

## Second-Harmonic Generation in “Cubic” PLZT Ceramics

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**Abstract.** The temperature-dependent optical second-harmonic generation in thermally depoled La-doped lead zirconate titanate (PLZT) ceramics of composition 8/65/35 and 9/65/35 has been studied. A microscopic model for the anomalous phase transition behaviour of these compounds is suggested.

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Transparent La-doped lead zirconate titanate (PLZT) ceramics have found a variety of applications including light modulators, optical memories and display devices [1–5]. Of particular interest are materials with compositions  $x/65/35$ , where  $x$  corresponds to the atom percentage of La, and 65/35 to the zirconium to titanium ratio. The  $\text{La}^{3+}$  ions are supposed to substitute  $\text{Pb}^{2+}$  ions, where charge compensation is achieved by A-site vacancies [6]. PLZT shows a number of phases and phase transitions, which influence its macroscopic properties, being essential in device applications.

For compositions  $x/65/35$  with  $x \leq 6$ , a paraelectric to ferroelectric phase transition occurs as the temperature is lowered through the Curie point  $T_c$ , and a second structural transition occurs at a lower temperature  $T_t$  [7, 8]. For  $x \geq 7$  no paraelectric to ferroelectric transition occurs as the temperature is lowered through  $T_c$ . Instead, the material remains in the so-called  $\alpha$ -phase. In this  $\alpha$ -phase the ceramic shows a broad peak in the low frequency dielectric constant,  $\epsilon(T)$ , which reaches a maximum at  $T_c$ . At somewhat lower temperatures a sharp increase in  $\tan \delta$  was found [9]. By applying an electric field or stress below a temperature  $T_p$ , where  $T_t < T_c$  a polar  $\beta$ -phase with orthorhombic structure is induced. When removing the field the  $\beta$ -phase is stable below  $T_p$ , but it converts back to the  $\alpha$ -phase at  $T_t$  and simultaneously a premaximum in  $\epsilon(T)$  occurs, which is

absent in the cooling cycle. X-ray, electrical and optical investigations showed that the  $\alpha$ -phase has cubic perovskite structure and is optically isotropic even in subgrain dimensions. In the absence of an external field there is no evidence for an  $\alpha$ - $\beta$  transition on cooling. On the basis of the most recent results, the “transition” at  $T_c$  was interpreted to be a cubic to cubic one, involving a decrease in unit cell size with increasing temperature [10].

In this paper we report on temperature-dependent optical second-harmonic generation (SHG) in thermally depoled samples, mainly of compositions 8/65/35 and 9/65/35. These ceramics are in the cubic  $\alpha$ -phase. SHG in PLZT 8/65/35 was already mentioned by Michel and Sicignano [11]. These authors interpreted their experiments, which were apparently performed at room temperature, by incomplete thermal depoling of the sample and by internal strain.

### 1. Experiment

The measurements of the second harmonic intensity as function of temperature were performed by using the experimental setup shown in Fig. 1. The light of a Q-switched  $\text{Nd}^{3+}$ -YAG-Laser ( $\omega_L \approx 1.064 \mu\text{m}$ ; repetition rate  $\approx 1 \text{ KHz}$ ; pulse length  $\approx 300 \text{ ns}$ ; peak power  $\approx 5 \text{ kW}$ ) served as fundamental beam. The sample

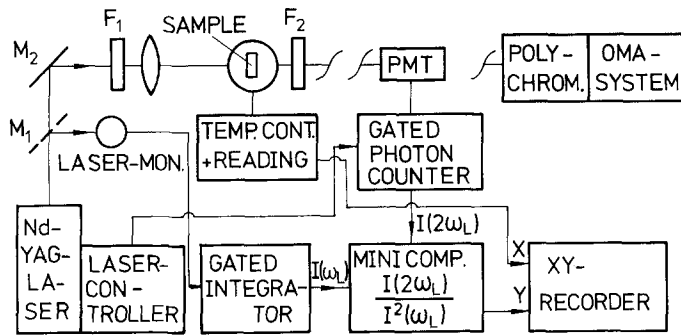


Fig. 1. Experimental setup for measuring the temperature dependence of the second harmonic intensity in PLZT. F1: edge filter RG 830 (Schott), F2: IR-blocking filter BG 18 (Schott). For the PMT system a 532 nm bandpass interference filter was added

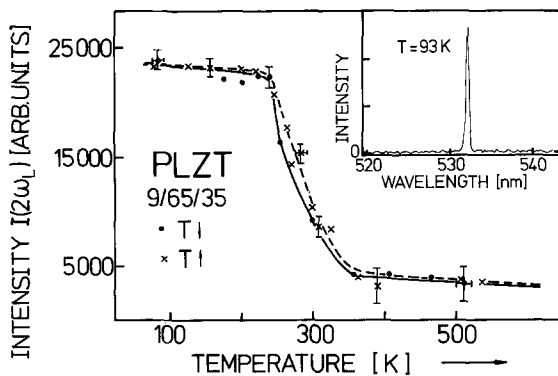


Fig. 2. Intensity of second harmonic for PLZT 9/65/35 as function of temperature. The measurements were performed with the OMA. ● decreasing temperature; × increasing temperature. Full and dashed lines are guides for the eyes. The inset shows a typical spectrum; the background is already subtracted

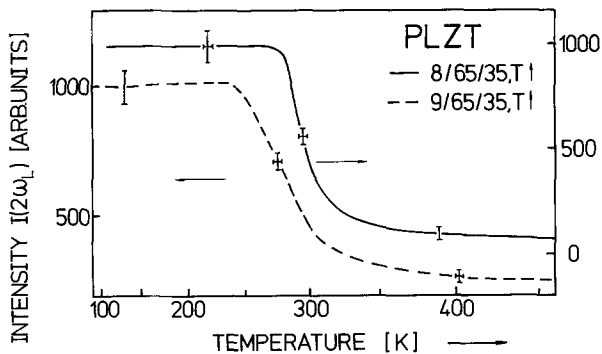


Fig. 3. Intensity of second harmonic for PLZT 8/65/35 and 9/65/35 as a function of temperature. The measurements were performed by using the photon counting system. The arbitrary units on left and right scale are not the same. In both measurements the temperature was increasing. The signal is divided by the square of the laser intensity,  $I^2(\omega_L)$ . The error bars give typical values in the respective regions of the measured curves

was mounted in a cryostat or an oven which allowed a temperature variation from 90 K up to 600 K. For detecting the SHG signal, an optical multichannel analyzer (PAR OMA II) and alternatively photon counting techniques were used: The vidicon of the

OMA was cooled to dry ice temperature and the signal was integrated over 200 s. The thermal background from the photocathode was subtracted from the spectrum centered  $\pm 10$  nm around  $2\omega_L$ . The photon counting system included an S11 photomultiplier tube and a gated dual channel photon counter. Using a minicomputer, the signal was corrected by normalizing it to the square of the laser intensity,  $I^2(\omega_L)$ . To avoid sample heating, only 5% of the laser intensity was used.

The samples used in the experiments were prepared by Härdtl from materials with compositions  $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ . The standard sintering process was followed by an isostatic hot-pressing procedure [6, 9]. This technique yields an average grain size of about 3–4  $\mu\text{m}$  and a residual porosity of  $\leq 10^{-3}$ .

## 2. Results

The temperature dependence of the second-harmonic intensity for PLZT 9/65/35 is shown in Fig. 2. The data were taken point by point by integrating the spectrum obtained with the OMA (net integral over SHG line). The inset shows such a typical low temperature spectrum. Between 90 K and 230 K the SHG is constant, and sharply decreases above this temperature to about 15% of its original value. Above 350 K the signal again stays constant or slightly decreases further up to the highest temperature measured, 600 K. On cooling, the original intensity is regained. No changes occur when cycling the sample for several times.

The hysteresis, if present, is within the accuracy of measurements. Figure 3 shows the results obtained with the photon counting system. The heating rate was about 2 K/min. The only difference from the data in Fig. 2 is the somewhat higher background level. This might be due to luminescence of the sample, which is subtracted by suitable integration when using the OMA. Figure 3 also shows the results for PLZT 8/65/35. The overall curvature is similar to that for the 9/65/35 sample. The decrease in intensity occurs in a smaller temperature range, and the whole curve has

shifted to somewhat higher temperatures. The temperature difference of the inflection points is about 10–15 K. The background level is less than 10% of the low temperature intensity.

For PLZT 9/65/35, samples with different thickness ( $d_1=0.2$  cm and  $d_2=0.025$  cm) were measured under the same conditions. The ratio for the change in signal between low and high temperatures was found to be  $I(2\omega_L, d_1)/I(2\omega_L, d_2) \approx 2.9$ . Theoretically, we expect for the intensity of the second harmonic under non-phase matching conditions

$$I(2\omega_L, x) \propto (\alpha_2 - 2\alpha_1)^{-1} I^2(\omega_L, 0) \cdot [\exp(-2\alpha_1 x) - \exp(-\alpha_2 x)], \quad (1)$$

where  $\alpha_1$  and  $\alpha_2$  are the absorption coefficients of the material at the laser and second harmonic frequency, respectively. For PLZT 9/65/35 absorption measurements did yield  $\alpha_1(1064 \text{ nm}) \approx 2.70 \text{ cm}^{-1}$  and  $\alpha_2(532 \text{ nm}) \approx 4.15 \text{ cm}^{-1}$ . Together with (1) we then obtain theoretically  $I(2\omega_L, d_1)/I(2\omega_L, d_2) = 3.4$ .

This value is in fairly good agreement with the experimental result. We therefore believe that the observed generation of the second harmonic is a bulk effect.

### 3. Discussion

The nonlinear (second-harmonic) polarization is given by

$$P_i(2\omega_L) = d_{ijk} E_j(\omega_L) E_k(\omega_L), \quad (2)$$

where  $d$  is a third-rank polar tensor which vanishes for any system with a center of inversion. Terms involving higher than third rank tensors (e.g. gradient and quadrupole terms) are neglected. Since

$$d_{ijk} \propto \sum_l \langle u_l \rangle \quad (3)$$

the temperature-or electric field – dependence of the SHG-coefficients in piezoelectric crystals yields detailed information concerning small displacements,  $u_i$ , of single ions [12–14]. In spite of the fact that the solid solution PLZT can not really have inversion symmetry, our measurements show that the SHG is small or even vanishes at higher temperatures. On the other hand, the intensity of the second harmonic observed at lower temperatures, clearly shows that in PLZT 8/65/35 and 9/65/35 the  $\alpha$ -phase is microscopically non-cubic – at least in the low temperature range. The “inversion” symmetry in paraelectric PLZT ( $x > 7$ ) may be relaxed by local displacements of ions which are not at ideal lattice positions. With decreasing temperature this local disorder increases until a saturation is reached, which reflects the constant intensity of the second harmonic.

Although the origin of the local disorder is unclear, we can tentatively explain it by the  $\text{La}^{3+}$  ions: The  $\text{La}^{3+}$  ions have an ionic radius which is about 4% smaller compared to the  $\text{Pb}^{2+}$  ions. Therefore, the  $\text{La}^{3+}$  ions might not sit at ideal lattice positions, but moved off-center as, e.g., Li or Na ions in  $\text{KTaO}_3$  [15]. Among the off-center positions, only the (100) and equivalent directions are compatible with the orthorhombic structure of the field induced  $\beta$ -phase.

On the basis of this model the experimental results can be interpreted in the following way: The  $\text{La}^{3+}$  ion sits in a 6-fold configurational degenerate potential. For further discussion, this potential will be simplified by a double-well potential. Because no cooperative ordering takes place, an interaction of single  $\text{La}^{3+}$  oscillators will be neglected. In this case the single particle Hamiltonian can be written in the form

$$H = \frac{p^2}{2m} + \frac{A}{2} u^2 + \frac{B}{4} u^4, \quad (4)$$

where  $A < 0$ . At “high” temperatures  $\langle u \rangle = 0$ . Therefore, according to (3) no SHG is observed. At somewhat lower temperatures the curvature of the “effective” potential decreases and the dielectric constant increases to the maximum at  $T_c$ . When lowering the temperature further,  $\langle u \rangle$  becomes different from zero, i.e. local disordering begins; this is observed in the increase in second-harmonic signal, the increase in  $\tan \delta$ , and the decrease in  $\epsilon(T)$ . At “low” temperatures the local order parameter becomes  $\langle u \rangle \approx (-A/B)^{1/2}$ . As a consequence, the intensity of the second harmonic stays constant. Due to the absence of any interaction between single oscillators, the  $\text{La}^{3+}$  ions are randomly distributed among the 6 potential minima. Because this local disorder is random and occurs in regions small compared to the wavelength of light, the material is “cubic” for X-rays, and does not show any birefringence, as verified in earlier experiments [8, 9]. The temperature shift of the inflection point in the SHG signal, which is about 10–15 K (see Fig. 3) directly reflects the shift in “transition” temperature  $T_c$  (for PLZT 9/65/35  $T_c \approx 363$  K, and for 8/65/35  $T_c \approx 371$  K).

By applying an electric field or mechanical stress to the ceramic, the 6-fold configurational degeneracy of the potential is lifted. The  $\text{La}^{3+}$  ions order cooperatively along (100) or one of the equivalent directions. The  $\beta$ -phase with a macroscopic polarization is induced. The fact that the  $\beta$ -phase has orthorhombic rather than tetragonal structure may be explained by the asymmetry produced by Ti and Zr ions, respectively. Actually, the deviation of the orthorhombic structure from a tetragonal structure is small; for PLZT 8/65/35 one finds  $a = 5.777$ ,  $b = 5.794$ , and  $c = 4.074$  [8].

Up to this point we have not yet taken into account the A-site vacancies, which are simultaneously produced in the La-doped samples. If these vacancies are statistically distributed, we find from [Ref. 16, Eq. (31)] that about 21% of the  $\text{La}^{3+}$  ions have a neighboring A-site vacancy. If the vacancies are not independent from the  $\text{La}^{3+}$  ions, nearly every La ion can have a neighboring A-site vacancy. This might favour a relaxation of the  $\text{La}^{3+}$  ion towards the vacancy, or in the perpendicular plane. The latter argument is based on the assumption that the 12 oxygen ions neighboring a vacancy relax towards it. The relaxation of the oxygen ions towards the A-site vacancy may also explain why highly La-doped PLZT ( $x > 7$ ) does not, in contrast to  $\text{PbTi}_{1-y}\text{Zr}_y\text{O}_3$  (PZT), exhibit a paraelectric to ferroelectric phase transition as the temperature is lowered through  $T_c$ . Due to the relaxation of oxygen ions towards A-site vacancies, the  $(d_s/p_\pi)$  hybridization between oxygen  $2p$  and  $\text{Ti}3d/\text{Zr}4d$  orbitals decreases. As discussed in [17], this  $(d_s/p_\pi)$ -hybridization, however, determines the paraelectric to ferroelectric transition in these materials.

### Conclusion

In summary, we can say that on the basis of the La off-center model, the SHG, dielectric, optical and X-ray results can be interpreted. In this model the anomalous phase transition behaviour observed in highly La-doped PLZT ( $x > 7$ ) is of different origin than the "normal" ferroelectricity in "conventional" compo-

sitions ( $x < 7$ ). This normal ferroelectricity has its origin in the relative displacements of Ti/Zr ions and oxygen ions. Both mechanisms, however, are related via the A-site vacancies which may induce a relaxation of the oxygen ions. This relaxation of the oxygen ions may be responsible for the fact that highly doped PLZT does not exhibit a "normal" paraelectric to ferroelectric phase transition as the temperature is lowered through  $T_c$ .

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