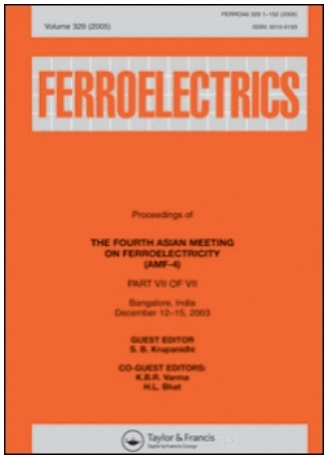

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Polar ordering in PLZT 8/65/35 studied by second harmonic generation

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Polar Ordering in PLZT 8/65/35 Studied by Second Harmonic Generation

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The second harmonic generation (SHG) of optically transparent ceramic PLZT 8/65/35 was measured in the temperature range from 10°C to 410°C. The spatial modulation of SHG intensity $I_{2\omega}$ with a period around 290 μm was observed by micro-scanning of the plane-parallel sample. During a heating run from the low temperature phase the averaged SHG intensity drops substantially at around 40°C reflecting the transformation into the relaxor phase, and a subsequent decrease occurs around 350°C (Burns temperature) indicating the transition into the high-temperature paraelectric phase, where also the spatial modulation of $I_{2\omega}$ is suppressed. The SHG intensity within the relaxor and high-temperature phases decreases linearly with the same small slope and the difference of $I_{2\omega}$ in these two phases depends on the heating rate. The results are in a good agreement with the concept of creation of polar nanoscopic clusters below the Burns temperature and transition into the nonergodic phase at low temperatures.

Keywords: SHG; PLZT 8/65/35; relaxor ceramics; polar ordering

INTRODUCTION

Measurements of second harmonic generation (SHG)[1] have been used not only for study of the breaking of inversion symmetry in macroscopic scale[2,3] (e.g. in structural phase transitions from paraelectric to ferroelectric phase) but also for detection of local dipoles in macroscopically centrosymmetric phases[4]. The asymmetric response of valence electrons to the electric field at optical frequencies responsible for the SHG signal is sensitive to the presence of a local polarization[2]. The SHG intensity was actually detected in pure cubic perovskite crystals[5,6] that indicates just either local fluctuations of polarisation or local static polarization induced by defects[4].

Lanthanum lead zirconate-titanate $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$, denoted as PLZT $100x/100y/100(1-y)$ is one of the most intensively studied ceramics with relaxor behaviour. Polycrystalline compositions PLZT x/65/35 for lanthanum content $x > 7\%$ have the cubic perovskite high-temperature

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phase and low-temperature rhombohedral phase below T_c[7,8]. Burns and Dacol[9] showed from linear optical measurements that PLZT ceramics *x*/65/35 possess local, randomly oriented and nonreversible polarization below a temperature T_d that is much higher than the phase transition temperature T_c. While T_c decreases with increasing lanthanum content *x* (e.g. T_c = 155°C for *x* = 7%, T_c = 110°C for *x* = 8% and T_c = 80°C for *x* = 9%), the temperature T_d is around 350°C independent on the lanthanum content from 7% to 9.5%. The Burns temperature T_d is very close to the temperature of phase transition in PLZT 0/65/35 and the local polarizations below T_d are expected[9] to appear in the neighbourhood of La ions with the Pb ions on the A sites (i.e. PZT 65/35 regions without La).

The temperature dependent SHG measured from -180°C to 250°C[10] revealed a sharp decrease of SHG intensity in heating run, around 30°C for PLZT 8/65/35 and around 0°C for PLZT 9/65/35. Field-induced SHG was studied in PLZT *x*/70/30[11] and in PLZT 9/65/35 at room temperature[12], but to our knowledge no detailed SHG measurements have been done in PLZT *x*/65/35 at higher temperatures around the Burns temperature. As the structure of relaxor crystals and ceramics is rather complex, also the second-harmonic signal generated by focused laser beam with the diameter of tens microns can vary with the beam position and with the temperature in a quite stochastic way[13]. This undesirable feature can be overcome using the average SHG intensities obtained by scanning the volume much bigger than the volume of focused beam.

The aim of this work is a detail study of the SHG signal in the temperature range 10°C - 400°C covering the relaxor-to-glass transition at around 40°C and in particular the Burns temperature (~ 350°C) region corresponding to the crossover from the paraelectric to relaxor behaviour. The experiment is based on the micro-scanning of the sample by the laser beam in order to obtain the average SHG intensities. The results obtained will be compared with the existing linear optical experiments and discussed within the concept of the polar microregions growing up below the Burns temperature.

EXPERIMENTAL

Samples of PLZT 8/65/35 were prepared by solid state synthesis and hot pressing. Constituent oxides were mixed together according to the formula

$$Pb_{0.92}La_{0.08}(Zr_{0.65}Ti_{0.35})_{(1-0.08\cdot4)}O_3 + 1 \text{ wt. \% PbO} \qquad (1).$$

Then the powder mixture were calcined at 850°C, cooled down, ball milled, and heated again at the same temperature. After milling the powder was cold pressed into pellets and heated in oxygen at 1200°C for 2 hours. Samples were additionally heat treated under pressure for 24 hours at 1250°C. Single phase fully dense ceramics were obtained as confirmed by XRD and optical microscopy. The number of grains per grain size is approximately constant and spreads from 2 μm to 12 μm, the average diameter of monocrystalline grains is 7 μm. Details of the processing procedure can be found elsewhere[14]. Plane-parallel samples were cut and polished to the thickness of 700 μm or wedge-shaped samples were prepared with an angle $\alpha = 6°$ and thickness varying from 2000 to 3000 μm.

The primary beam generating the double-frequency signal in the sample was launched by a pulsed Q-switched Nd-YAG laser of the following parameters: energy per pulse 0.15 mJ, pulse duration 7 ns with repetition frequency 20 Hz and wavelength $\lambda = 1064$ nm. The SHG intensity was detected by a Hamamatsu photomutiplier, the output signal was measured by a gated boxcar integrator connected with a computer. Micro-scanning of samples was provided by means of a micro-shift system with a minimum distance step of 0.1 μm controlled by a computer. The experimental set-up is shown in Fig. 1 where also scanning parameters are presented. The laser beam with the diameter of 7 mm is focused by a lense with the focus distance of 550 mm to the waist diameter of 50 μm.

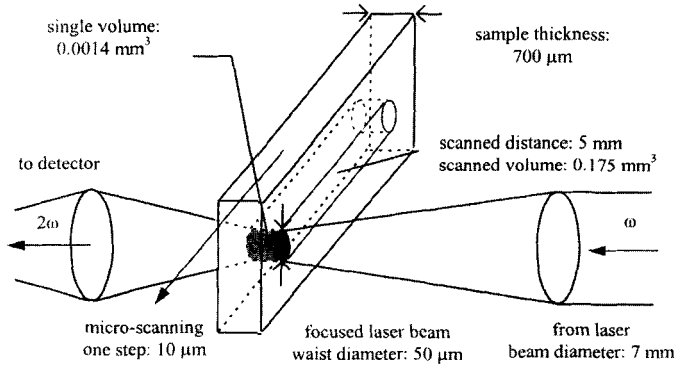

FIGURE 1. Set-up of sample micro-scanning and scanning parameters.

The plane-parallel plate sample of thickness 700 μm was scanned by the laser beam along the distance of 5 mm. This allows to collect the SHG intensity coming from the total volume of 0.175 mm^3 (125 times bigger than single volume, see Fig.1) that contains about 5 x 10^5 grains. Such averaging procedure removed unwanted irregular features of the SHG in the ceramics. Temperature measurements were performed using a non-commercial oven with temperature stabilization accuracy of 0.05°C and with controlled heating/cooling rates from 0.02°C/min to 160°C/min.

RESULTS

The micro-scanning of a plate PLZT 8/65/35 sample by the laser beam over 5 mm with single steps of 10 μm showed that the SHG intensity is not constant in space for temperatures from 10°C to 350°C, but it exhibits a space modulation with a typical period of about 290 μm. Fig. 2 shows that the observed SHG intensity modulation (SHGIM) has not regular dependence, it is significantly lowered near 350°C and disapeared around 400°C. The SHGIM behaves differently during the first heating run than during the subsequent ones. In the virgin sample the spatial Fourier transform of the scanned SHG intensity exhibits several peaks in the period range from 400 μm to 500 μm. In subsequent runs SHGIM is

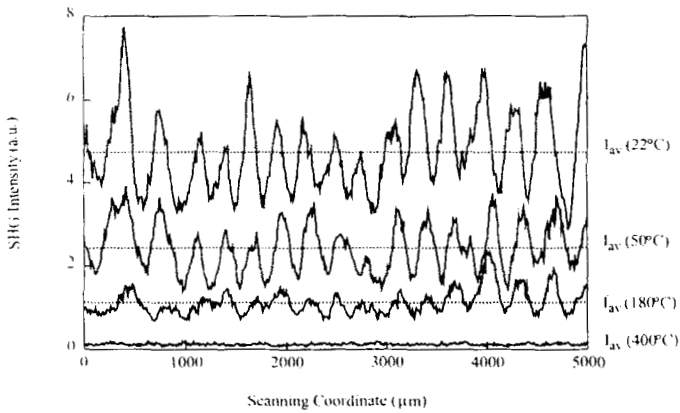

FIGURE 2. Space modualtion of SHG intensity and averaged intensity I_{av} per scanning volume in different temperatures obtained from micro-scanning of a plane-parallel PLZT 8/65/35 sample.

more regular and a single well-defined Fourier peak corresponding to the period of 290 μm was obtained. We observed SHGIM at room temperature also in a wedge-shaped PLZT 8/65/35 sample and it appeared also in a wedge-shaped PLZT 9.5/65/35 sample (for both samples, $\alpha = 6°$) at room temperature when a static electric field was applied ($E > 0.5$ kV/cm).

The temperature dependence of the averaged SHG intensity I_{av} is given in Fig. 3. I_{av} drops substantially at around 40°C and the subsequent decrease occurs below 350°C. The SHG intensity decreases with the same slope in the range 120°C - 300°C and above 350°C. Each I_{av} point corresponds to the measurement time of 10 min (the micro-scanning of the sample takes 6 min and the stabilization to a new temperature 4 min); the average heating rate was 0.5°C/min in the range 20°C - 100°C and 0.34°C/min in the range 300°C - 400°C.

Repeated heating measurements after zero-field cooling confirm a slow relaxation of SHG. The influence of different average heating rates HR in the temperature interval from 20°C to 100°C on the SHG intensity I_{av} is illustrated in Fig. 4. For heating rates HR = 0.5°C/min and 1.6°C/min I_{av} is the same at high (above 350°C) and at low (20°C) temperatures, but it differs in the relaxor phase, i.e. in the interval 100°C - 300°C. For HR = 160°C/min I_{av} does not drop around 40°C, the slope of the decrease of the SH intensity is five time higher than that for heating rates

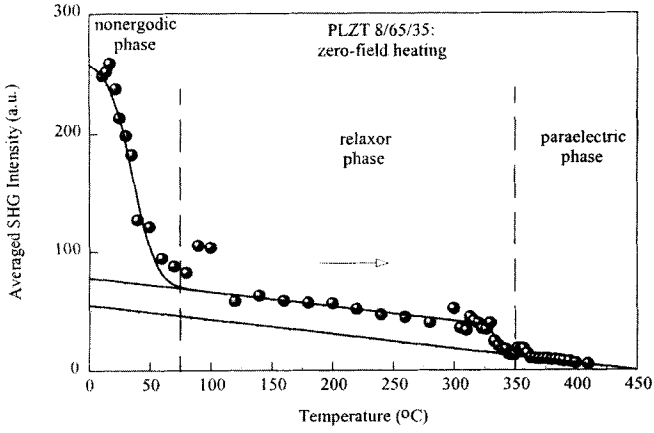

FIGURE 3. Temperature dependence of the averaged SHG intensity in PLZT 8/65/35 during zero-field heating.

0.5°C/min and 1.6°C/min. Moreover, no anomaly is observed around 350°C for HR = 160°C/min.

DISCUSSION

We discuss: (i) the origin of the temperature dependent behaviour of SHG in the cubic phase of PLZT 8/65/35 and (ii) the long-range spatial modulation of SHG intensity.

(i) In PLZT ceramics $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$, of the La^{3+} concentration $x = 0.08$, the mean nearest neighbour distance of La^{3+} ions is $d = \frac{a}{\sqrt[3]{x}} = 2.3a$, for PLZT 8/65/35[7] the lattice spacing $a = 0.409$ nm and $d \cong 0.95$ nm. Since the wavelength $\lambda_{2\omega}$ of the double-frequency wave is much longer ($\lambda_{2\omega} = 532$ nm), the sample inside the grain can be treated as homogeneous medium. On the other hand there is a distribution of grain sizes in the range 2 - 12 μm, random orientation of grains, and grain boundaries. All these features influence the resulting SHG signal and they are responsible for the observed irregular features that will be discussed elsewhere. Here we assume that the sample (disordered crystal) of cubic symmetry has randomly distributed local dipoles appearing due to the positionally disordered La^{3+} ions disturbing the lattice and giving

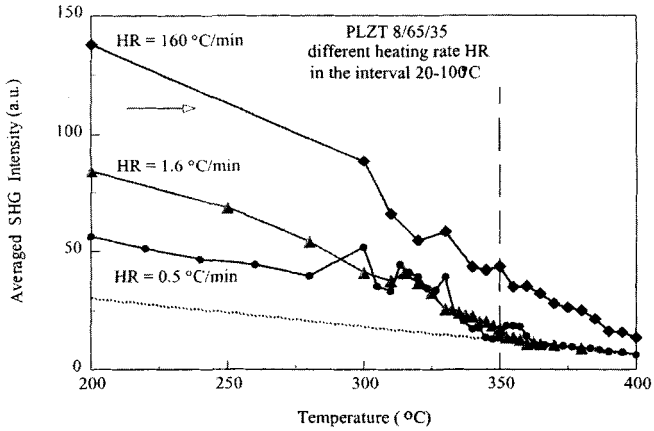

FIGURE 4. Temperature dependence of the averaged SHG intensity for different heating rates HR in the range from 20°C to 100°C.

rise to the existence of local fields. The amplitude of SHG field $E_{2\omega}$ is proportional to the second power of the single-frequency field $E_{2\omega} \propto \beta E_{\omega}^2$ (tensor notation is omitted for simplicity). The effective nonlinear coefficient β can be expressed[2,15,16] as $\beta = \gamma P$ where polarization $P = \frac{1}{V}\sum_{x} p(\mathbf{x})$ stands for the sum over existing local dipoles $p(\mathbf{x})$ in the volume V of the sample and γ is the third-order nonlinear coefficient. Although the mean value $\bar{\beta} = 0$ in the macroscopically centrosymmetric sample, the SHG intensity can still be generated due to the fluctuations of polarization[4]:

$$I_{2\omega} \propto \langle E_{2\omega}^{*} E_{2\omega} \rangle \propto \gamma^2 \langle P^{*} P \rangle E_{\omega}^2 = \gamma^2 \frac{1}{V^2} \sum_{x,x'} \langle p^{*}(\mathbf{x}) p(\mathbf{x}') \rangle E_{\omega}^2 = \gamma^2 \frac{1}{V^2} \sum_{\mathbf{X}} \langle p'(\mathbf{X})^2 \rangle E_{\omega}^2 \tag{2}$$

where $p'(\mathbf{X}) \equiv \sum_{\mathbf{x} \in v} p(\mathbf{x})$. It was assumed that the local dipoles $p(\mathbf{x})$ are correlated so that the superparaelectric clusters of volume v with the dipole moment $p'(\mathbf{X})$ are well defined. The large-scale coordinate $\mathbf{X}$ denotes the position of a superparaelectric cluster and the clusters at different positions are considered independent.

Then the increase of the SHG signal at 350°C is attributed to the growth of the fluctuations of local dipoles and creation of small polar Pb rich microregions as reminiscent of the phase transition in PZT. Below 350°C the plateau of the SHG intensity means that there are no substantial development of the clusters with decreasing temperature. Further increase of the SHG intensity occurs when approaching the freezing temperature from above. This can be interpreted within the concept (2) as the increase of the effective cluster sizes as was also proposed in [17].

(ii) Nonhomogeneous SHG signal has been reported[18] in a single crystal of $K_{0.85}Na_{0.15}TaO_3$ where variation of SHG intensity by a factor of three has been found. In the case of PLZT 8/65/35 ceramics the observed dependence of SHG intensity $I_{2\omega}(x)$ on the scanning coordinate x can be considered as almost periodic with an average period of 290 μm and with the mean ratio of maximum and minimum SHG intensity approx. 1.6.

This feature was observed both in samples of constant thickness 0.7 mm and in wedge-shaped samples with thickness varying from 2.0 mm to

3.0 mm, in the compounds PLZT 8/65/35 without bias and in PLZT 9.5/65/35 with a bias field. In all these cases no significant thickness dependence of the SHG signal was found. The observed modulation of $I_{2\omega}$ therefore should be a bulk effect, not influenced by sample surfaces. Concerning the grains influence on the discussed modulation no fine structure of the grain ordering inside the samples was observed on the scale of 300 μm. The origin of the long-range SHG modulation is still unclear and more detailed experimental studies are needed[19].

ACKNOWLEDGMENT

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