

Light-induced grating spectroscopy studies of hole transport in LaGaO₃ crystals

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The results of the absorption and photocurrent measurements and light-induced grating spectroscopy of undoped LaGaO₃ crystals near room temperature are presented. Several absorption bands in the visible and near-ultraviolet region have been detected. Reversible photochromic effect has been observed in the nonoxidized crystals. The results of measurements show that the main absorption band in crystals annealed in air, peaked at 22 500 cm⁻¹, which also coincides with the main band in the photocurrent spectrum, is associated with the hole-related defect. The diffusion of holes is revealed in the light-induced grating's experiments. The diffusion is thermally activated with an activation energy equal to 0.75 ± 0.03 eV. This value of the activation energy of hole diffusion is responsible for large changes of the diffusion coefficients, which increase more than two orders of magnitude between 20° and 70 °C. [S0163-1829(99)00448-8]

I. INTRODUCTION

Lanthanum gallate (chemical formula: LaGaO₃) bulk crystals have recently been a subject of interest due to their possible applications as a substrate material for the epitaxy of high T_c superconductors^{1,2} and as a base material for electrolyte for solid fuel cells³⁻⁵ and for membranes for oxygen permeation.⁶ Bulk large LaGaO₃ crystals are grown by the Czochralski method. LaGaO₃ polycrystals could be also obtained by other methods such as flux,⁷ solid-state reactions,⁸ or a sol-gel method.⁹

Lanthanum gallate crystal belongs to orthorhombically distorted centrosymmetric GdFeO₃-type perovskitelike structures¹⁰ (space group $Pbnm$) (Ref. 10) at room temperature with the following parameters: $a = 5.52298(8)$, $b = 5.49139(9)$, and $c = 7.7725(1)$.¹¹ It is almost unique among other compounds with the GdFeO₃ structure, since in LaGaO₃ $a > b$.¹² At $T = 151$ °C LaGaO₃ crystals undergo first-order phase transition and transform into a rhombohedral $R3c$ structure.¹⁰⁻¹² This is one of the reasons for inducing structural imperfections in the crystals. The strong tendency to twinning limits appreciably their application as a substrate or as a laser active material (if doped with luminescent ions). Although several attempts have been made to reduce twinning, this problem still remains unsolved. It has been known that the application of stress removes twinning at least partially and also decreases the temperature of the phase transition, even for a few tens of degrees.¹³

Little is known about the intrinsic defect structure of LaGaO₃ crystals, since large and good quality crystals of that compound have been obtained only recently. The aim of this paper is to study the properties defect centers in these crystals, detectable in optical absorption and responsible for their different coloration, dependent on thermal treatment and il-

lumination. Unfortunately, strong twinning makes it difficult to use the electron paramagnetic resonance technique for studying the defects in this compound. We apply for that purpose absorption and photocurrent measurements, and also the light-induced gratings (LIG) technique. The LIG is a holographic technique that turned out to be a powerful tool for obtaining information about the nonlinear properties of solids, which is very often difficult to obtain by the other methods. It is especially useful for studying the excitation energy migration on the system of dopants or charge transfer in solids. In this technique two crossed coherent laser beams interfere inside the examined medium. Being in resonance with the optical transitions in solid, they can create LIG's of the excited states or concentration gratings of the certain charges. The grating can induce changes of absorption and/or refractive index, which could be detected by the other laser beam, scattered from the LIG. This way the scattering efficiency of the LIG and its dynamics can be probed.

The paper is organized in the following way: experimental details are described in the Sec. II. The results of absorption measurements are presented in Sec. III A and photocurrent studies are reported in Sec. III B. The results of LIG measurements are described in the Sec. III C of the paper. Interpretation of the results and discussion are given in Sec. IV.

II. EXPERIMENT

The crystals used in these studies were grown by the Czochralski technique in an iridium crucible in a nitrogen atmosphere with 1% oxygen. Some of the crystals were additionally annealed in air (oxidized) at temperatures above 1300 °C for several hours. Oxygen ions are known to be incorporated into the crystal in such a process.⁶ The crystals were cut to

form slabs of thickness between 0.5 and 1 mm and polished on a diamond powder.

The absorption of the crystals has been measured with the Hitachi U2001 and U3501 spectrophotometers at room temperature.

Transient induced absorption was measured in a setup with a MDR-2 (LOMO) monochromator and S-20 type photomultiplier. The absorption was induced by the pulses of an argon-ion laser with different wavelengths. A halogen lamp or He-Ne laser was used for probing the absorption changes. The induced absorption value, ΔK , was determined as

$$\Delta K = \frac{1}{d} \ln \frac{T_1}{T_2}, \quad (1)$$

where d is the sample thickness, and T_1 and T_2 are the crystal transmissions before and after irradiation, respectively.

The photocurrent measurements were performed with use of Keithley model 617 electrometer, MDR-2 (LOMO) monochromator and xenon or halogen lamps, depending on the spectral region of measurements. Silver paste electrodes were used. The spectra have been corrected for the quantum efficiency of the excitation system and for the penetration depth of the illumination due to strong absorption.

The LIG experiments were performed in a setup described elsewhere.¹⁴ The argon-ion laser was used as a source of write beams, and a He-Ne laser was applied for probing the grating properties. The grating decay kinetics was recorded with a lock-in SR 510 amplifier and stored in a computer or recorded in a storage oscilloscope, depending on their time persistence. The decay kinetics of transient gratings were measured with a Newport Shutter model 846 for light chopping with the closing transient time equal to about 20 ms. For elevated temperature measurements the samples were mounted at a heated metal finger in a vacuum chamber. The temperature of the finger was controlled by a temperature controller.

III. EXPERIMENTAL RESULTS

A. Absorption measurements

The room-temperature absorption spectrum of LaGaO₃ crystals, as grown or illuminated by blue-yellow light, is presented in Fig. 1 (line *a*). The crystal, kept in the darkness, has a weak yellowish tint associated with the absorption bands with peaks at 25 000 and 33 000 cm⁻¹. At about 40 000 cm⁻¹ another absorption band could be observed that is overlapped with a very strong absorption in the UV, which is presumably the band-edge absorption. Such a crystal was subsequently annealed in air at a temperature of 1400 °C for 4 h. The absorption spectrum of the annealed crystal (see Fig. 1, line *b*), besides the bands present in the nonannealed crystal, contains an additional nonsymmetrical strong band peaking at 22 500 cm⁻¹, approximately, which is responsible for the brown-reddish color of the sample. The differential absorption spectrum (which is a difference between the absorption spectrum of annealed and nonannealed crystal) is also shown in Fig. 1 (line *c*). More detailed analysis of the shape of this band shows that it is a convolution of at least two bands centered at 22 500 and 27 500 cm⁻¹. The relative ratio of intensity of these bands is equal to 1:0.12, respec-

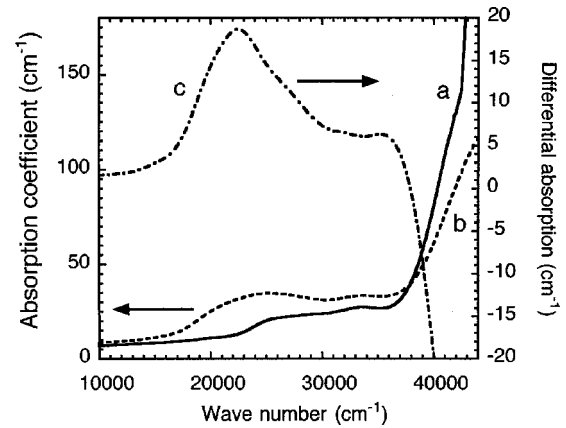


FIG. 1. Room-temperature absorption spectra of LaGaO₃ crystals: *a*, as grown; *b*, annealed in air at 1400 °C for 4 h; *c*, differential absorption spectrum of the crystal annealed in air (curve *b*-curve *a*).

tively. This spectrum also exhibits strong negative differential absorption close to the band edge. A subsequent annealing of the crystals in vacuum or in a neutral atmosphere leads to bleaching of the absorption peaked at 22 500 cm⁻¹ and restoration of the absorption in the band-edge region. This way the process of coloration of the crystals by proper annealing is reversible.

Illumination of the as-grown crystal with sunlight or with UV light with a wavelength in the range of 350 nm leads to darkening of the sample. This is associated with a light-induced absorption band with a peak at about 22 000 cm⁻¹, very similar to the band associated with the annealing in oxygen. The spectra of this crystal before and after illumination with UV light are shown in Fig. 2. The differential absorption spectrum induced by such an illumination is also presented in Fig. 2. The induced absorption in the region of 22 000 cm⁻¹ is accompanied by a weaker bleaching of the crystal in the region of 30 000 cm⁻¹, and also by induced absorption close to the band-gap absorption. The subsequent illumination with light resonant with the 22 000 cm⁻¹ absorption band (as, for instance, argon ion laser lines) restores completely the previous spectrum. The absorption changes associated with this reversible photochromic effect are in the order of a few cm⁻¹. The induced changes of absorption last

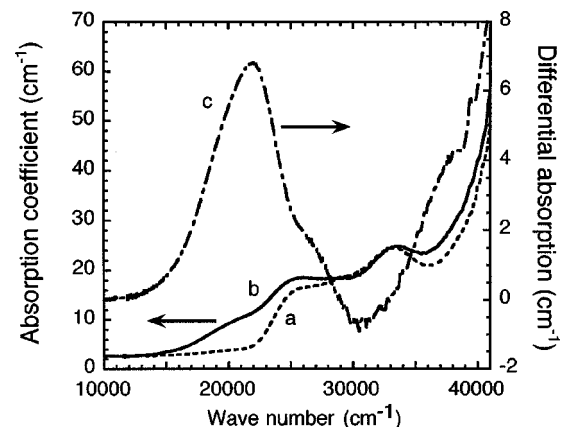


FIG. 2. Absorption spectra of nonoxidized LaGaO₃ crystal: *a*, illuminated by 514.5-nm argon-ion laser light; *b*, subsequently illuminated by 350-nm light; *c*, differential absorption.

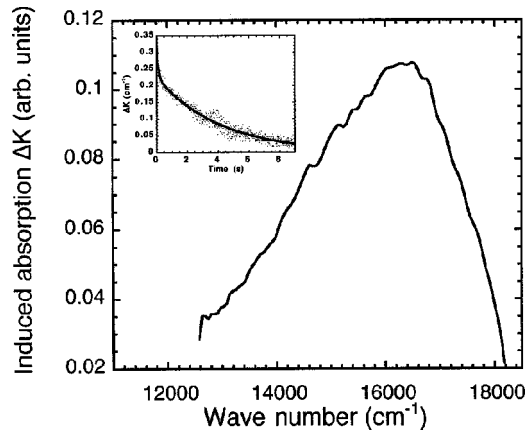


FIG. 3. Room-temperature transient absorption spectrum of the LaGaO₃ crystal, annealed in air, induced by 514.5-nm argon-ion laser light. The decay dynamics of the transient absorption is shown in the inset. The solid line in the inset is the computer fit of the two-exponential decay to the experimental data.

for a long time (at least a few weeks) if samples are kept at room temperature in darkness.

No change of absorption of the bands peaked at 25 000 and 33 000 cm⁻¹ has been observed under the influence of illumination in any of the examined samples. Annealing in oxygen or in reducing atmosphere does not affect the intensities of those bands.

No long-lasting changes of absorption upon illumination have been revealed in the sample annealed in air. Only weak transient absorption changes were observed under the influence of different wavelengths of the argon-ion laser in these samples. The absorption spectra and decay times of this type of absorption depend on the energy of the light, which induces them. Under the influence of 514.5-nm laser light, a broad transient absorption spectrum with a peak at about 16 100 cm⁻¹ (about 620 nm) is observed in the sample annealed in air. The room-temperature transient absorption spectrum induced in the sample is shown in Fig. 3. A decay kinetics of this absorption is presented in the inset in Fig. 3. The spectra of this absorption and the decay kinetics are very similar at temperatures between room temperature and 70 °C. The decay kinetics can be deconvoluted into two-exponential decay with the decay times equal to 5.1 ± 1 and 0.25 ± 0.1 s, approximately. The total peak absorption changes are in the order of 0.4 ± 0.15 cm⁻¹.

The transient absorption changes were also observed in nonoxidized crystals. The more detailed studies of this type of absorption and its relation with the shallow charge trap levels in LaGaO₃ crystals will be a subject of a forthcoming paper.¹⁵

No luminescence associated with the described above absorption bands has been detected in the crystals, even at a temperature of 10 K. In some samples, contaminated with traces of nonintentional impurities such as Cr³⁺ or Nd³⁺, luminescence associated with the intrashell transitions of those ions was observed.

B. Photocurrent measurements

The photocurrent spectra of the LaGaO₃ crystals are shown in Fig. 4. The spectrum of the nonoxidized crystal

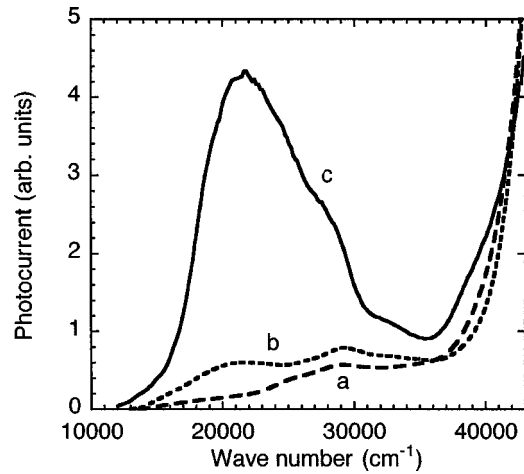


FIG. 4. Photocurrent spectra of LaGaO₃ crystals: *a*, nonoxidized crystal illuminated by 514.5 nm light; *b*, nonoxidized crystal after short illumination with 350-nm light; *c*, annealed in air.

contains two distinct peaks close to 22 000 and 30 000 cm⁻¹. Their spectral positions agree very well with positions of the photochromic absorption, observed in these crystals. In contrast to that, the photocurrent spectrum of the sample bleached with the argon-ion laser light, resonant with the 22 000 cm⁻¹ band, exhibits much lower photocurrent at the region of this band.

The crystal annealed in air exhibits a very strong photocurrent peak near 22 000 cm⁻¹, much stronger than in the nonoxidized crystals. There is also a weaker photocurrent peak with the maximum around 27 500 cm⁻¹ visible in this spectrum on the shoulder of the 22 000 cm⁻¹ band. The positions of the photocurrent peaks agree very well with the positions of the absorption bands in this crystal.

C. Light-induced grating measurements

For light-induced grating creation a 514.5-nm argon-ion laser line has been mostly used in our studies, although it has been checked that the gratings could be created by any argon-ion laser line between 457.9 and 514.5 nm.

The LIG's, created by coherent laser beams, could be destroyed due to the decay of the states (or species), which form the grating, and/or it could be erased by diffusion of the states (species) from the peaks to the valleys of the grating. Rapid diffusion means here faster decay of the grating due to faster filling of the valleys by the diffusing states (species). The grating would also decay faster if the grating spacing is smaller. This is, in fact, the advantage of the LIG technique since the grating spacing, Λ , could be controlled by changing the crossing angle, Θ , between the two write beams, and it is equal to¹⁶

$$\Lambda = \frac{\lambda}{2 \sin(\Theta/2)}, \quad (2)$$

where λ is the wavelength of the write beam. The grating decay rate, R_g , is expressed by the equation¹⁷

$$R_g = \frac{2}{\tau} + \left[32 \left(\frac{\pi}{\lambda} \right)^2 \sin^2 \left(\frac{\Theta}{2} \right) \right] D, \quad (3)$$

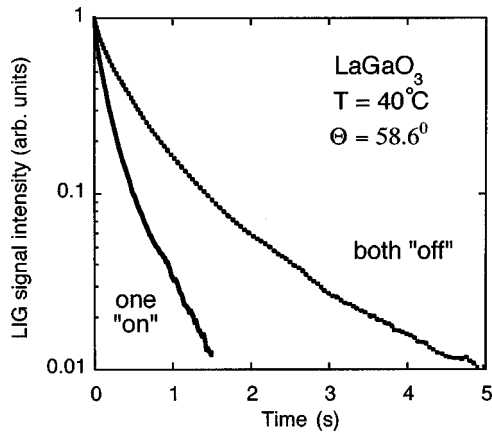


FIG. 5. An example of LIG decay in the crystal annealed in air, excited by weak intensity write beams. Θ is the crossing angle between the write beams.

where D is the diffusion constant and τ is the intrinsic lifetime of the diffusing species. Thus the grating decay rate is a linear function of the square of the reciprocal of the grating spacing and the diffusion constant could be easily deduced from the plot of the grating decay rate vs $\sin^2(\Theta/2)$. The intrinsic lifetime of the diffusing species can be calculated from the crossing point of this dependence with the grating decay rate axis. In the absence of diffusion the grating decay rate is independent of the grating spacing and LIG decays with a rate equal to double that of the decay rate of the absorption or refractive index changes.

In nonoxidized crystals, formerly illuminated by the UV light, only very weak gratings with the relative scattering efficiency on the order of 10^{-5} in about 1-cm-thick samples could be observed for the write beams from the argon-ion laser. These gratings are associated with the photochromic reversible phototransformation of the 22 000 and 30 000 cm^{-1} bands. They exhibit saturation behavior at room temperature. Their scattering efficiency decreases after prolonged illumination due to not exactly equal intensities of the write beams or/and due to parasitic noncoherent scattering from crystal imperfections, as for example, twin boundaries. Such scattering illuminates also the valleys of the interference pattern and destroys the grating by the phototransformation of defects also in the valleys.¹⁸ This type of the gratings has not been a subject of studies in this paper.

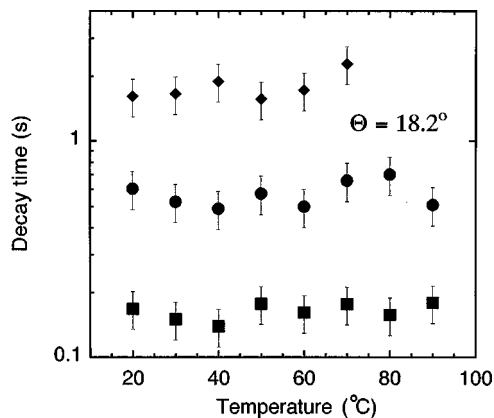


FIG. 6. Examples of decay constant of transient LIG's vs temperature in LaGaO₃ crystal annealed in air.

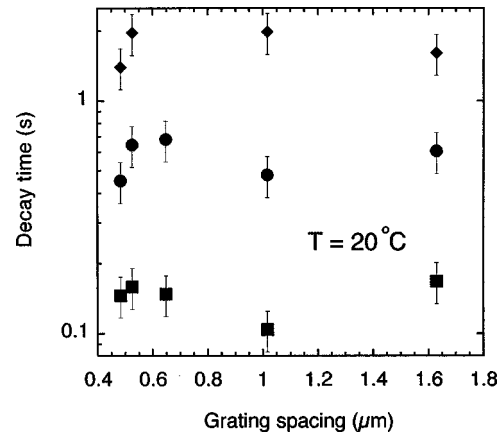


FIG. 7. Examples of decay constants of transient LIG's vs the grating spacing in LaGaO₃ crystal annealed in air.

On the other hand, the more efficient LIG's can be easily produced in samples annealed in air. Two different types of gratings could be produced in these crystals depending on the intensity of the write beams. The gratings created by low intensity write beams, below 0.1 W cm^{-2} , are transient, that is, they decay with decay times no longer than about 2 s in the examined range of temperature. The typical decay kinetics of this type of grating is presented in Fig. 5. The gratings undergo optical erasure if one of the write beams is not switched off during the measurements of the grating decay. This is also shown in Fig. 5. The decay kinetics of those gratings could be deconvoluted into three-exponential decays with the decay constants equal approximately to $0.14 \pm 0.05 \text{ s}$, $0.5 \pm 0.15 \text{ s}$, and $1.9 \pm 0.4 \text{ s}$. The longest component of the grating decays is weaker and for this reason sometimes has not been observed. The decay times of these gratings seems to be not dependent (within the error bars) on the grating spacing between 0.48 and $1.64 \mu\text{m}$ and temperatures between 20° and 80°C . The examples of behavior of the grating decay time as a function of temperature and the grating spacing are presented in Figs. 6 and 7, respectively.

Scattering efficiency of this type of gratings depends on the power of the write beams. A typical example of such dependence is shown in Fig. 8. The grating efficiency is proportional to the square of the intensity of the write beams

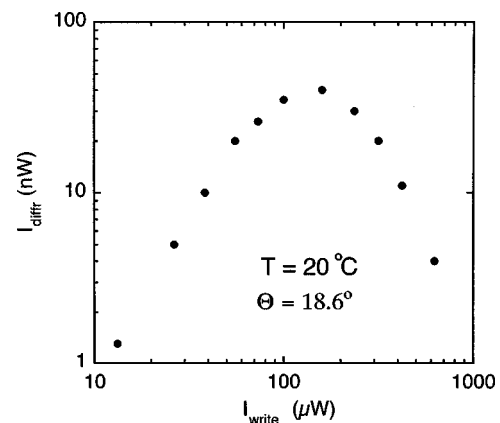


FIG. 8. An example of scattering efficiency of the transient LIG's on the power of the write beams in the oxidized LaGaO₃ crystal.

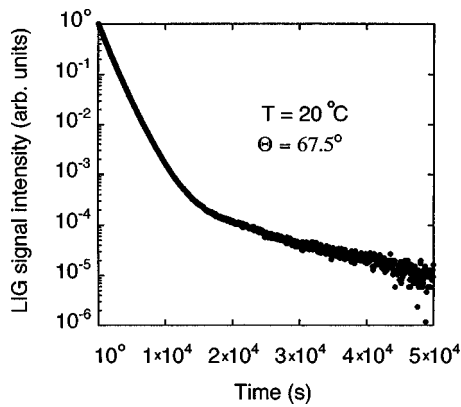


FIG. 9. An example of decay of persistent LIG's in oxidized LaGaO₃ crystal.

for very small intensity of the write beams. For higher intensities it reaches a maximum and subsequently decreases if the intensities of the write beams are further increased. This behavior, similar to the behavior of the LIG's in nonoxidized crystals, is also consistent with saturation of the absorption changes and influence of incoherent illumination due to non-equal intensity of the write beams or scattering of the write beams from the crystal imperfections. Maximum scattering efficiency of this type of gratings reached upon conditions of grating recording shown in the graph is equal to about 4×10^{-5} in the 0.8-mm-thick sample, that is, at least an order of magnitude more than scattering efficiency of gratings associated with photochromic absorption in the nonoxidized crystals.

Drastically different behavior is observed if larger intensities (above 30 W cm^{-2}) of the write beams are used. The gratings created this way exhibit much more persistent character, with the decay lasting between a few days and few minutes, being dependent on the grating spacing and temperature. The recording time of those gratings takes a few minutes. The grating decays could be decomposed into two exponential decays, with the second one much weaker (about two to three orders of magnitude) than the first one. The typical decay of the persistent gratings is shown in Fig. 9. Scattering efficiency of the persistent gratings is in the range of 1.5×10^{-4} in the 0.8-mm-thick sample (for the same write conditions as in Fig. 8).

The typical dependencies of the grating decay rate on the angle between the write beams are shown in Fig. 10. The decay rates of both components of the grating decays depend linearly on the $\sin^2(\Theta)$ (i.e., inverse of square of the grating spacing). The extrapolated crossing points with the decay rate axis are equal to zero within the error bars of measurements for both components of the decay. The persistent gratings exhibit this behavior at any temperature between 17 °C and 70 °C. However, the decay rate of the permanent gratings increases strongly with increase of temperature for any crossing angle of the write beams.

At temperatures higher than 80 °C the weak laser beams also create gratings that have permanent behavior if the temperature is decreased rapidly after grating recording.

IV. INTERPRETATION OF RESULTS AND DISCUSSION

A. Nature of absorption centers in pure LaGaO₃ crystals

The defect associated with an absorption band with a peak at $22\,500 \text{ cm}^{-1}$ is a dominating defect center in the LaGaO₃

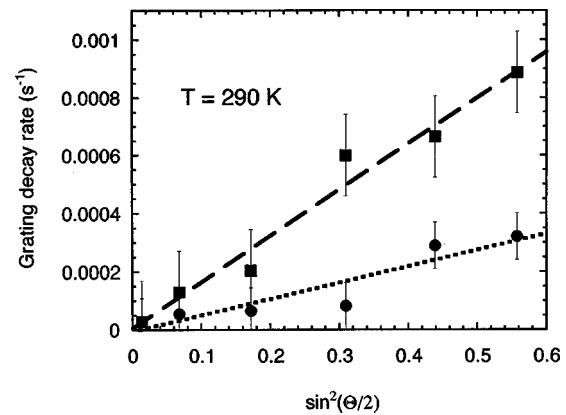


FIG. 10. An example of dependence of the grating decay rate on the angle between the write beams in oxidized LaGaO₃ crystal.

crystals annealed in oxygen containing atmosphere. In perovskite YAlO₃ (YAP) crystals,^{19,20} which are very similar in many ways to the LaGaO₃, exists the absorption band in the similar spectral region, which exhibits the same properties as the band peaked at $22\,500 \text{ cm}^{-1}$ band in LaGaO₃ crystals annealed in air. Doping the crystals with ions with a possible valence state larger than 3 [as, for example, Mn in the 4+ or 5+ valence state in YAP (Ref. 19) or V in the 4+ valence state in LaGaO₃ (Ref. 21)] removes this band, even if crystals are grown in an oxygen environment.

The above described properties of the $22\,500 \text{ cm}^{-1}$ allow to associate it with the hole center (or centers) in the LaGaO₃ or YAP crystals since the band occurs when the electrons are bound by the additional nonstoichiometric centers introduced into the crystals (as, for example, oxygen ions). Even a relatively small amount of electron donors, such as Mn or V ions, leads to a complete removal of this band. The band is likely to be associated with the so-called V^- center (a hole trapped on an oxygen ion neighboring a cation vacancy), self-trapped hole, or more complicated defect associated with holes. In YAP crystals it has been noticed that the intensity of this band is related to the cation nonstoichiometry, i.e., it is stronger in the crystals containing more yttrium than aluminum ions. Therefore it has been supposed that the intensity of the band is associated with the yttrium antisities¹⁹ (yttrium ions replacing aluminum ions in the crystal host). This is also possible in LaGaO₃ crystals, in addition to the possibility of trapping holes at cation vacancies. Lack of luminescence associated with the observed absorption additionally confirms that it is related to the hole centers. It seems to be much less probable that it is related to an F^+ center (oxygen vacancy occupied by one electron) since such centers are likely to be removed by the oxidizing process. The additional weaker band with a peak at $27\,500 \text{ cm}^{-1}$ shows that other defects are also present in the crystals. They could be associated with the same main defect modified by the presence of the other imperfections of the crystallographic structure.

The photocurrent data show that this absorption band is associated with the photoionization of the centers, that is with the photoionization of the holes. The photoionized holes are subsequently trapped by the same or another center. The holes are stable in this sample in the examined temperature region, they are only transferred between the defect centers.

The photocurrent data also prove that the bands peaked at energy of 22 000 and 30 000 cm^{-1} in the LaGaO_3 nonoxidized crystals are associated with the recharging of the defects. The diminished photocurrent in the region of 22 000 cm^{-1} in the sample bleached by the argon-ion laser light testifies that the process of recharging is metastable at room temperature, as it was observed in the absorption measurements. In this not oxidized sample several absorption bands are visible in the spectra (see Figs. 1 and 2). Similarity of the band with a maximum at 22 000 cm^{-1} to the band with a peak at 22 500 cm^{-1} in the oxidized sample would suggest that these bands are associated with the same defect. Persistent changes of absorption under the influence of light have not been observed in the sample annealed in air, where only stable hole centers have been observed. It is possible that bands with a peak at 30 000 cm^{-1} and close to the band gap in the nonoxidized sample could be associated with the electron defect centers, as, for example, F^+ or F centers (vacancies at anion sites, charged with one or two electrons, respectively). These centers could be destroyed by annealing in oxygen containing atmosphere, since the electrons are likely to be trapped by the oxygen ions introduced to the crystal during annealing.

The observed transient absorption is likely to be associated with the shallow charge traps present in the crystals, detected there by electrical methods as thermally stimulated depolarization. It will be a subject of a forthcoming paper.¹⁵

No photocurrent associated with centers with the absorption peaks at 25 000 and 33 000 cm^{-1} was observed. Therefore they are likely to be associated with internal transitions of nonintentional dopants. Iron ions are likely to be in our crystal with a level of concentration in the order of a few ppm. These ions are known to produce some absorption bands in the same spectral region in the other oxides. In order to identify more exactly the nature of these defect centers in LaGaO_3 additional studies are necessary.

B. Origin of the light-induced gratings in LaGaO_3 crystals

1. Origin of transient LIG's

The LIG's in LaGaO_3 crystals, created by argon-ion laser light, seem to be the absorption type of holographic grating. Such gratings usually have low scattering efficiency,¹⁶ which is observed in our crystals.

The origin of the gratings, which are created in the oxidized crystals, with weak argon-ion laser beam intensity is consistent with the transient photochromic absorption, related with shallow charge levels detected in the crystals.¹⁵ Lack of dependence of the LIG decay rate on the grating spacing testifies that this transient absorption is associated with local changes of the absorption coefficient, induced in phase with the interference pattern of interfering laser beams. The dynamics of the LIG signal associated with this absorption is consistent with the scattering from two superimposed, laser induced gratings. The LIG's signal is proportional to the square of the change of the complex refractive index induced in the material by the interference of the laser write beams, which in this case is the sum of the two exponential components of the transient absorption changes. This way the LIG signal is described by

$$I_s \propto (\Delta K)^2 = (\Delta K_1)^2 \exp\left(-\frac{2t}{\tau_1}\right) + 2\Delta K_1 \Delta K_2 \exp\left(-\frac{t}{\tau_3}\right) + (\Delta K_2)^2 \exp\left(-\frac{2t}{\tau_2}\right), \quad (4)$$

where $\Delta K_{1,2}$ are the absorption changes associated with two components of the transient absorption decay, and $\tau_{1,2}$ are the decay constant of those two components. The decay rate $1/\tau_3$ is equal to

$$\frac{1}{\tau_3} = \frac{1}{\tau_1} + \frac{1}{\tau_2}. \quad (5)$$

This way three-exponential LIG decay is observed. The long and short components of this type of LIG's have decay rates in very good agreement with the decay rates of the transient absorption. The intermediate decay rate $1/\tau_3$ is also consistent with the presented model. This confirms the assignment of this type of LIG's observed in oxidized LaGaO_3 with the transient absorption changes.

The scattering efficiency, η , of the LIG's is expressed by the Kogelnik formula:²²

$$\eta = \exp\left(-\frac{Kd}{\cos \alpha}\right) \left(\sin^2 \frac{\pi \Delta n d}{\lambda \cos \alpha} + \sinh^2 \frac{\Delta K d}{4 \cos \alpha} \right), \quad (6)$$

where K is the absorption of the crystal at wavelength λ , d is the sample thickness, α is the Bragg angle, Δn are the refractive index changes, and ΔK are the absorption coefficient changes. The first term in this equation describes the phase gratings and the second one absorption gratings. Neglecting the first term and substituting observed values of the absorption and absorption changes (about $K = 8 \text{ cm}^{-1}$ and $\Delta K = 0.4 \text{ cm}^{-1}$, respectively, at 632.8-nm wavelength) we obtain a theoretical value of scattering efficiency for the Bragg angle of about 10° equal to about 3×10^{-5} . This is in a very good agreement with the observed value of the scattering efficiency. This additionally confirms that this type of gratings is associated with the transient changes of the absorption coefficient.

2. Origin of persistent LIG's

We associate the origin of the persistent gratings in the crystals annealed in air with the hole transfer mechanism between defect centers in the crystal. The reasons that corroborate this conclusion are presented below.

The linear dependencies of the decay rates of both components of the decay of persistent gratings on the reciprocal of the square of the grating spacing agree very well with the diffusion mechanism of the grating decay. The extrapolated crossing points of those dependencies with the decay rate axis show that the diffusing species are stable. The diffusion coefficients could be calculated from the slopes of the dependencies using Eq. (2). The calculated diffusion coefficients for short and long components of the decay, $D^{1,2}$, depend strongly on temperature, T . Both dependencies have thermally activated character, presented in Fig. 11, and can be well described by the formula⁴

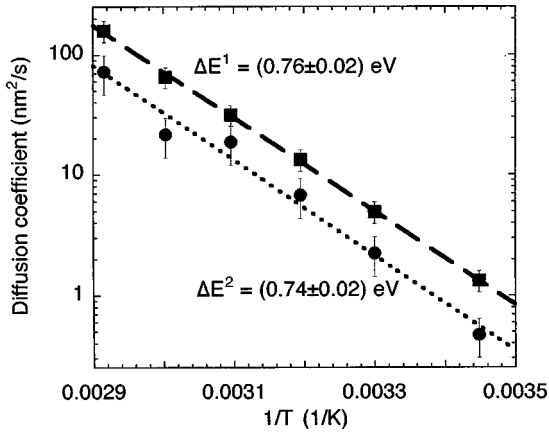


FIG. 11. Temperature dependencies of the diffusion coefficients for both components of the LIG's decay in oxidized LaGaO₃ crystal.

$$D^{1,2}(T) = D_0^{1,2} \exp\left(-\frac{\Delta E^{1,2}}{k_B T}\right), \quad (7)$$

where $\Delta E^{1,2}$ are the activation energies for the two components of the diffusion process, associated with the grating decay, and k_B is the Boltzmann constant. The calculated activation energies for both components of the grating decay are quite similar to each other and equal to 0.75 ± 0.03 eV. This means that the diffusion constants change about two orders of magnitude between room temperature and 70 °C, at 70 °C reaching values of about 200 nm²/s and 65 nm²/s for the short and long components of the grating decay, respectively. The values of the diffusion constant of the faster component of the decay D^1 are approximately 2 to 3 times larger in the temperature range of measurements than the values of diffusion constant D^2 associated with the much weaker and slower decay. Although the value of activation energy of diffusion agrees very well with the calculated activation energy for the oxygen vacancy transport in this compound (0.73 eV),²³ it seems to be quite improbable that such an ionic current could be induced by illumination in this compound close to room temperature. Illumination by argon-ion laser is resonant within the absorption (photoionization) band of the center associated with holes and leads to release of the holes upon illumination. Therefore we associate the origin of persistent gratings with the hole hopping conductivity of LaGaO₃. Hole conductivity has been observed in LaGaO₃,²⁴ being more than two orders of magnitude weaker than the ionic conductivity in the range of 1000 °C, important for solid fuel cells. Its activation energy was estimated to be about 1.1 eV at the same temperature range.²⁴ We are not aware of any other measurements of the hole diffusion in LaGaO₃ close to room temperature. Since our measurements are done below the phase transition temperature (151 °C), therefore the activation energies can be quite different from those observed around 1000 °C, also due to different mechanisms of conductivity than at high temperatures.

There is an important difference between the low intensity write beam illumination, which does not produce persistent grating in the examined temperature range, and the high intensity illumination, which leads to this effect. This is associated with heating of the crystal by the relatively strong

write beams, which was observed during a process of grating recording. The process of heating occurs due to strong absorption of the crystals, associated with the 22 500 cm⁻¹ absorption band. Although the temperature of the illuminated spot during LIG's recording increases considerably, it did never exceed the temperature of the phase transition, since we did not observe characteristic changes of the diffraction pattern related to the reorientation of twins present in the crystals that occur reversibly at phase transition temperature. The hole conductivity at high temperature is much higher than at lower temperatures due to the high value of their activation energy, which has been shown in our studies. This leads to the increased probability of the hole transport out of the illuminated regions of the interference pattern. Such a transport is greatly decreased at lower temperatures due to much lower conductivity of the crystal. Therefore the mechanism of grating formation under influence of weak write beams is different from that under strong illumination. The hole transport is probably limited at higher temperatures by the formation of space charge. Switching the light off leads to a rapid cooling of the formerly illuminated spot, which freezes the state of charge separation in the crystal, induced by the interference pattern. The possibility of recording of permanent gratings at higher temperatures by the weak laser beams and the possibility of observing them after cooling the crystal confirms our conclusion. After reaching the equilibrium temperature, at which the measurements of the grating decay kinetics were performed, the diffusion of holes back to formerly illuminated regions erases the grating. We associate the faster component of the grating decay with the hole diffusion in the bulk of the crystal. The much weaker, slower component of the decay could be associated with the hole diffusion in a much more perturbed environment, perhaps along the twin boundaries present in the crystals or in the presence of the other defects.

The charge separation must produce an electric field between peaks and valleys of the grating. Such a field is a source of electro-optic gratings in photorefractive materials. However, it seems that the persistent gratings formed in LaGaO₃ are not of electro-optic origin since the crystallographic structure of the crystal is not electro-optic. Thus the linear electro-optic effect should not occur in those crystals. We also have checked that the grating formation is independent of the crystallographic orientation of the sample. Thus the diffusion of the holes leads to changes of the absorption coefficient and formation of the absorption type persistent gratings in the LaGaO₃ crystal.

The absence of persistent changes of absorption in the crystals grown or annealed in an oxygen atmosphere under the influence of the strong argon-ion laser light is related to the low value of the diffusion constant for transport of the holes. The diffusion length is expressed by the formula

$$L_{\text{diff}} = \sqrt{2Dt}. \quad (8)$$

Assuming that the temperature of the illuminated spot is equal to about 140 °C (very close to the phase transition temperature) we can estimate the diffusion length of holes at this temperature during the recording time of the hologram, equal to about 2 min. Using the value of the faster diffusion constant at about 140 °C, extrapolated from our data, equal to about 14 400 nm²/s, the diffusion length of the holes at

140 °C would be about 1.85 μm . In order to transfer them on the distance of about 1 mm, required for the absorption measurements in the typical spectrophotometer it would be necessary to illuminate a spot on the sample for about 10 000 h. Although this type of estimation is very crude, it supports the conclusion that the diffusion constants are too small to transfer the holes at large distances necessary for effective absorption measurement. In the LIG's experiments the diffusion occurs only on few micrometer distances, which agrees very well with calculated value of the diffusion length.

V. CONCLUSIONS

The results of our studies of the light-induced gratings, absorption, and photocurrent of LaGaO_3 crystals allowed to identify the absorption band associated with the hole photoionization process in oxidized crystal. LaGaO_3 is considered to be an almost purely ionic conductor,²³ at least at higher temperatures. However, our experiments show that the hole conductivity dominates close to room temperature in

LaGaO_3 . Due to the high value of the activation energy of the hole transport in those crystals the hole conductivity increases strongly at temperatures above room temperature. The hole transport at micron distances is responsible for the creation of persistent LIG's in the oxidized crystals. The other mechanism of LIG's formation, associated with the transient light induced absorption and probably the charge transfer between various defect centers, is present in both nonoxidized and oxidized crystals. More precise identification of the defects observed in LaGaO_3 crystals requires additional studies.

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