

INFLUENCE OF OXIDIZING TREATMENTS ON THE PHOTOREFRACTIVE PROPERTIES OF FERROELECTRIC LEAD GERMANATE CRYSTALS

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The influence of oxidizing treatments on the photorefractive properties of nominally pure ferroelectric lead germanate crystals is investigated. In two-wave mixing experiments the dark conductivity, the intensity dependence of the photoconductivity, the effective charge density and the factors that reduce the space-charge field are determined. Oxidizing treatments increase the photoconductivity and the effective charge density, but decrease the electron-hole-competition factor. The experimental results can be explained in terms of a one-center model with electron-hole competition.

Keywords: photorefractive properties; lead germanate; nonlinear optics

1. INTRODUCTION

Photorefractive materials have attracted much interest for many potential applications, such as reversible optical data storage and signal processing. Nonuniform illumination of the materials leads to spatially modulated refractive index gratings via the electro-optic effect and such gratings can remain for a definite time after the recording beams are switched off. Ferroelectric lead germanate crystals $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (PGO) are photorefractive materials with fairly large linear electro-optic coefficients: $r_{33} = 15.3$ pm/V and $r_{13} = 10.5$ pm/V [1]. Holographic gratings can be formed within one second with a recording light intensity of about 1 kW/m^2 . The photorefractive properties of PGO crystals have been discovered in [2]. Detailed investigations of nominally pure crystals, of crystals

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doped with Fe or Rh and of $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ solid solutions were performed by Yue *et al.* [3]. Here electron-hole competition is suggested to be the main factor to limit the amplitude of the light-induced space-charge fields.

Doping of transition-metal ions is the usual way to improve the photorefractive properties. In this way the effective charge density can be increased. But in [3] no evidence has been found that the effective charge densities are increased in doped PGO or in $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ samples. Therefore, the charges responsible for the photorefractive effects in these crystals probably originate from intrinsic defects.

In order to check the above statement and to find a way to enhance photorefractive effects, we anneal nominally pure crystals in an oxygen atmosphere. The influence of these oxidizing treatments on the photorefractive properties is studied and light-induced charge transport properties involved in the photorefractive process are discussed.

2. SAMPLES AND ANNEALING TREATMENTS

Nominally pure PGO crystals melt congruently and can be grown using a standard Czochralski equipment. Crystallization takes place at 738°C . At the Curie temperature $T_c = 178^\circ\text{C}$ the crystals undergo a second-order phase transition from the paraelectric phase (point group $\bar{6}$) to the ferroelectric phase (point group 3). At room temperature their relative permittivity is $\epsilon_{33} = 39.5$ (low frequency value) and refractive indices are $n_e = 2.197$ and $n_o = 2.160$ at $\lambda = 515$ nm [4]. Two samples used in our experiments are grown in the crystal growth laboratory of the University of Osnabrück. One of them is cut into two pieces, denoted by A_1 and A_2 , with the same dimensions of $3.5 \times 3.2 \times 3.2$ mm³ ($a \times b \times c$). Three pieces cut from the second sample are denoted by B_1 , B_2 and B_3 , with the dimensions of $3.8 \times 2.3 \times 3.0$ mm³.

As the experimentally investigated samples are grown in argon atmosphere, we oxidize them in order to change their photorefractive properties. Oxidizing treatments are performed with an arrangement described in detail in [5]. The samples are put in a tube which can be floated with oxygen under a partial pressure of about 1 bar. They are at first heated to the desired temperature at a rate of $1^\circ\text{C}/\text{min}$, and then annealing treatments are carried out for a certain time. Afterwards the samples are cooled down slowly to room temperature. The following treatments are performed: A_2 is oxidized at 400°C (denoted as Ox.400) at first, then at 500°C (Ox.500) and at 700°C (Ox.700), respectively. Each of the above treatments takes 24 hours. After the oxidation at 700°C (near the crystallization

temperature) the sample was damaged. B₂ and B₃ are oxidized at 600°C (Ox.600) for 16 hours and at 680°C (Ox.680) for 12 hours, respectively. A₁ and B₁ are left in the as-grown state (AG).

After each treatment the crystals have to be poled again. They are first heated to a temperature slightly above $T_c = 178^\circ\text{C}$ and then slowly cooled down to room temperature under an external electric field of about 0.25 kV/cm.

3. EXPERIMENTAL METHODS AND EVALUATION

Optical absorption spectra of the annealed and the as-grown crystals are measured with extraordinarily polarized light in the wavelength range 400 – 800 nm with a CARY-17D spectrometer. We calculate the bulk absorption coefficients α_e by taking into account the reflections at the surfaces of the samples.

Measurements of light-induced absorption changes are performed as follows. The crystals are illuminated with an Ar⁺ laser beam ($\lambda = 515$ nm) as a pump beam, and additionally with the probe light of a He-Ne laser ($\lambda = 633$ nm). Intensities of the transmitted probe light with the pump beam off and on are determined, respectively.

Holographic experiments are carried out utilizing a conventional two-beam interference arrangement. The 515 nm line of the Ar⁺ laser is split into two extraordinarily polarized beams which are at first expanded and then used to symmetrically record transmission holograms with grating vectors parallel to the *c*-axis of the crystals. The evolution of the grating is monitored by a weak, ordinarily polarized beam of a He-Ne laser incident under the Bragg angle. The diffraction efficiency η is defined as

$$\eta = \frac{I_d}{I_t + I_d}, \quad (1)$$

where I_d and I_t are the intensities of the diffracted and transmitted beam, respectively. The intensities are measured with a digital storage oscilloscope using photodetectors and amplifiers. Once the gratings are written we block the recording beams and erase the grating with an additional ordinarily polarized expanded beam of the Ar⁺ laser. With different glass filters as attenuators we record the time dependence of the diffraction efficiency for different intensities of the erasure beam. We assume that the time evolution of the gratings is monoexponential. We determine the time constant τ , the dark conductivity σ_d , the photoconductivity σ_p , the specific photoconductivity κ , and the sublinearity coefficient x of photoconductivity using the relations

$$\tau^{-1} = \frac{\sigma_d + \sigma_p}{\epsilon_0 \epsilon}, \quad \sigma_p = \kappa I^x, \quad (2)$$

where ϵ_0 and ϵ are the dielectric permittivity in vacuum and the relative permittivity.

Using the same experimental setup, we record holographic phase gratings and measure the logarithmic gain coefficient at steady state, defined as

$$\Gamma = \frac{1}{l_{\text{eff}}} \ln \left(\frac{I'_1 I_2}{I_1 I'_2} \right). \quad (3)$$

Here I_1 and I_2 are the transmitted signal and pump beam intensities without coupling, I'_1 and I'_2 are the corresponding values with coupling and l_{eff} is the effective interaction length, $l_{\text{eff}} = l (1 - \pi l \sin \theta_e / 4nD)$ [6], with the thickness l of the crystal, the (half) incident angle θ_e (in air), the refractive index n and the diameter D of the incident light beam. If we consider the influence of the dark conductivity, the space-charge field is reduced by the factor $\chi = 1/(1 + \sigma_d/\sigma_p)$. The electron-hole-competition factor ξ is supposed to be another important factor reducing the space-charge field. It is defined as

$$\xi = \frac{\sigma_e - \sigma_h}{\sigma_e + \sigma_h}, \quad (4)$$

with $\sigma_e \propto (N_D - N_D^+)/N_D^+$ and $\sigma_h \propto N_D^+/(N_D - N_D^+)$ [5,7–9], where $N_D - N_D^+$ and N_D^+ are the densities of filled and empty traps. The dependence of the gain coefficient on the grating spacing Λ is utilized to determine the product of the effective electro-optic coefficient r_{eff} and the reducing factor of the space-charge field C as well as the effective trap density N_{eff} by a fit to the experimental results according to

$$\Gamma = \frac{4\pi^2 n^3 (C r_{\text{eff}}) k_B T}{\lambda \Lambda e \cos \theta_{\text{in}} [1 + (2\pi l_s / \Lambda)^2]}. \quad (5)$$

Here $k_B T$ is the thermal energy, e the elementary charge, θ_{in} the crossing half-angle of the incident waves inside the sample and $l_s = (\epsilon \epsilon_0 k_B T / e^2 N_{\text{eff}})^{1/2}$ is the Debye screening length [6].

4. EXPERIMENTAL RESULTS

The absorption coefficients α_e as a function of wavelength are shown in Figure 1 for the samples B₁, B₂ and B₃. Oxidizing treatments lead to an increase of the absorption in the investigated range. These changes of the absorption coefficients are more pronounced in the shorter wavelength range. The influence of oxidation

on sample A at 500°C is similar to that on B, only a treatment at 400°C does not change the absorption spectrum. The values α_e for all tested crystals at $\lambda = 515$ nm are listed in Table I. We do not observe any absorption changes for pump intensities up to 30 kW/m².

TABLE I Measured parameters of oxidized and as-grown PGO crystals. Here α_e is the bulk absorption coefficient of extraordinarily polarized light, σ_d the dark conductivity, κ the specific photoconductivity, x the sublinearity coefficient of photoconductivity, Cr_{eff} the product of the effective electro-optic coefficient r_{eff} and the reducing factor of the space-charge field C , N_{eff} the effective trap density, and ξ the electron-hole-competition factor

	$A_2(\text{Ox.500})$	$A_1(\text{AG})$	$B_3(\text{Ox.680})$	$B_2(\text{Ox.600})$	$B_1(\text{AG})$
$\alpha_e(\lambda=515 \text{ nm}), \text{m}^{-1}$	1.7×10^2	7.5×10^1	1.9×10^1	2.4×10^2	1.1×10^2
$\sigma_d, 10^{-9}(\Omega\text{m})^{-1}$	1.03	1.04	1.17	1.22	1.32
$\kappa, 10^{-13}(\Omega\text{m})^{-1}/(\text{Wm}^{-2})^x$	232	19.2	28.7	16.0	3.40
x	0.51	0.70	0.66	0.70	0.85
$Cr_{\text{eff}}, \text{pm/V}$	2.8	4.3	4.2	3.9	3.9
$N_{\text{eff}}, 10^{21}/\text{m}^3$	38	17	8.3	14	7.1
$\xi (\Lambda=1.3 \mu\text{m})$	0.26	0.50	0.53	0.56	0.66
$\alpha_e/N_{\text{eff}}, 10^{-21} \text{ m}^2$	4.4	4.5	23	18	15

Holographic gratings with a period of $\Lambda = 1.3 \mu\text{m}$ are recorded to saturation with the intensities $I_1 = 1.8 \text{ kW/m}^2$ and $I_2 = 1.0 \text{ kW/m}^2$. Then optical erasure experiments are performed with intensities up to 40 kW/m². In our cases the time evolution of the refractive index change is found to be monoexponential and a single time constant can be determined. Figure 2 shows the dependences of the inverse time constant on the intensity of the erasure beam for the crystals B_1 , B_2 and B_3 . The fitting parameters σ_d , κ and x according to the Eqs. (2) are presented in Table I for all crystals. Oxidizing treatments practically do not change the dark conductivity, but obviously change the specific photoconductivity and the sublinearity coefficient x .

With the same recording intensities as in the above experiments, we measure the gain coefficient of two-wave mixing as a function of grating period. The experimental results and the fitted curves according to Eq. (5) are shown in Figure 3 for the samples A_1 and A_2 (Ox.500). The fit parameters Cr_{eff} and N_{eff} of each tested crystal are also listed in Table I. After the oxidizing treatment the maximum of the gain coefficient shifts apparently to shorter grating period, i.e., the Debye screening length becomes smaller and the limiting space-charge field becomes larger. We also deduce the electron-hole-competition factor by consid-

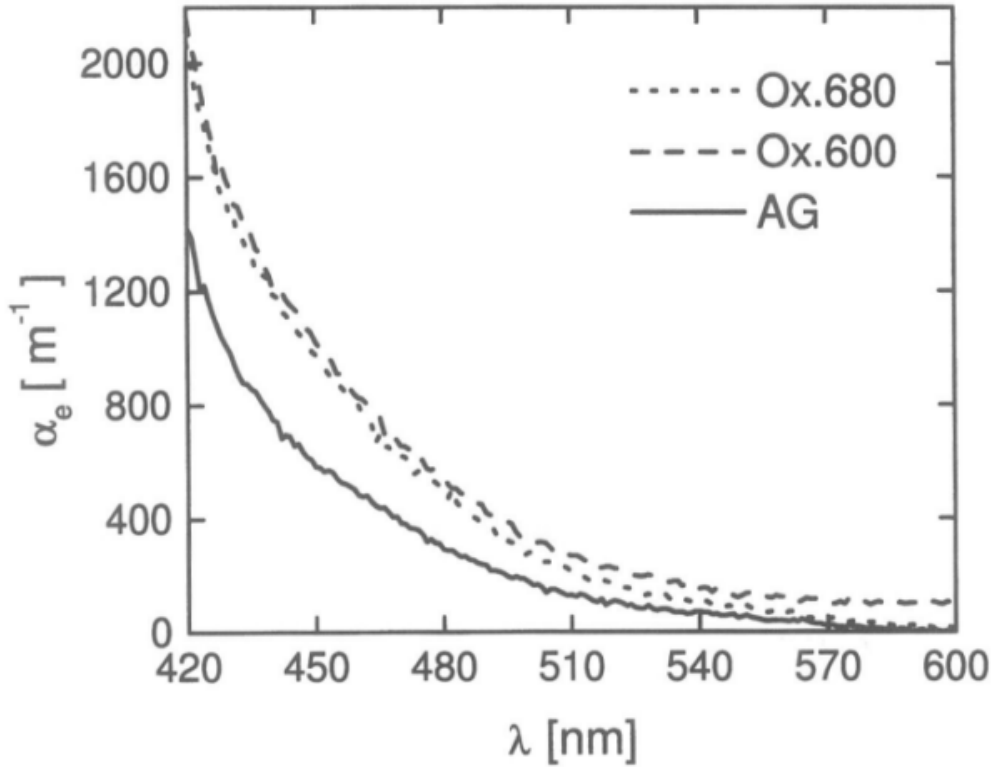


FIGURE 1 Optical absorption coefficients α_e of the crystals B_1 , B_2 and B_3 for extraordinary polarization versus light wavelength λ : AG, Ox.600 and Ox.680 denote the as-grown state and oxidations at 600 and 680°C, respectively

ering $r_{\text{eff}} \approx r_{33}$ due to the experimental configuration and taking into account the factors χ of the corresponding crystals for an intensity of 2.8 kW/m^2 . The values for all samples at $\Lambda = 1.3 \mu\text{m}$ are again listed in Table I. The competition coefficients are decreased by oxidation.

We estimate that the relative measuring errors of our experimental results are limited within $\pm 20\%$.

5. DISCUSSION

The measured data listed in Table I show that oxidizing treatments obviously change optical and photorefractive properties of undoped PGO crystals.

The absorption coefficients α_e for the treated and as-grown crystals cut from the same boule are proportional to their effective charge densities N_{eff} (see Table I). This linear relation gives first hints that the optical absorption indeed leads to the excitement of charge carriers at the photorefractive centers. Because

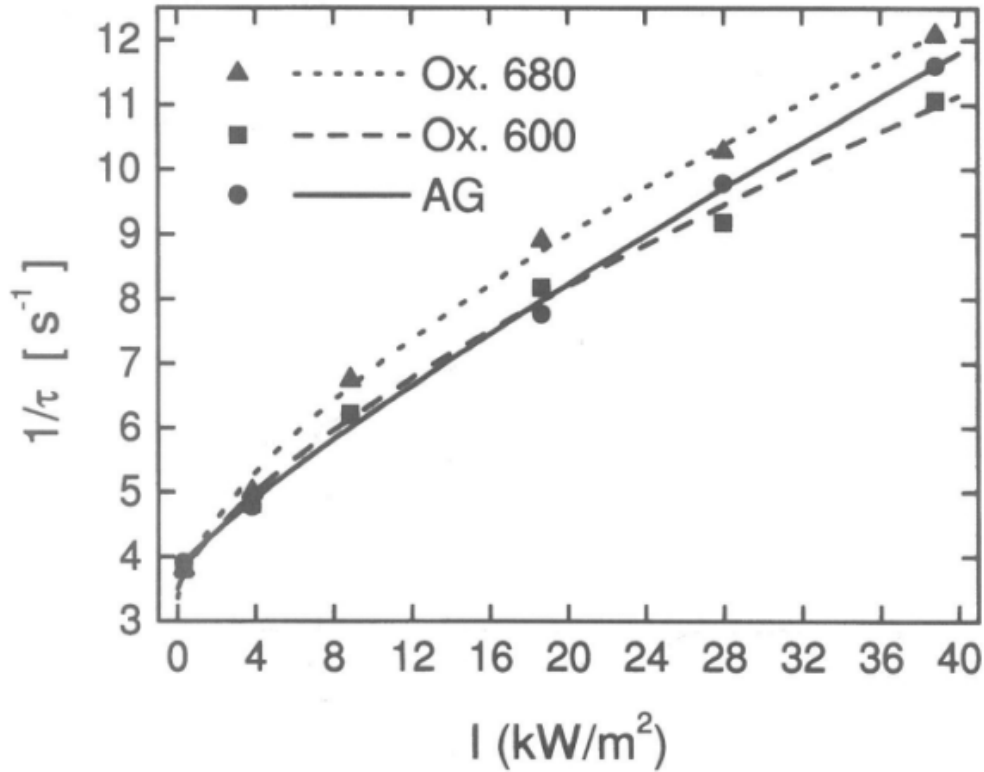


FIGURE 2 Inverse decay time constant τ^{-1} of the crystals B_1 , B_2 and B_3 as a function of erasure beam intensity I . The symbols correspond to measured data and the lines are fits according to the Eqs. (2)

light-induced absorption changes are never found experimentally, we explain our results in terms of a one-center model with electron-hole competition, and not in terms of a two-level model [10,11]. The one-center model assumes one type of photorefractive centers with photoionization of electrons (holes) from filled (empty) traps and recombination at empty (filled) traps. After the oxidizing treatments of the PGO crystals the effective charge densities ($N_{\text{eff}} = N_D^+(N_D - N_D^+)/N_D$) can be increased by a factor of two compared to that of the as-grown ones. This can be understood if we assume $N_D^+ \leq N_D - N_D^+$. Oxidation leads to an increase of the density N_D^+ of the empty traps, and to a decrease of the density $N_D - N_D^+$ of the filled traps, just like in the case of potassium tantalate-niobate [5]. Under these assumptions the decrease of the electron-hole-competition factor after oxidation can also be interpreted (Eq. (4)).

In terms of a one-center model the sublinearity coefficient x of photoconductivity may be explained by limitations of the space charges. This coefficient changes after the annealing treatment, too. A similar influence of oxidation on

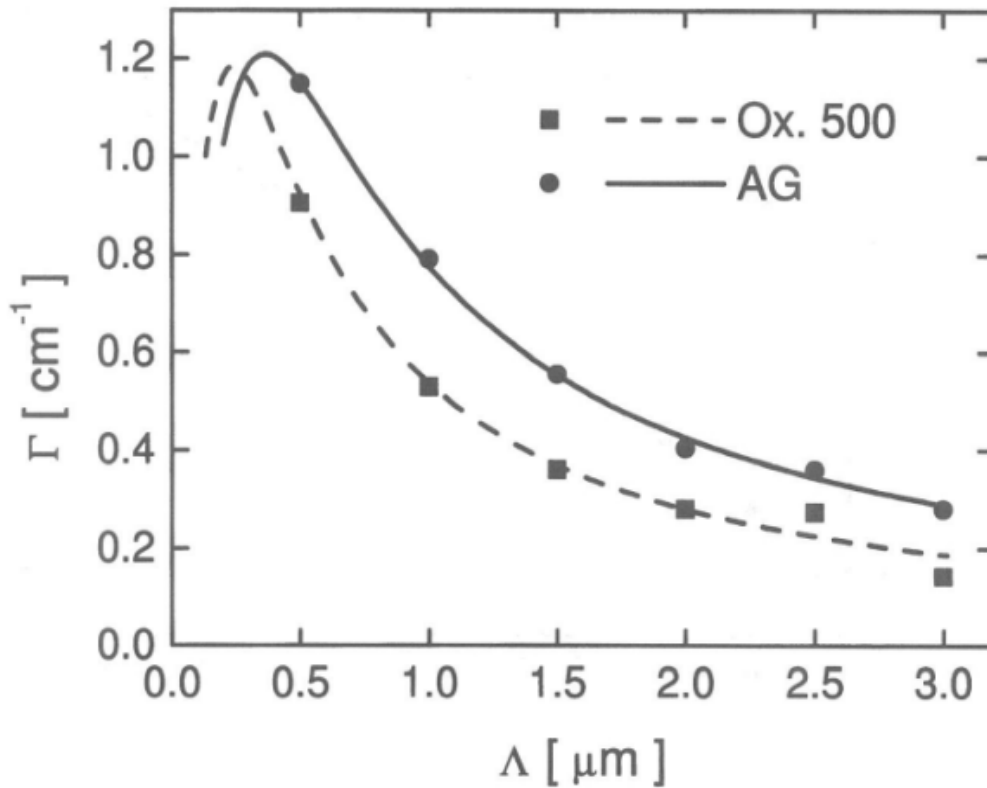


FIGURE 3 Gain coefficient Γ for A_1 and A_2 as a function of grating spacing Λ . The symbols correspond to measured data and the lines are fits according to the Eq. (5)

photoconductivity was observed for BaTiO_3 crystals [8]. At present, no explanation for this decrease after oxidation can be given.

Although A and B are nominally pure crystals, the measured photorefractive parameters are different. This is plausible because the charges responsible for photorefractive effects originate most probably from intrinsic defects. It is the difference of the effective charge densities in A and B that leads to the difference of the photorefractive properties.

6. CONCLUSIONS

Oxidizing treatments affect the photorefractive parameters of lead germanate crystals and may positively change the photorefractive properties by increasing the effective charge density and the photoconductivity. The one-center model with electron-hole competition can be used to explain the experimental results.

The charge carriers responsible for the photorefractive effects originate most probably from intrinsic defects.

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