Phase gratings in Fe$^{3+}$-doped triglycine sulphate single crystals recorded in the ultraviolet spectral region

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Phase gratings have been recorded in ferroelectric triglycine sulphate crystals doped with iron by interference of two ultraviolet laser beams in the 350 nm wavelength range. The recording sensitivity increases with temperature and a diffraction efficiency exceeding 60% has been reached in a 5.5-mm-thick crystal after several hours of writing with intensities of 0.1 W/cm$^2$. The photoinduced refractive index changes are anisotropic. The recording mechanism is not connected with the photorefractive effect and is believed to be due to the redistribution of hydrogen bonds leading to structural and refractive index modifications.

In ionic crystals two classes of mechanisms have been employed for recording volume phase holograms. The first is based on color centers; the second on the space-charge-induced photorefractive effects. In the latter case the effort has been mostly concentrated on ferroelectrics and photoconductive electro-optic materials. In organic compounds, a wide spectrum of photoinduced phenomena has been recognized as leading to grating recording based on the relative ease of breaking and redistributing bonds in molecular crystals.

In this note the recording of volume phase holograms in single crystals of ferroelectric triglycine sulphate is presented for the first time. While all previous ferroelectrics studied in this context can be classified as inorganic ionic crystals, (NH$_4$CH$_2$COOH)$_2$H$_2$SO$_4$ (TGS) has an organic constituent in the form of three glycine molecules per formula unit. TGS is a proper ferroelectric of symmetry group 2 with a Curie point $T_C = 49.5$°C at which the symmetry changes to the paraelectric point group 2/m. Nominally pure crystals, grown from a water solution, are transparent and colorless. The absorption edge lies between 4.8 and 5.0 eV. As we checked in some preliminary studies, pure TGS crystals are not sensitive to light at $\lambda = 351$ nm. When TGS is doped with trivalent Fe cations, a broad absorption band arises centered around 280 nm which extends up to 350 nm. This makes TGS:Fe$^{3+}$ a candidate for investigating the possibility of writing holographic gratings in the ultraviolet (UV) region.

The crystal used in this study was grown in the paraelectric phase by the temperature decrease method from a saturated aqueous solution of TGS and 5% of iron sulphate, Fe$_2$(SO$_4$)$_3$,9H$_2$O. It revealed fully developed faces and except for the seed it was optically uniform and transparent, with a light yellowish tint. The volume of the crystal of about 4 cm$^3$ allowed the preparation of several samples.

For absorption measurements a plate perpendicular to the polar b axis was used. Spectra were taken at room temperature with a Perkin–Elmer spectrometer in the region of 200–1000 nm. The curve shows a shoulder adhering to the intrinsic absorption region, giving evidence of an absorption band centered around 280 nm. At $\lambda = 280$ nm we measure an absorption coefficient $\alpha = 1.3$ cm$^{-1}$ in unpolarized light. Comparing this value with previous measurements for different doping contents, we can estimate that the Fe concentration is less than 400 ppm.

For holographic experiments two cubes A and B were cut with the edges along the $a'$, $b$, and $c$ axes and thicknesses of 6.3 and 5.5 mm, respectively. The faces perpendicular to the $c$ and $b$ axes were optically polished. Two ultraviolet beams ($\lambda = 351$ or 364 nm) from an argon ion laser interfered in the crystal volume creating a holographic grating. The typical intensity was 0.15 W/cm$^2$ with a modulation ratio of 0.99. At these wavelengths we have $\alpha = 0.3$ cm$^{-1}$; thus along a 6 mm path the beam is attenuated by 16%. The hologram was monitored by detecting the diffracted light of a He-Ne laser beam ($\lambda = 633$ nm) falling on the crystal at the Bragg angle. In this way we studied either the grating buildup (both UV beams on), the grating dark decay (both UV beams off), or the grating erasure (illumination with only one homogeneous UV beam). The presence of the He-Ne beam with an intensity of 0.03 W/cm$^2$ did not affect the dynamics of either buildup, erasure, or decay. The grating period $\Lambda = \lambda/(2 \sin \theta)$ ($\lambda$ is the recording wavelength, $\theta$ is the angle between the writing beams) was chosen in the region 0.8–2 μm.

The buildup of the holographic grating at room temperature is shown in Fig. 1 together with the subsequent dark decay and erasure processes. Values of the refractive index change have been calculated from the measured diffraction efficiency $\eta$ using the well known Kogelnik formula for phase holograms. We see that long writing times are needed to reach an appreciable diffraction efficiency at the writing intensity used (115 mW/cm$^2$). Illuminating with one UV beam enhances the decay velocity. However both dark decay and erasure dynamics are strongly nonex-

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FIG. 1. Time dependence of the light-induced refractive index change $\delta n$ and diffraction efficiency $\eta$ during grating buildup and decay or erasure at room temperature. Both recording and reading beams were polarized along the $a'$ axis. Erase intensity $I_e = 51$ mW/cm$^2$. The grating wave vector $K = 2\pi/\Lambda = 4.6 \times 10^5$ cm$^{-1}$ was parallel to the $c$ axis (cube B).

Exponential and by increasing the starting value of $\delta n$ it becomes more and more difficult to erase the grating. This is seen in Fig. 2 where the erase dynamics are shown for different writing times. During the recording, a kind of self-fixing of the hologram seems to occur.

To investigate the influence of temperature, the samples were mounted in a stabilized oven with transparent windows. The recording mechanism was found to be strongly temperature dependent, as evidenced by measuring the grating strength after 1 min writing at different temperatures. The results are shown in Fig. 3 where $\delta n \sim \eta^{1/2}$ is plotted in arbitrary units. The increase in $\eta$ is particularly strong above 50°C. A grating written in cube B at 60°C reached an efficiency $\eta = 61\%$ ($\delta n = 3.2 \times 10^{-5}$) after 8 h of recording ($I_e = 130$ mW/cm$^2$) without showing any saturation effect. No appreciable decay of this strong grating is observed even after cooling to room temperature. The diffraction efficiency $\eta$ for another grating recorded at the same temperature for 1 h decreased by only 10% of the maximum value after 12 h.

In other words, the self-fixing mechanism illustrated in Fig. 2 is enhanced by recording the grating at high temperatures.

The holographic sensitivity $S_0$ can be defined as the refractive index change per absorbed energy per unit volume, $S_0 = \frac{dn}{dW}, \eta = \alpha W_0$, where $W_0$ is the incident optical energy. For gratings written at 60°C we get $S_0 \approx 2 \times 10^{-8}$ cm$^2$/J. This value reduces by a factor of about 20 at room temperature and is about 500 times smaller than the one reported for photorefractive LiNbO$_3$ crystals.

We also investigated the influence of electric fields up to 1 kV/cm applied along the $b$ direction of the sample A. No detectable change of the diffracted intensity was observed at any temperature.

The change in refractive index is anisotropic, being maximal for light polarized in the $a'$ direction which was therefore employed for the reading He-Ne beam. After recording several holograms at high temperatures (60–70°C), diffuse scattering of light could be observed by the naked eye in the illuminated region. Quantitative measurements showed that this scattering is also a maximum for light polarized in the $b$ direction. As an example, in sample A the scattering reduced the transmission for $a'$ polarized light from 87 to 62% at $\lambda = 600$ nm and from 53% to 9% at 300 nm. For light polarized along $b$ the reduction was from 91% to 82% at 600 nm and from 67% to 27% at 300 nm. In the strongly scattering region the recording of further gratings becomes difficult.

The large diffraction efficiencies mentioned above, which have been obtained for longer recording times and higher temperatures, prove that the hologram has the character of a phase grating. The recording configuration would allow for the presence of space-charge-induced photorefractive effects. Due to the fact that the linear electrooptic effects are strongly temperature dependent, reaching peak effects at $T_c$ and dropping to zero above this temperature, one would also expect the largest photorefractive effects near $T_c$, provided that the refractive index changes would be induced by photo-generated space-charge fields. However, the holographic sensitivity increases in our experiment even in the paraelectric phase (Fig. 3), where
photorefraction could only occur due to the quadratic electro-optic effect. Also, the Bragg angle for reading is the same as below \( T_c \), so that a doubling of the grating \( \mathbf{K} \) vector is excluded. The photorefractive effect plays therefore a minor or negligible role. This is also confirmed by the previously described fact that an electric field applied to the sample did not affect the value of the diffraction efficiency.

A tentative model to explain the observed UV sensitivity of TGS:Fe\(^{3+}\) crystals can be based on some previous observations. Detailed x-ray investigations showed that pure TGS can exist in two configurations.\(^9^{,10}\) One, called the A structure, applies to a virgin crystal. The other, structure B, occurs when the crystal is x-ray irradiated. The most essential difference between A and B is that the hydrogen H(12)\(^6\) bonding the glycine I molecule to the sulphate group is transferred from the glycine's nitrogen in A to the sulphate's oxygen in B. At the same time it is known\(^1\) that the x-ray irradiation leads to refractive index changes for \( \lambda \) between 270 and 750 nm. The effect is temperature dependent. Above room temperature, the largest changes occur for light polarized along the \( a' \) axis if the wavelength lies between 300 and 500 nm.\(^11\) The effect, named "x-ray refraction effect,"\(^12\) is stable in the sense that the refractive index changes cannot be erased either optically or thermally.\(^13\) It may be assumed that these changes are a straightforward consequence of the A to B structure transformation.

The doping Fe\(^{3+}\) can form two different complexes in TGS.\(^14^{,15}\) One of them is incorporated regularly in the crystal lattice with the iron ion located in a position between the two glycine molecules II and III. The Fe\(^{3+}\) creates directed bonds with two nitrogen atoms and two oxygens. It further couples to two oxygens from neighboring SO\(_4\) groups. The second complex is an iron ion surrounded by glycine molecules located in lattice defects.\(^15\) Within the unit cell occupied by Fe, the interstitial ion of the lattice complex is situated near the H(12) hydrogen that plays the crucial role in the A to B transition. It is reasonable to suggest that due to the presence of the Fe ions the transformation from the A to the B structure or to another related structure with a disturbed hydrogen bonding network may occur with irradiation by UV photons. The structural modification is then connected with the refractive index change in the same way as in the "x-ray refraction effect." The role which may be played by the second iron complex is not clear at the present stage of the investigations.

The above model would easily explain the increase of the holographic sensitivity at higher temperatures as well as the relative stability of the recorded grating. In agreement with our observation, the ferroelectric state would not play any role and, since the photorefractive mechanism is also excluded, no anomaly is observed near \( T_c \). The enhanced decay rate by a uniform UV illumination (Fig. 1) is due to the generation of a homogeneously perturbed index. The grating dark decay is connected with the reverse transformation processes.

In conclusion, we have shown that TGS:Fe is a new medium for holographic recording. The main features of the recording mechanisms, like the grating buildup and decay dynamics and its temperature dependence, have been described. A redistribution of hydrogen bonds in the neighborhood of the doping ion is believed to be responsible for the observed refractive index change. To the best of our knowledge, the presented data demonstrate holographic storage in a crystal by using UV light for the first time. However, more data will be needed to understand the mechanisms involved and to work out a model which would explain additional features such as the difference between the erasure and decay processes. Further work should include the study of the structure of the illuminated region by x-ray and electron spin resonance methods.

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