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Stokes parameters for characterizing the polarization state of the second optical harmonic reflected from lead zirconate titanate thin films

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Received July 31, 2024
Revised October 24, 2024
Accepted October 24, 2024

Crystallites in lead ziriconate-titanate films have been studied using the technique of nonlinear optical polarization microscopy. 2D maps of the Stokes parameters S_0, S_1, S_2, S_3 are determined. Nonlinear polarization components are analyzed.

Keywords: PZT, nonlinear optical microscopy, second harmonic generation, spherulites, Stokes parameters.

DOI: 10.61011/TPL.2025.02.60639.20079

Nonlinear optical microscopy based on measuring the local response of the second optical harmonic is sensitive to crystal anisotropy and allows analyzing the crystallographic parameters of the material [1]. This technique is widely used, in particular, to study domain walls in ferroelectric films [2], to detect crystallographic defects [3]. From the intensity of the second harmonic (SH) signal, nonlinear susceptibility of the material [4] can be estimated. The SH field strength is related to the dielectric polarization of the material, so by analyzing the Stokes [5] parameters, we can describe the dielectric polarization behavior in different parts of the crystallites and the sample as a whole. The nonlinear optical microscopy technique has been successfully applied to study polarization switching in ferroelectric [6] samples. The crystal orientation characterization method based on the analysis of Stokes parameters is currently used as an alternative to electron backscatter diffraction (EBSD) [7]. Thin films of lead zirconate titanate (PZT) are now being studied as a material for microelectromechanical systems [8], nonlinear optical components in integrated optics [4]. In this paper, the nonlinear optical microscopy technique using the Stokes parameter formalism has been used to characterize the behavior of the nonlinear optical response in thin ferroelectric films.

PZT films on platinized silicon substrates with the structure $Si{-}SiO_2{-}TiO_2{-}Pt{-}PbZr_xTi_{1-x}O_3+10\,\%\,PbO$ were used as samples, (sample sputtering time 1 h, $T_{sputt} = 150\,^\circ C$, annealing time 1 h, $T_{ann} = 570\,^\circ C$, heating rate300 °C/h, cooling together with the furnace, PZT film thickness 300 nm).

The heating rate, as well as the crystallization temperature, affects the rate of lead evaporation from the film during the crystallization of the perovskite phase. This in turn affects the perovskite crystallization process. Given suboptimal parameters, crystallization will be incomplete. Slow cooling of the samples leads to stress relaxation in the film−substrate system, which prevents cracking and delamination of the film.

The ratios of Zr and Ti atoms used in the samples are close to the morphotropic phase boundary near which the ferroelectric properties of the material have a maximum, so such ratios are of interest to study. A laser pumping Witec alpha 300 confocal optical microscope was used in the experiment. The pumping wavelength was 800 nm, the pulse duration was 100 fs, and the repetition rate was 80 MHz. The pumping laser beam passed through a polarizer, hit the sample, was reflected at right angles, and passed through filters that allowed only SH radiation with a wavelength of 400 nm to pass through. Then the SH beam passed through the analyzer and into the photomultiplier tube. The pumping radiation for all images had the same vertical polarization (along the y axis in the laboratory coordinate system). The technique of measuring Stokes parameters is a powerful tool for describing the polarization state of the nonlinear optical response of anisotropic [9] samples. The following Stokes parameters were used, including the degree of linear polarization (DOLP) [10,11]:

$$S = \begin{bmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} I_0 + I_{90} \\ I_0 - I_{90} \\ I_{45} - I_{-45} \\ I_{\mathrm{RCP}} - I_{\mathrm{LCP}} \end{bmatrix}, \qquad (1)$$

$$\mathrm{DOLP} = \sqrt{\frac{S_1^2 + S_2^2}{S_0}}, \qquad (2)$$

where I — the SH intensity at the corresponding analyzer angle, RCP and LCP — right and left circular polarization, respectively.

The direction of SH linear polarization from the sample can be expressed through the Stokes parameters as

$$\theta = \frac{1}{2}\,\mathrm{Arg}(S_1 + iS_2), \qquad (3)$$

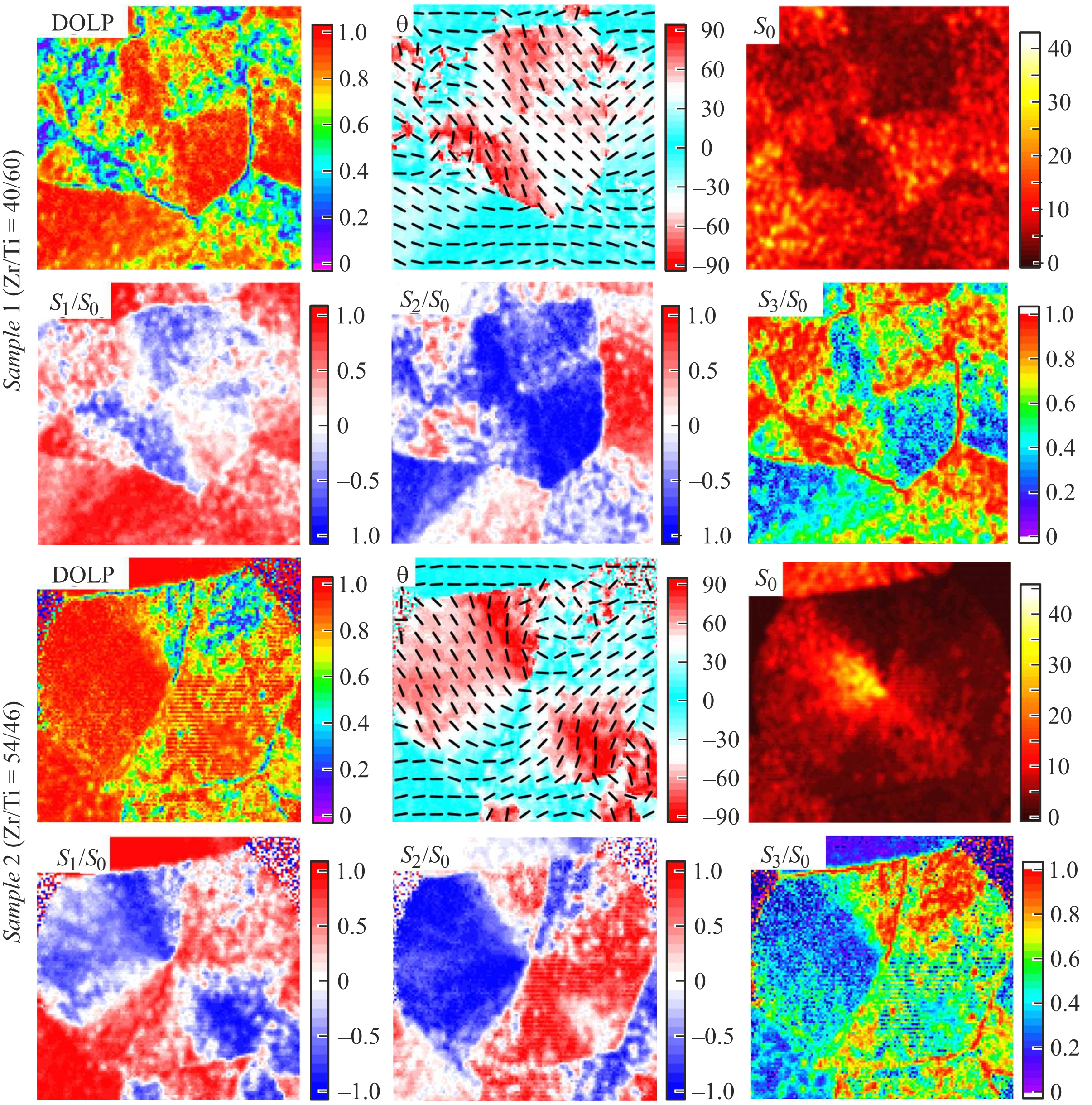

Figure 1. 2D maps of the Stokes parameters. The top two rows correspond to sample №1, the bottom two rows — sample №2 (see the Table). DOLP — degree of linear polarization (second harmonic), θ — direction of linear polarization of the second harmonic, S_0, S_1/S_0, S_2/S_0, S_3/S_0 — Stokes parameters. The dimensions of all images are $30 \times 30\,\mu$m. A color version of the figure is provided in the online version of the paper.

where $S_1 + iS_2$ — complex intensity of SH with linear polarization.

In case of monochromatic radiation, the Stokes parameters are related as follows:

$$S_0^2 = S_1^2 + S_2^2 + S_3^2. \tag{4}$$

The parameters S_0, S_1 and S_2were measured in the experiment, and the parameter S_3 was calculated by formula (4), so the modulus of this parameter is shown in the corresponding map. The expression used is valid for fully polarized light. In the experiment, the incident and reflected radiation from the sample had a high degree of polarization. The maps show (Fig. 1) that the degree of linear polarization of the SH radiation on the fused and non-fused spherulites has an inhomogeneous distribution. There is a nonlinear response in the spherulites, which has a circular polarization of SH. Comparing the S_3 (circular polarization intensity) and DOLP maps, it can be seen that the circular polarization is present in the areas with low degree of linear polarization.

The S_0 parameter maps are maps of the SH intensity. It is different from zero only in the crystallized regions with perovskite structure. This intensity in crystallized regions depends on the direction of polarization of the incident beam with respect to the crystallographic directions of

Film parameters

Sample number	Zr/Ti	Perovskite phase fraction, % (film continuity to the)	Crystal structure according to phase diagram
1	40/60	100	Tetragonal
2	54/46	90–95	Mixture of tetragonal and rhombohedral
3	54/46	20–30, islands	Same
4	60/40	5–10, islands	Rhombohedral

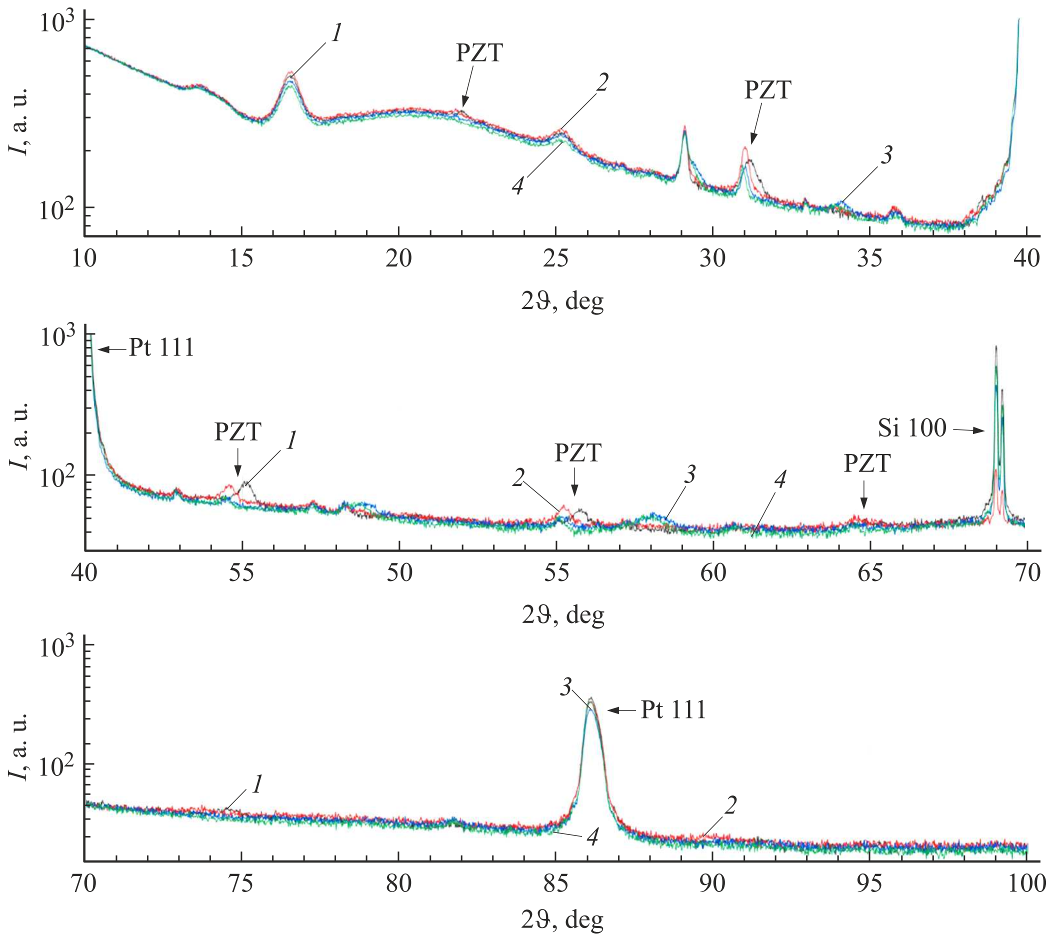

Figure 2. Diffraction patterns of four PZT samples. The curve numbers correspond to the sample numbers. In sample №1, which has only tetragonal phase, the peaks from PZT are shifted to the right and correspond to smaller interplanar spacing. The different intensity of the PZT peaks is related to the continuity of the crystallized regions (it was higher in samples №1 and 2).

individual crystallites. The heterogeneity of the SH intensity distribution indicates that the crystallites that make up the spherulite have different crystallographic directions.

The Stokes parametersS_1, S_2 and S_3 are normalized to S_0 (i.e., shown as relations S_1/S_0, S_2/S_0 and S_3/S_0) to make them easier to analyze. These relations (unlike the parameters S_1, S_2 and S_3) themselves) have values from -1 to 1.

The parameter S_1 represents the difference between the vertical and horizontal polarization components. If it is positive, the vertical component predominates, and if it is negative, the horizontal component predominates. Both polarization components were present in the spherulites.

In samples №1 and 2 (differing in Zr/Ti ratio and crystal structure, see the Table), where there are fused spherulites, the parameters S_1 and S_2 have sharp boundaries between spherulites because the crystallographic directions of the crystallites are mainly determined by the crystallization centers. In all maps, it can be seen that the crystallites have a radial growth direction. The SH polarization from neighboring crystallites can vary dramatically. Along a single crystallite (along the radial direction), the polarization state of SH changes only slightly. The direction of linear polarization of θ changes at the boundaries of spherulites. In some spherulites this direction changes smoothly.

Diffraction patterns (Fig. 2) were obtained on the X-ray diffractometer DRON-8T with copper cathode in the following configuration: on the leg of the X-ray tube — Soller slit $1^\circ 30'$, equatorial slit 2 mm, on the detector leg — Soller slit $1^\circ 30'$, equatorial slit 0.25 mm, nickel beta filter. Scanning parameters: discrete, step 0.02°, accumulation time 20 s, with rotation.

The diffraction patterns show peaks from the substrate and sublayers (Si, Pt, and also SiO_2 and TiO_2). These peaks for all four samples are the same since the substrate and sublayers were the same. The peaks of lead zirconate titanate in the diffraction patterns are different. From samples №1 and 2, these peaks (in the regions 31, 45, and $55-56^\circ$) are more intense, which is due to the greater continuity of these films. In sample №1, the PZT peaks are shifted to the right, which is probably due to the different Zr/Ti ratio (40/60) and the presence of only tetragonal phase.

Our findings suggest the following conclusions.

— according to Stokes parameter maps, the spherulites have inhomogeneous distribution of SH linear polarization;

— there is a circular polarization component;

— the spherulites consist of separate radially directed crystallites with different crystallographic parameters, which is consistent with the diffraction patterns.

Funding

The research was supported by RSF (grant 23-72-01110).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by J.Savelyeva