appl. Phys. Lett. 86 (2005) 202907.
[14] O. Tikhomirov, M. Labardi, C. Ascoli, M. Allegrini, Ferroelectrics, in press.