Optical second-harmonic generation in thin films of ferroelectric ceramics

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The microstructure of thin films of ferroelectric ceramics is investigated by measuring the azimuthal dependence of the intensity and the scattering indicatrix of the optical second harmonic. The distribution function of the crystallites over orientations in the plane of the film is calculated, as are the correlation length of the fluctuations of the nonlinear sources and the degree of ordering of the films. © *1996 American Institute of Physics.* [S1063-7834(96)02710-4]

Nonlinear optical studies of thin films of ferroelectric ceramics are of great interest from both the applied and fundamental standpoints. Films of the type ABO_3 are used in various microelectronic devices such as nonvolatile memory elements, sensors, and actuators. In addition, since these films have appreciable values of the nonlinear optical constants, they can be used in optoelectronic devices as well. The properties of these films depend strongly on their structure. For local diagnostics of this structure one can use the method of optical second-harmonic generation (SHG), whose unique possibilities have been demonstrated over the last decade in research on the properties of thin films (down to monolayers), surfaces, and interfaces (see the reviews[1,2]). The efficacy of the SHG method derives from the high sensitivity of the nonlinear response to the symmetry of the system under study. This makes it possible to obtain additional information about the structural properties of molecules beyond the capabilities of other optical methods. For example, in the electric dipole approximation an optical process of order n can be sensitive only to a symmetry of degree $n+1$ or lower (Ref. 3). This means that in a linear optical experiment only a twofold axis can be discerned, whereas the SHG method is also sensitive to a threefold symmetry. The diagnostic capabilities of the SHG method have been expanded through the use of modern femtosecond lasers, which enable one to study the optical properties of materials without appreciably taking them out of a state of thermodynamic equilibrium (even if the pump radiation lies in the absorption band).

In addition, the study of SHG in ceramic films is an extremely urgent fundamental problem in nonlinear optics. A unique feature of these objects is that they are practically isotropic and homogeneous as regards their linear optical properties, but reveal themselves to be substantially anisotropic and randomly inhomogeneous systems in the quadratic optical response. This feature is due to the structure of the films, which consist of microcrystals with a random orientation of crystallographic axes in the plane of the film. It should be noted that SHG on random sources has been investigated previously only in the bulk of a material.[4,5] The study of SHG in thin films with random sources encounters problems that require modern experimental techniques which have hitherto been employed separately for studying single-crystal samples and ultradisperse systems. In the first case it is necessary to measure the azimuthal dependence of the intensity of the second harmonic for various combinations of polarizations of the pump and second-harmonic radiation; from such measurements one can obtain the values of the components of the quadratic susceptibility tensor of the crystal.[6] In the second case, measurements of the scattering indicatrix of the second harmonic yield information about the second-order susceptibility tensor (or the hyperpolarizability) of individual scatterers (as in the case of hyper-Rayleigh scattering on molecules[5]).

At present there is are only a few papers on the study of SHG in ferroelectric thin films.[7,8] In this paper we present results from an experimental study of the morphological and nonlinear optical properties of thin films of the ferroelectric $Pb_x(Zr_{0.53}Ti_{0.47})O_3$ (PZT), the structure of which was varied by changing the parameters of the preparation procedure. The nonlinear optical technique used in this study is based on joint measurements of the scattering indicatrix at the second harmonic and the azimuthal dependence of the intensity of the second harmonic.

1. EXPERIMENT

PZT films with different crystal structures were prepared by the sol–gel method[9] with a Pb excess in the film-forming solution varying from $y=0$ to 0.5 with respect to the stoichiometric value and were then annealed at 650 °C. With this technology one can grow films consisting of columnar microcrystallites with a transverse dimension varying in the range 100–1000 nm (Ref. 10). The Pb concentration x in the film was 5–10% lower than in the solution on account of the evaporation of lead during annealing.[10] X-ray diffraction experiments revealed the presence of microcrystallites of the perovskite phase, with faces lying in the film plane in the

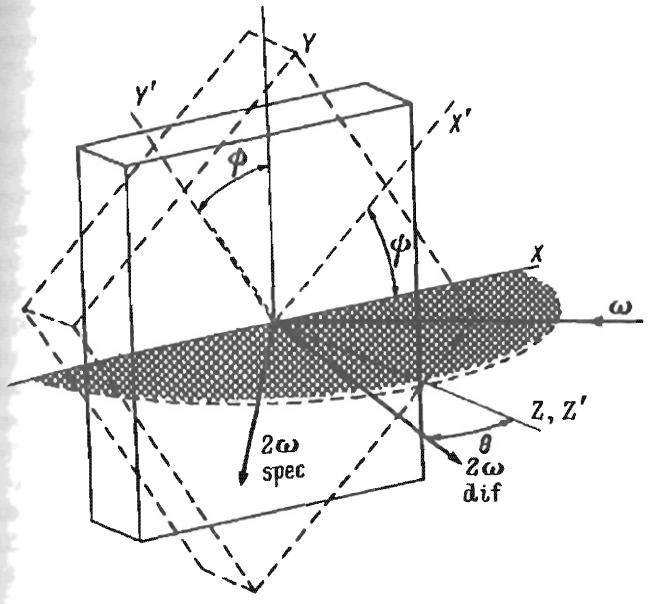

FIG. 1. Experimental geometry. The coordinate system XYZ is in the laboratory (stationary) reference frame, $X'Y'Z'$ is a coordinate system tied to the film, and ψ and θ are the azimuthal and polar angles, respectively.

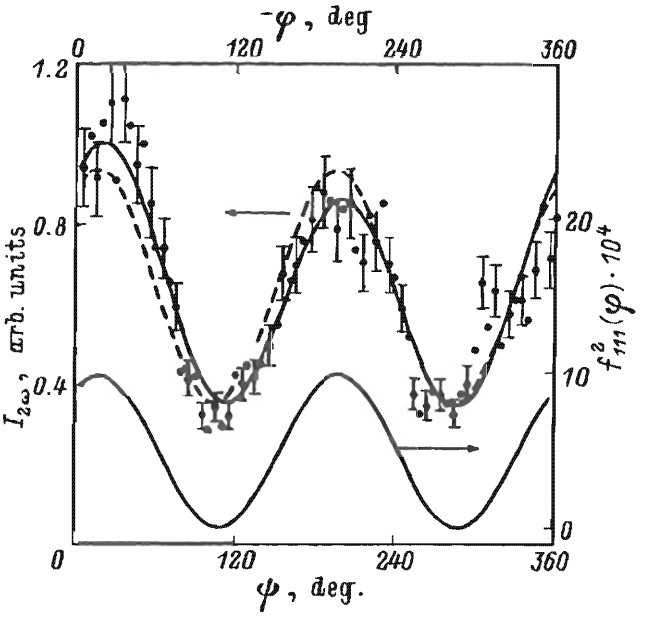

FIG. 2. Azimuthal dependence of the intensity of the second harmonic in PZT films with $n_{(111)}=0.92$ (left-hand scale). The points are experimental data, the solid curve is an approximation in Fourier harmonics up to $n=7$, the dashed curve is the result obtained by fitting the zeroth and second Fourier harmonics. The right-hand scale is for the plot of the square of the distribution function $f_{(111)}(\varphi)$ over orientations as a function of the azimuthal angle, as calculated according to formula (1) with the parameter values $S_1=-0.007$, $C_1=0.028$.

(111) and (100) orientations, with the relative concentration of the (111) orientation varying in the range $n_{(111)}=0.2$–0.97 (Ref. 11). The linear optical properties and thickness of the films were determined by spectroscopic ellipsometry in the range from 200 to 1000 nm.

In the nonlinear optical experiments we used pump radiation with a wavelength of 739 nm from a titanate–sapphire laser with a pulse duration of 100 fs, a pulse repetition rate of 82 MHz, and an average power of 100 mW, focused to a spot around 100 μm in diameter. The angle of incidence was 45°. The pump and second-harmonic radiation were polarized perpendicularly to the plane of incidence (s, s geometry). Figure 1 shows a sketch of the experimental geometry.

An anisotropic dependence of the second-harmonic intensity $I_{2\omega}(\psi)$ was measured in the specular direction as the sample was rotated about the normal (z) to the surface of the film (xyz are the coordinates in the stationary laboratory frame, $x'y'z'$ is a coordinate system moving with the film, and the azimuthal angle ψ was measured between the x and x' axes). The scattering indicatrices at the second harmonic were measured as the detection system was rotated about the vertical axis y. The axis from which the polar angle θ was measured was chosen such that θ was equal to zero in the direction normal to the surface of the film and negative in the direction of the pump radiation.

Figure 2 shows the azimuthal dependence $I_{2\omega}(\psi)$, and Fig. 3 shows the scattering indicatrix of the second harmonic for a sample with $y=0.05$ ($n_{(111)}=0.92$). The function $I_{2\omega}(\psi)$ is a superposition of a large isotropic background and an anisotropic component with two maxima. Anisotropic azimuthal dependences of this kind were observed for all the samples except for the one with $y=0$ ($n_{(111)}=0.97$), for which $I_{2\omega}(\psi)$ was completely isotropic.

All the scattering indicatrices were measured at the maximum and minimum of the anisotropic component. It is easy to see that the scattering indicatrix at the maximum of the anisotropic component consists of two parts: a sharp peak in the specular direction, superposed on a very wide dependence of the second-harmonic intensity on the polar angle (background). At the minimum of the anisotropic dependence the scattering indicatrices consist of the background alone, which agrees within the experimental error with the background for the scattering indicatrices at the maximum. This means that the diffuse part of the signal is completely

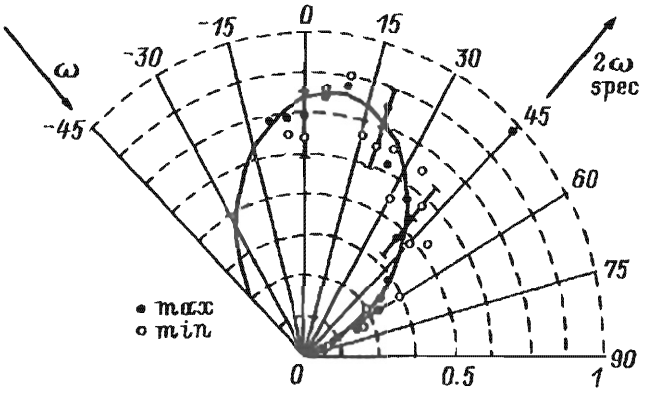

FIG. 3. Scattering indicatrix for the second-harmonic radiation at the minimum and maximum of the anisotropic azimuthal dependence. The solid curve is the result of an approximation of the experimental data according to formula (5).

isotropic, while the specular part (after subtraction of the diffuse background) is completely anisotropic, i.e., it vanishes at the minima of the azimuthal dependence.

2. INTERPRETATION OF THE RESULTS

For a theoretical analysis of the experimental data, let us treat the film as a random mixture of (111) and (100) crystallites uniformly filling the film and having surface concentrations of $n_{(111)}$ and $n_{(100)}=1-n_{(111)}$, respectively. The anisotropic linear response of the crystallites is negligible, and from the standpoint of linear optics the film is a homogeneous medium with an isotropic local dielectric constant. Here, retardation effects (including optical interferometry effects in the film) at the pump and second-harmonic frequencies are taken into account with the help of the local field factors for a three-layer medium.[12] At the same time, the substantial anisotropy of the bulk dipole quadratic response of the crystallites of each type is taken into account in the structure of their quadratic susceptibility tensor.

The orientation of an individual crystallite in the plane of the film is characterized by an azimuthal angle φ relative to the X' axis in a coordinate system tied to the film. The angle φ is a random quantity describable by a distribution function $p_i(\varphi)=1/2\pi+f_i(\varphi)$, where $i=(111)$ or (100) and $\int d\varphi f_i(\varphi)=0$. In this paper we will consider only the function $f_{(111)}(\varphi)$ for a sample with $n_{(111)}=0.92$, assuming for simplicity that it is a single-component system.

The periodic function $f_{(111)}$ can be represented as a Fourier series in the angle φ:

$$f_{(111)}(\varphi)=\sum_n (C_n\cos(n\varphi)+S_n\sin(n\varphi)). \qquad (1)$$

The specular and diffuse components of the second harmonic, $I_{2\omega}^{\text{spec}}$ and $I_{2\omega}^{\text{dif}}$, can be expanded in an analogous way in Fourier series in the azimuthal angle ψ, where the coefficients of these expansions depend in a known way on the coefficients C_n and S_n (for brevity we will omit these relations). A reasonable approximation to the experimental azimuthal dependence of the specular component (Fig. 2) is given by the expression

$$I_{2\omega}^{\text{spec}}(\psi)=I_0^{\text{spec}}+I_{c2}^{\text{spec}}\cos(2\psi)+I_{s2}^{\text{spec}}\sin(2\psi). \qquad (2)$$

At the same time, the diffuse component of the second harmonic is practically isotropic:

$$I_{2\omega}^{\text{dif}}(\psi)=I_0^{\text{dif}}. \qquad (3)$$

It follows from approximations (2) and (3) that the coefficients C_n and S_n with $n=2$, 3, 4, 6 in expansion (1) are negligible. This serves as an empirical justification for setting to zero all the C_n and S_n with $n>1$. Thus the expression for $f_{(111)}(\varphi)$ includes only Fourier harmonics with $n=1$, and $|C_1|$ and $|S_1|$ can be calculated using the experimental values of I_{c2}^{spec}, I_0^{spec}, and I_0^{dif}. The function $(f_{(111)}(\varphi))^2$ is given in Fig. 2 (see the units of measure on the right-hand axis). The onefold symmetry of the distribution function indicates the existence of an axis of symmetry in the plane of the film. This means that there is a predominant orientation of the microcrystallites, which may have been caused by the preparation procedure or by the properties of the substrate. The quantity

$$\sigma\equiv\left(1/2\pi\int_0^{2\pi}f_{(111)}^2(\varphi)d\varphi\right)^{1/2}=\sqrt{1/2(S_1^2+C_1^2)}$$

characterizes the deviation of the distribution function from uniform (isotropic). Therefore, we call σ the degree of ordering, which determines the fraction of the crystallites giving an anisotropic contribution to the second-harmonic radiation. The quantity σ defined in this way is given by the expression

$$\sigma=1/\pi\sqrt{I^s{}_0/(I_0^s+K\Omega I^{\text{dif}})}, \qquad (4)$$

where Ω is the angular aperture of the detection system, $K=2\pi\cos(\theta_0)(l_{\text{cor}}/\lambda_{2\omega})^2$, and l_{cor} is the spatial scale of the correlation function of the nonlinear sources. This last quantity can be calculated from the experimental dependence of $I_{2\omega}^{\text{dif}}$ on the polar angle θ, since the form of the scattering indicatrix of the diffuse component of the second harmonic is determined by the correlation function of the fluctuations of the nonlinear polarization induced in the film. These fluctuations are caused by two types of structural disorder: randomness in the orientation and randomness in the distribution of the crystallites in the film plane. Using a formalism analogous to that described in Ref. 13, we obtain the following expression for the scattering indicatrix.

$$I_{2\omega}^{\text{dif}}(\theta)\propto\cos^2(\theta)\left(a-c\left(\frac{2\pi}{\lambda_{2\omega}}\right)^2(\sin(\theta)-\sin(\theta_0)^2)\right), \qquad (5)$$

where a and c, which we treat as adjustable parameters, determine the correlation length: $l_{\text{cor}}=\sqrt{2c/a}$. The results of a fitting of the scattering indicatrix (for the sample with $n_{(111)}=0.92$) and the inferred dependence of the correlation length on $n_{(111)}$ are shown in Fig. 3 and 4, respectively.

In spite of the fact that we have for simplicity limited discussion to a one-component sample, the approach we have used is quite general, since expression (5) is valid for

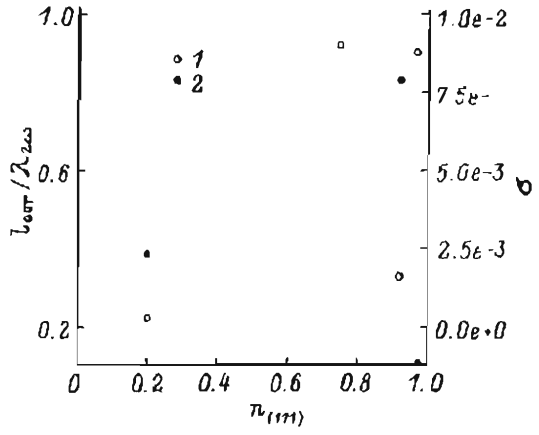

FIG. 4. Correlation length in units of the second-harmonic wavelength (left-hand scale) (1) and a measure of the ordering of the crystallites (right-hand scale) (2).

two-component films as well. This makes it possible to estimate the degree of ordering σ for the entire set of samples (Fig. 4).

In summary, joint measurements of the azimuthal rotational anisotropy and the scattering indicatrix for second-harmonic radiation yields quantitative and qualitative information about the morphological properties of films of ferroelectric ceramics, specifically, information about the correlation length of fluctuations of nonlinear sources in the film and about the lower harmonics of the distribution function over orientations in the film plane. For the films investigated here, the direction of predominant azimuthal orientation of the crystallites in the film plane coincides with the maximum of the anisotropic azimuthal dependence, and the structural ordering σ of the films does not exceed 0.01.

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