Ferroelectrics, 1997, Vol. 190, pp. 143–148
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OPTICAL SECOND HARMONIC GENERATION STUDIES OF THIN FERROELECTRIC CERAMIC FILMS

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(Received March 26 1996)

Abstract: The microscopic structure of thin PZT films with various Pb concentrations is studied by optical second-harmonic generation. From the azimuthal anisotropic dependence and scattering indicatrices of the nonlinear optical response information about the orientation distribution of microcrystallites is obtained..

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INTRODUCTION

Ceramic thin ferroelectric films are of interest for their application in nonvolatile memories, sensors and actuators, but also for their possible nonlinear optical properties. Thin films of $Pb_X(Zr_{0.53}Ti_{0.47})O_3$ (PZT) are isotropic and homogeneous as far as their linear optical properties are concerned, but they are anisotropic and inhomogeneous for nonlinear optics. The properties of these films depend strongly on their composition, homogeneity and structure and therefore require a thorough characterization of these structural aspects.

The motivation for optical Second Harmonic Generation (SHG) studies of thin ceramic ferroelectrics is two-fold: to probe their intrinsic nonlinear optical properties and to use this nonlinear optical technique to probe the symmetry and microstructure of these films. For example, it can simply be shown that in the electric dipole approximation an n-th order optical process can only be sensitive for symmetries up to (n+1) [1]. This means that in a linear optical experiment, only two-fold axes can be distinguished, whereas SHG is also sensitive for three-fold rotational symmetries. Traditionally, SHG has been frequently used to study the nonlinear optical properties of bulk - mostly single crystal - materials (including ferroelectrics [2]). More recently, the unique potential of SHG for studying the properties of very thin films (down to monolayers), surfaces and interfaces has been proven (see for review [3,4]). This is based on the high sensitivity of the nonlinear optical response to the local electronic and symmetry properties, and on the use of modern femtosecond lasers that do not destroy these thin films even within the fundamental absorption band. SHG has already been shown to be successful for the study of ferroelectric phase transitions in thin films [5], but the possibility of structural analysis has been recognised only recently [6].

SHG studies of single crystals or of random structures call for different approaches. For single crystals, the azimuthal anisotropic dependencies of the SHG intensity should be measured

for different polarization combinations, that provide the values of the second order susceptibility tensor components [7]. For random structures, SHG scattering indicatrices are important that give information about the second order susceptibility (or hyperpolarisability) tensor of a single scatterer (as Hyper-Raleigh scattering from molecules [8] or SHG from small metal particles [9]). So far, single crystals and random structures have always been studied separately. Ceramic films simultaneously possess the properties of both structures, consisting of microcrystallites with various orientations of crystallographic axes in the plane of the film with an appropriate distribution function. Therefore, the study of ceramic films requires the combination of the two approaches and thus measurements of both azimuthal anisotropic dependencies and SHG scattering indicatrices.

In this paper we present the results of experimental and theoretical studies of the structural and nonlinear optical properties of thin PZT ceramic films based on polarization, rotational anisotropic and scattering indicatrix SHG measurements. The structure of the films was varied by the preparation procedure. We will show that the nonlinear optical response consists of two parts: a specular, polarized and anisotropic part and a diffuse, depolarized and isotropic one. The former permits to study the symmetry of the second-order susceptibility tensor components of single microcrystallites and their predominant orientation, the latter to obtain the correlation length of the random SHG sources. A comparison of these two allows a measure of the orientational ordering of the microcrystals.

EXPERIMENT

In order to get films with various crystal structures we fabricated them by the sol-gel technique [10], varying the lead excess in the precursor solution relative to the stoichiometric quantity from 0 to 0.5, and then annealed them at 650°C. The lead concentration x in the film in comparison with solution is less by 5-10 % due to evaporation during annealing [11]. This gives films with column-like microcrystals with transverse size varying in the range of 100 - 1000 nm [10]. X-ray diffraction showed only microcrystallites of a perovskite phase having (111) and (100) orientation with relative concentration $n_{(111)}$ that varied as a function of the lead excess from 0.2 to 0.97. The linear optical constants as well as the thickness were determined by spectroscopic ellipsometry in the range of 200-1000 nm.

For the SHG experiments we used a fundamental radiation at 739 nm from a Ti:Sapphire laser with a pulse width of about 100 fs, repetition rate 82 MHz, average power 100 mW focused onto a spot of about 100 μ m in diameter. The angle of incidence was 45°. Both fundamental and

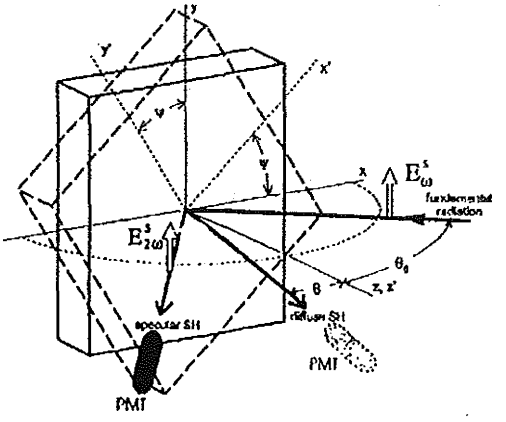

FIGURE 1. Schematic picture of the experimental configuration (shaded plane is normal to the sample surface).

SHG radiation were polarised perpendicularly to the plane of incidence (s-in, s-out). Fig. 1 gives a schematic picture of the experimental configuration.

The azimuthal SHG anisotropy $I_{2\omega}(\Psi)$ was measured in the specular direction by rotating the sample around its normal Z (XYZ is the laboratory frame, X'Y'Z' is the film frame, the azimuthal angle ψ was measured between the X and X' axes).

The SHG scattering indicatrix (SI) was measured by rotating the detection system around the vertical Y-axis. The polar angle θ is defined to be zero for the direction normal to the film surface and negative in the direction towards the incoming beam.

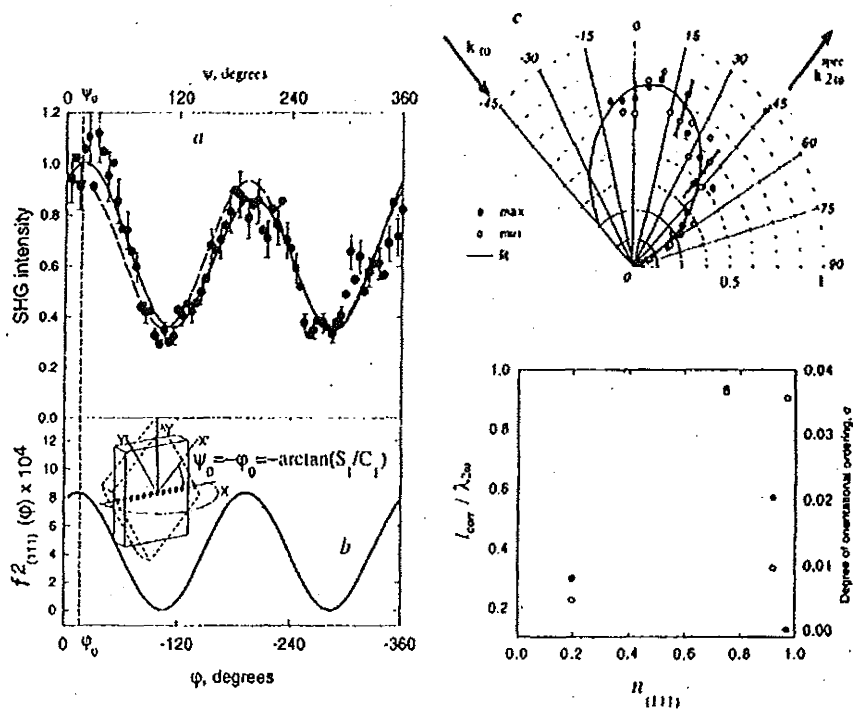

FIGURE 2. SHG measurements for PZT film with $n_{(111)}$=0.92.

a) Azimuthal SHG dependence. Points: experimental data, solid line - fit by complete Fourier transform, dashed line - fit by Fourier transform only using zero and second order terms.

b) Orientation distribution function versus azimuthal angle calculated using (1) with the following parameters: S_1=-0.007, C_1=0.028.

Insert: position of the sample drawn by dashed line corresponds to maxima of SHG intensity (at angle ψ_0). Bold dashed line on the sample shows the direction of predominant microcrystallites orientation.

c) SHG scattering indicatrices at the minimum and the maximum of the anisotropic dependence. Solid line is a fit to the experimental data

d) Correlation length in SHG wavelengths units (filled circles, left scale) and degree of ordering (hollow circles, right scale).

Fig. 2 shows as an example the SHG angular dependence $I_{2\omega}(\Psi)$ and the SHG scattering indicatrix for the sample with x=0.05 ($n_{(111)}$=0.92). In $I_{2\omega}(\Psi)$, a strong anisotropy with an approximately one-fold symmetry is added to a significant isotropic background. Such anisotropic dependences were observed for the whole set of samples, except for x=0 ($n_{(111)}$=0.97), for which $I_{2\omega}(\Psi)$ was completely isotropic.

All scattering indicatrices were measured both at the maxima and the minima of the anisotropic dependences. The SI at the maximum of the anisotropic dependence (SI_{max}) consists obviously of two parts: a sharp peak in the specular direction that is added to a very broad dependence of the SHG intensity on the polar angle. The SI in the minimum of the anisotropic dependence (SI_{min}) shows only a background that coincides with the background for SI_{max} within the error bar. It means that the diffuse part of the signal is completely isotropic with a specular component being completely anisotropic.

RESULTS AND DISCUSSION

In our theoretical analysis of the experimental data we consider the film as a statistically distributed mixture of (111)- and (100)-crystallites that homogeneously fill the film with the surface concentrations $n_{(111)}$ and $n_{(100)}$=(1 - $n_{(111)}$) respectively. The anisotropy of the linear response of the crystallites is negligibly small. Therefore, in linear optical terms the film can be treated as a uniform medium with a local and isotropic dielectric function. The retardation effects (including the optical interference in the film) at both the fundamental and SHS frequencies can be described by means of Fresnel-like local-field factors. At the same time we take into account the anisotropy of the bulk dipole quadratic response of the crystallites through the structure of their nonlinear susceptibility tensor.

The azimuthal anisotropic dependences could be analysed on the base of an orientation distribution function. The orientation of each crystallite in the plane of the film is characterized by the azimuthal angle φ relative to X' axes of the film frame. The angle φ is supposed to be a random quantity described by the distribution function $p_i(\varphi) = 1/2\pi + f_i(\varphi)$, where i=(111), (100) and $\int d\varphi f_i(\varphi) = 0$. In this paper we restrict ourselves to studying the function $f_{(111)}(\varphi)$ for the sample with $n_{(111)}$=0.92 which is considered as an one-component system for the sake of simplicity.

The periodic function $f_{(111)}(\varphi)$ can be expanded in the Fourier series:

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

In the same way both specular and diffuse components of the SHG intensity $I_{2\omega}^{spec}$ and $I_{2\omega}^{dif}$ can be expanded in Fourier series in the azimuthal angle Ψ. The Fourier coefficients of $f_{(111)}(\varphi)$ with odd and even n are related to the Fourier coefficients of $I_{2\omega}^{dif}(\Psi)$ and $I_{2\omega}^{spec}(\Psi)$, respectively, through known expressions that we omit for brevity. In particular, the experimental azimuthal dependence of the specular component can be reasonably approximated by

$$I_{2\omega}^{spec}(\Psi) = I_0^{spec} + I_{c2}^{spec}\cos(2\Psi) + I_{s2}^{spec}\sin(2\Psi), \qquad (2)$$

the coefficients C_n and S_n with odd $n \geq 3$ being negligibly small (Fig. 1). Moreover, as the diffuse SHG component is practically isotropic ($I_{2\omega}^{dif}(\Psi) = I_0^{dif}$),

we conclude that C_n and S_n with even $n \geq 2$ can also be neglected. Hence the expression for $f_{(111)}(\varphi)$ includes only Fourier harmonics with n=1 and $|C_1|$ and $|S_1|$ can be calculated with the use of the experimental values I_{c2}^{spec}, I_0^{spec} and I_0^{dif}. The function $\left(f_{(111)}(\varphi)\right)^2$ is shown in Fig. 2 b). The one-fold type of distribution function shows the presence of symmetry axes in the plane of the film. It means the presence of a predominant orientation of the microcrystallites that could be due to the preparation procedure or to substrate properties. The quantity

$$\sigma \equiv \left(1/2\pi \int_0^{2\pi} f_{(111)}^2(\varphi) d\varphi \right)^{1/2} = \sqrt{1/2\left(S_1^2 + C_1^2\right)} \tag{3}$$

characterizes the deviation of the distribution function from a uniform (isotropic) one. For this reason we call σ the degree of ordering that determines the fraction of crystallites giving the anisotropic contribution to SHG. On the other hand, we can relate σ to the observable parameters as follows:

$$\sigma = 1/\pi \sqrt{I_0^{spec} / (I_0^{spec} + K\Omega I^{dif})}, \tag{4}$$

where Ω is the angular aperture of the detection system, $K = 2\pi\cos(\theta_0)\left(l_{corr}/\lambda_{2\omega}\right)^2$. The latter can be obtained from the diffuse SHG.

The analysis of the diffuse SHG components calls for a different approach. The scattering indicatrix for the diffuse component of the SHG radiation is determined by the correlation function of the static fluctuations of the nonlinear polarization induced in the film. These fluctuations result from two types of structural disorder: random orientations and positions of the crystallites in the film plane. Using a formalism analogous to that described in [12] we obtain the following approximation for the scattering indicatrix:

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

where the adjustable fit parameters a and c express the characteristics of the correlation function of the nonlinear polarization fluctuations. The correlation length could be obtained from (5) as $l_{cor} = \sqrt{|2c/a|}$. The results for the scattering indicatrix and correlation length are shown in Fig. 2 c) (for the sample with $n_{(111)}$=0.92) and Fig. 2 d), respectively.

Though the analysis above was done for a single sample that could be considered as a one-component structure, the approach is rather general and therefore Eq. (4) is valid for any two-component system as well. That permits to estimate the degree of ordering σ for the whole set of samples in the same way. The values of σ calculated from this expression for various samples are shown in Fig. 2 d). Of course, the present set of data is too limited to draw extensive conclusions, other than stating that l_{cor} and σ do depend on the sample preparation. The important message at this stage is that it is possible to distract such parameters from thesenonlinear optical experiments. In order to reconstruct the distribution function $f_{(100)}(\varphi)$, additional experimental data (for example, azimuthal anisotropic dependences in the p-p polarization configuration) should be used.

In conclusion, combining rotational anisotropy and scattering indicatrix SHG measurements one can obtain quantitative information about the morphological properties of thin ceramic films. From the azimuthal anisotropic dependences, a predominant orientation can be obtained directly, the anisotropy of single microcrystallite being completely hidden. The anisotropy of SHG turns out to be extremely sensitive to the structural ordering of the films.

This work is supported by the Russian Foundation of Basic Research (RFFI) Grants 96-02-19533, 95-02-05893a and ISSEP 683p.

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