Photorefractive effect in $Cd_{13}P_4S_{22}I_2$

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The mechanism of the photorefractive effect in $Cd_{13}P_4S_{22}I_2$ (CPSI) has been investigated with holographic methods. Our experimental results reveal that the photorefractive properties of CPSI do not originate from the electro-optic effect but from a different type of mechanism, probably a light-induced ionic transport process.

I. INTRODUCTION

$Cd_{13}P_4S_{22}I_2$ (CPSI) was recently discovered to be a very efficient holographic recording material[1] with a remarkable photoinduced change of the refractive index of more than 1×10^{-4} at room temperature. This photorefractive effect is reversible, i.e., the photoinduced refractive index pattern can be erased by homogeneous illumination without apparent fatigue. Thus the holographic recording properties of CPSI crystals are comparable with those of the most efficient oxide crystals known today, namely, $LiNbO_3$, where the high refractive index changes arise from its large photovoltaic effect, and KTN which profits from its large electro-optic coefficients. The observation of large photoinduced refractive index changes of CPSI is also astonishing because no attempts to improve the crystal quality or to optimize the crystals by suitable doping were made. The potential for further optimization is thus far from being exhausted. The important question of the mechanism of the photorefractive effect in CPSI is answered in this paper by considering experimental results on photorefraction and on electrical conductivity in these crystals.

II. EXPERIMENTAL AND DISCUSSION

Several platelets of CPSI were grown by vapor transport and used in the experiments as grown.[1] We obtained only the cubic modification of point symmetry $\overline{4}3m$ exhibiting characteristic (111) faces.[2]

To check the symmetry and orientation of the platelets, optical second harmonic generation (SHG) measurements were used. In the SHG experiment the incoming beam ($\lambda = 1064$ nm) hits the CPSI sample perpendicularly to the assumed (111) plane. The polarization γ of the incoming light is varied within this (111) plane of the crystal as sketched in Fig. 1. The second harmonic light ($\lambda = 532$ nm) is measured behind the crystal as a func-

tion of γ. The polar diagram in Fig. 1 shows an example for a measurement with fixed analyzer position.

A careful analysis of the generated second harmonic light reveals that its intensity does not depend on the incident polarization γ whereas its polarization angle is a characteristic function of γ. The behavior is exactly that which theoretical considerations predict for a crystal with point symmetry $\overline{4}3m$ in (111) orientation (the corresponding theoretical result for the example in Fig. 1 is plotted as dashed line). Thus the SHG measurements prove that the samples perfectly exhibit the assumed symmetry and orientation, and, furthermore, are definitively not polycrystalline. At most, the SHG results allow for crystallographic twins because SHG measurements cannot discriminate 180° twinning with respect to the [111] axis in crystals of $\overline{4}3m$ symmetry.

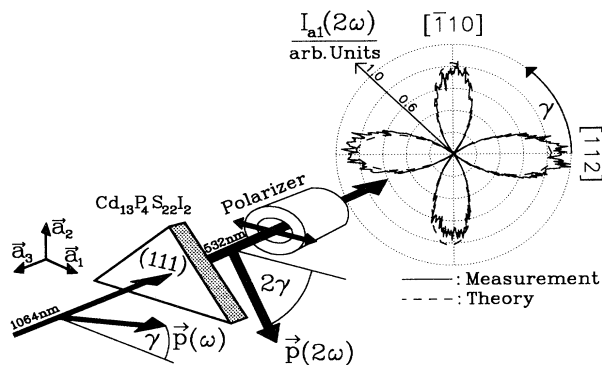Occurrence of second harmonic generation implies that

FIG. 1. Second harmonic generation in CPSI. The polarization of the second harmonic light depends characteristically on the polarization γ of the incoming beam. A fourfold symmetry is simulated, because the polarization of the incident wave is rotated with respect to the polarizer instead of the sample.

there is also an electro-optic effect. It seems therefore reasonable to assume that the photorefractive effect originates from the well-known mechanism based on light-induced charge transport, generation of a space-charge field, and the electro-optic effect. Since such a mechanism has specific symmetry characteristics we can test for it by the following holographic experiments: Holographic gratings are written for 2 min at a total intensity of $56\,kW/m^2$ ($\lambda = 488$ nm) with different angles γ between the [112] direction and the plane of incidence (Fig. 2). Thereby both writing beams are polarized perpendicularly to the plane of incidence. The result of Bragg-diffraction experiments with these gratings is that neither the intensity nor the polarization of the diffracted beam depends on the angle γ. The polarization of the diffracted beam is always found to be parallel to the incident one.

If the photorefractive effect is based on the electro-optic effect, a calculation for cubic crystals of point symmetry $\overline{4}3m$ shows, that diffraction is in general anisotropic, i.e., the Bragg-diffracted beam has not the same polarization state as the readout beam. This has been verified experimentally using GaAs as an example of a cubic crystal with point symmetry $\overline{4}3m$.[3] Therefore the observation, that neither the diffraction efficiency nor the polarization of the Bragg-diffracted beam depend on γ, excludes that the photorefractive effect in CPSI is of electro-optic nature. This conclusion does not only hold for monocrystalline samples, but also for samples containing crystallographic twins, because the refractive index change of two twins may only differ in sign. A change of the sign of Δn, however, does neither affect diffraction efficiency[4] nor the polarization state of the diffracted beam,[3] i.e., there should be anisotropic diffraction regardless of the presence of twins and of the mechanism of formation of the space charge field.

If we induce an external phase shift ϕ_{ext} of the recording pattern, relative to the storage medium, after the pattern is recorded at $\phi_{ext} = 0$, the intensities of the transmitted beams vary as a function of ϕ_{ext}. This type of experiment is called a beam-coupling measurement. In contrast to diffraction experiments, the intensity behind the sample depends in beam-coupling measurements on the sign of the refractive index change.[5] Presence of twins will therefore make a difference: If we have constructive interference for one of the crystallographic twins, there is destructive interference for the other. We measured the total intensity integrated over the contributions of
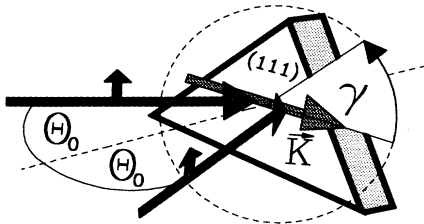
the twins, which means that we measured in diffraction experiments an average of the diffracted intensity contributions and in beam-coupling experiments the magnitude square of the average of the diffracted wave field contributions. Consequently, the average refractive index amplitude Δn calculated from a diffraction efficiency experiment would be larger than the one from a beam-coupling experiment if there are twins in the sample. We obtain, however, $\Delta n = 1.5 \times 10^{-4}$ from both experiments which excludes the presence of crystallographic twins in our samples.

The beam-coupling experiment shows that the refractive index pattern is in phase with the intensity pattern used for recording. This observation is also not consistent with the assumption that the photoinduced refractive index change originates from an electro-optic effect with diffusion as the major driving force for the formation of a space charge field. Additionally, the beam-coupling measurement in Fig. 3 shows that the photoinduced refractive index change (after 2 min) is accompanied by an extinction grating (after 10 min). This is indicated by the differing amplitudes of the intensity modulation of both readout beams behind the sample as a function of ϕ_{ext}, which is the phase shift between the hologram and the recording intensity pattern.[6]

The above experimental results demand that the photorefractive effect is isotropic, which excludes an explanation via the electro-optic effect as well as any other explanation involving material tensors higher than of rank two. This means that the field modulated by the light intensity pattern must be a scalar field such as the temperature field or the concentration field. The latter is the only possible explanation for CPSI, because the decay time for holographic gratings in CPSI stored in the dark is longer than one month.[1] So the photorefractive effect in CPSI is due to a light-induced concentration modulation and the chemo-optic effect. The chemo-optic effect describes a change

$$\Delta \epsilon_{ij} = \sum_{\nu} (\delta \epsilon_{ij}/\delta C^{(\nu)}) \Delta C^{(\nu)}$$

of the dielectric tensor at optical frequencies, where $\Delta C^{(\nu)}$ is the concentration change of the species ν.[7]

As holographic writing in CPSI is reversible and saturable,[1] the formation process of the concentration grating must have the same properties. This excludes not only all kind of stable photochemical reactions, but also metastable ones. The necessary condition for reversible holographic recording processes is that a photon triggers a spatial shift of some state of the solid from one place to another without changing the state itself. For example, photochromiclike effects, where an initial state is erased by a photon at the writing wavelength and a different final state is created at the same or another place, do not fulfill this condition, because the initial and final states are different. As they have different absorption bands, erasure and hence reversibility at the writing wavelength are prevented.

Reversible recording is characteristic for polaronic photoconductivity. By this we mean that there are self-trapped electrons (or holes) in the medium, usually

FIG. 2. Holographic recording in CPSI. The orientation of the grating vector $\vec{K}$ within the (111) plane of the crystal is given by γ.
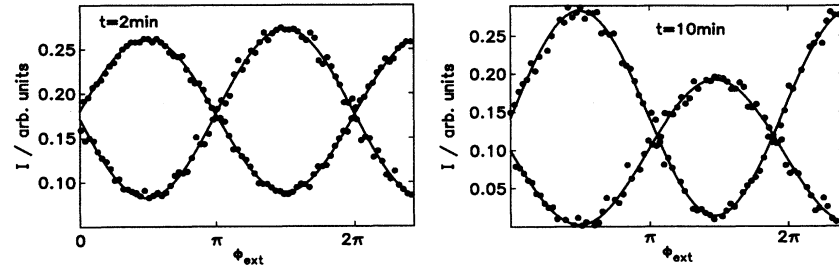
FIG. 3. Beam-coupling measurement in CPSI. The intensity of both holographic writing beams is recorded as a function of the externally induced phase shift ϕ_{ext} of the recording pattern relative to the holographic grating. After 2 min ($I = 56\,\text{kW/m}^2$, $\lambda = 488\,\text{nm}$) we obtain a pure refractive index grating and after 10 min an additional extinction grating.

trapped at some trapping site, which can move only by photon-assisted hopping. Let us assume that in the initial equilibrium state the charge of the self-trapped electrons is locally compensated by ions or hole polarons (or electron polarons) and that these complexes are distributed statistically over the medium contributing to the average absorption and refractivity, respectively. Holographic recording redistributes the polarons, resulting in a modulated space-charge density and a primary modulation of absorption and refractive index. This primary modulation of absorption and refractive index is local if the polaronic charge transport is due to diffusion and nonlocal for drift in an electric field. For holographic recording with a spatially periodic light pattern the pertinent contribution to an absorption or refraction grating is in phase for diffusion and phase shifted by $\pi/2$ for drift. Space charges with their space-charge field can give rise to secondary modulations if the crystal is electro-optic or an ionic conductor. Both material properties may result in large contributions to the refractive index or absorption modulations, even larger than the primary contributions.

In our case we have already excluded a mechanism based on the electro-optic effect, because the mechanism is isotropic and because there is no phase shift between refractive index and light intensity pattern for holographic recording without an applied electric field. As we will show now, measurements of the electrical conductivity of CPSI suggest, that the refractive index grating observed in CPSI is due to an ionic grating which compensates for the space-charge field.
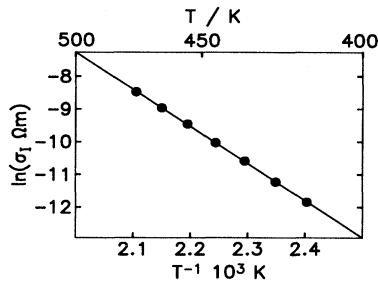
For the measurements of the electrical conductivity

powder of CPSI was pressed to a pellet and contacted by platinum electrodes. We measured the complex resistance (Cole-Cole-plot) as a function of temperature. From this measurement we obtained the electrical conductivity of CPSI and, additionally, the electrical circuit diagram.[8,9] This diagram represents the platinum electrodes as capacitors, which is characteristic for ionic conductivity because platinum electrodes are impermeable for ions. Figure 4 shows the Arrhenius plot of the ionic conductivity as a function of temperature in the range of 143 °C to 201 °C. The experimental values, represented as dots in Fig. 4, are described by $\sigma_I \propto \exp\left(-W/k_BT\right)$ with an activation energy of $W = 1\,\text{eV}$. This function is shown as a solid line in Fig. 4.

The time development of the thermal fixing process is connected with two time constants,[10] namely, the time constant τ_e due to electronic (polaronic) photoconductivity and the ionic time constant τ_i. With ϵ^{st} from Ref. 1 and by extrapolation of the ionic conductivity to room temperature we get a value of $\tau_I = \epsilon^{st}\epsilon_0/\sigma_I \approx 0.5\,\text{s}$ for the characteristic time constant of the ionic relaxation at room temperature. The above extrapolation is allowed, because no phase transition is reported for the temperature region between 25 °C and 143 °C, a fact which we also assured by difference thermal analysis. If we compare τ_I with the characteristic time constant for the hologram build-up in CPSI, which is $\tau \approx 260\,\text{s}$, it is obvious that mobile ions in CPSI can compensate for a holographically produced space-charge field. If this process is running for quite a period of time, it may lead to rather large refractive index changes depending on the ionic species. In the case of CPSI the mobile ion is expected to be the Cd^{2+} ion which would contribute with a rather high refractivity.

III. CONCLUSIONS

Our holographic experiments show that the photorefractive effect in CPSI is isotropic in the sense that neither the diffraction efficiency nor the polarization of the Bragg-diffracted light depends on the crystal orientation. This result is not compatible with a mechanism based on the electro-optic effect.

Our conductivity measurements support the assumption that the holographically induced refractive index change in CPSI is caused by mobile ions, presumably

FIG. 4. Arrhenius plot of the ionic conductivity of CPSI.

Cd^{2+}, which compensate for a holographically induced space-charge field. Besides the fact that the large refractivity of the Cd^{2+} ion provides a large refractive index change, the mechanism is practically the same as the thermal fixing process.[11,12]

We predict that holographic writing with an applied electric field will result in a phase-shifted refractive index grating and, consequently, in two-beam coupling. Unfortunately we presently cannot prove this obvious consequence of our model ourselves due to the lack of samples suitable for electric field measurements. But as we measured already a refractive index change of more than 1×10^{-4} for a diffusion mechnism, we can expect a correspondingly large holographic gain for drift transport in an electric field. It might therefore be possible that CPSI fulfills all necessary conditions for applications in photonics, dynamical holographic storage, and optical information processing.

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