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Spectroscopy of defect centers in $LaGaO_3$ crystals

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Abstract

It is shown that the process of thermal relaxation of the photochromic effect in $LaGaO_3$ crystals proceeds due to transfer of the charges between defects involved in the effect and shallow traps. The crystals exhibit luminescence of Cr^{3+} ions, which are an unintentional dopant. However, the emission observed in the thermally stimulated luminescence of the crystals with residual concentration of chromium is associated with luminescent centers different from typical isolated Cr^{3+} ions. The spectral properties of these centers are studied.

Keywords: Optical materials; Insulators; Point defects; Crystal field

1. Introduction

Recent interest in $LaGaO_3$ lanthanum orthogallate bulk crystals is driven by possible applications of this material as a substrate for epitaxy of high T_c superconductors [1,2] and as a base material for an electrolyte for solid fuel cells [3–5]. It has been recently shown that the Czochralski grown $La_{1-x}Nd_xGaO_3$ mixed crystals exist in the full concentration range [6]. For composition $x=0.33$, they are perfectly lattice matched to YBCO superconductors. In addition, the temperature of the first-order phase transition, equal to $T_c=153°C$ in pure $LaGaO_3$, is increased in mixed crystals with $x=0.33$ to about 800°C, much above the epitaxial deposition temperature. This reduces the surface roughness caused by twinning associated with the phase transition [6].

The lanthanum gallate crystal belongs to orthorhombically distorted centrosymmetric $GdFeO_3$ type perovskite-like structure (room temperature space group *Pbnm*) [7]. Knowledge about the intrinsic defect structure of $LaGaO_3$ crystals is still quite limited. Recently we have studied properties of some defects in $LaGaO_3$ crystals using absorption, light-induced gratings, and photocurrent techniques [8]. It has been shown that several defect centers exist in these crystals. Close to room temperature some of these defects are stable and others are transient. The defect structure of the crystal is strongly affected by the crystal stoichiometry [9], annealing in various atmospheres and also by illumination of the crystal. Stable and transient photochromic processes have been detected under illumination with light of various wavelengths. Electronic hole transport has also been detected by light-induced gratings technique. It has been shown that the crystals contain some electronic traps, which strongly affect their optical and electrical properties.

The main aim of this work is to reveal the influence of those traps on photochromic properties of $LaGaO_3$ crystals. For this purpose, we have used thermally stimulated luminescence (TSL) and photoinduced absorption techniques. The emission spectra of TSL have also been studied in order to reveal the nature of the processes leading to TSL.

2. Experimental

The crystal 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 1400°C for several hours. Oxygen ions are known to be incorporated into the crystal in such a process [5]. The crystals were cut to form slabs of thickness between 0.5 and 1 mm and polished with diamond powders. The luminescence spectra of the crystals exhibited unintentional traces of Cr^{3+} ions (and also Nd^{3+} in some crystals). Electron probe microanalysis (EPMA) of the crystals shows some deviation from stoichiometric composition with a small excess of La over Ga [6]. This is due to faster evaporation of gallium from the melt.

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The absorption of the crystals has been measured with use of a Hitachi Perkin-Elmer model 340 spectrophotometer. Luminescence was excited by various argon-ion laser lines and recorded in a set-up with a GDM-1000 monochromator and a S-20 photomultiplier or with a Jobin-Yvon-Spex Triax 320 monochromator and a JY2000 CCD camera. The luminescence excitation spectra were measured with use of a xenon lamp filtered by a small crystal monochromator and detected with a CCD camera. The spectra have been corrected for quantum efficiency of the excitation and detection systems and for the penetration depth of the illumination due to strong absorption.

The decay kinetics of the luminescence were recorded with the use of a SR 430 multichannel scaler. The luminescence was excited by various argon-ion laser lines and chopped with a fast mechanical chopper with transient time shorter than 100 μs.

Transient-induced absorption was measured in a set-up 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:

$$\Delta K = \frac{1}{d} \ln \frac{T_1}{T_2} \tag{1}$$

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

For TSL measurements, the samples were loaded into a closed-cycle cryostat equipped with a temperature controller, which also allowed heating the samples with a constant (linear) temperature rate. After cooling to a temperature of about 10 K, the samples were illuminated by a 100 W xenon lamp. Then the samples were heated with a heating rate, which was equal typically to about 0.1 K/s. The TSL light was detected by a S-20 photomultiplier. TSL optical spectra have been measured with the use of a Jobin-Yvon-Spex Triax 320 monochromator and a JY2000 CCD camera. This system allows measurement of emission spectra in a very short time during the TSL experiments.

3. Experimental results

The results of the TSL experiment in the 50–300 K temperature range are presented in Fig. 1 for the as-grown and annealed in oxygen samples. Several TSL peaks are observed in the spectra. There is one dominant TSL peak, observed at $T_1 = 112$ K for both samples. Oxygen annealing removes some of the TSL peaks, observed at higher temperatures.

The TSL intensity, $I(T)$, as a function of temperature, T, is described by the following equation [10,11]:

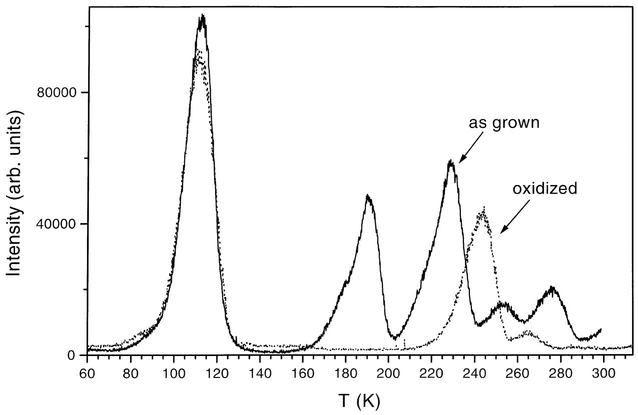

Fig. 1. The results of the thermally stimulated luminescence experiment in the 50–300 K temperature range for as-grown (solid line) and oxidized (dashed line) $LaGaO_3$ crystals.

$$I(T) = \sum_i A_i \cdot \omega_i \cdot \exp\left[\left(\frac{-E_i}{kT}\right) - \int_{T_0}^{T} \frac{\omega_i}{\beta} \exp\left(-\frac{E_i}{kT'}\right) \mathrm{d}T'\right] \tag{2}$$

where E_i is the activation energy of the trap i, k is the Boltzman constant, ω_i is the frequency prefactor, β is the heating rate, and A_i is a parameter. Computer fits of this equation to experimentally observed TSL curves yield the values of activation energies and frequency prefactors of each trap involved in the process. They are presented in Table 1 for both samples examined.

The crystals studied were unintentionally doped with a small amount of Cr^{3+} ions. They were detected in photoluminescence measurements at low temperature. Characteristic R-lines of Cr^{3+} luminescence were observed at $T = 10$ K around 727 nm, with a vibronic side-band at longer wavelengths [12]. The optical spectrum of TSL is localized close to the Cr^{3+} luminescence (with a maximum around 712 nm), and it could be easily mixed up with it, especially at higher temperatures, when the spectrum is broadened. However at low temperatures, the optical spectrum of TSL is well separated from the Cr^{3+} luminescence. The Cr^{3+} and optical spectra of luminescence

Table 1
Parameters of the TSL peaks for the $LaGaO_3$ crystals, as-grown and annealed in oxygen

Peak	As-grown sample			Annealed in O_2 sample		
	$T_{\max}$ (K)	E_i (eV)	ω_i (s^{-1})	$T_{\max}$ (K)	E_i (eV)	ω_i (s^{-1})
A	90	0.1	5.7×10^{3}	85	0.11	6.0×10^{6}
B	112	0.164	3.3×10^{5}	112	0.162	1.4×10^{7}
C	190	0.482	8.5×10^{10}			
D	230	0.716	8.2×10^{13}			
E	255	0.756	1.6×10^{13}	243	0.76	8.0×10^{14}
F	277	0.853	4.4×10^{13}	264	0.85	2.0×10^{15}

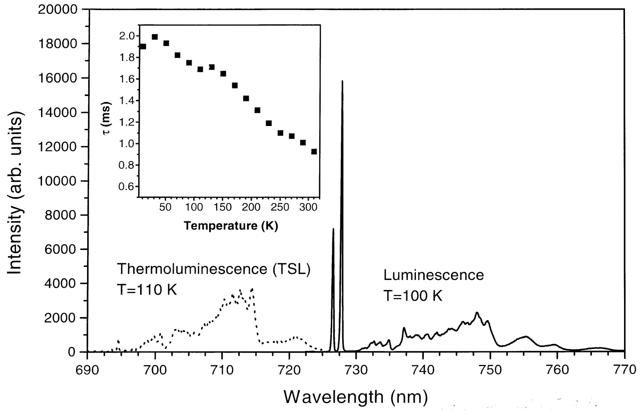

Fig. 2. The Cr^{3+} luminescence excited by the 457-nm Ar-ion laser line at temperature $T=100$ K and optical spectra observed in TSL experiments at temperature $T=110$ K; in the inset: temperature dependence of the photoluminescence decay times of the defect associated with TSL in the $LaGaO_3$ crystals.

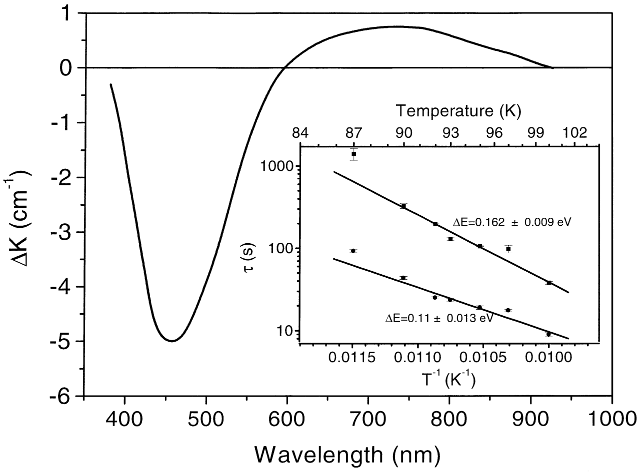

Fig. 4. The absorption changes induced in the oxidized $LaGaO_3$ crystals by the 488-nm argon-ion laser line at $T=100$ K. The inset shows the Arrhenius plot of the temperature dependencies of the decay times of the light-induced absorption changes in the $LaGaO_3$ as grown crystal.

associated with TSL process are presented in Fig. 2. The spectrum of optical emission, observed in the TSL process, is the same for each of the TSL peaks.

The emission detected in the TSL process can also be observed in the photoluminescence experiments. The decay kinetics of this luminescence are single-exponential. At low temperatures the decay time is equal to about 2 ms. Temperature dependence of the decay time is shown in the inset in Fig. 2.

On the other hand, in the crystals which are intentionally doped with a higher concentration of Cr^{3+}, the emission associated with those ions dominates the optical spectrum of the TSL, although the weaker luminescence with the peak at 712 nm is also observed in such samples.

In order to distinguish the spectral properties of both types of luminescence we have measured their photoluminescence excitation (PLE) spectra and the results are presented in Fig. 3. It can be seen that the excitation spectra of both types of luminescence are well separated from each other. The absorption spectrum of the as-grown crystal is also shown in this graph. It has a different shape from both PLE spectra. This means that defects different to those active in luminescence dominate the absorption spectrum of $LaGaO_3$ crystals.

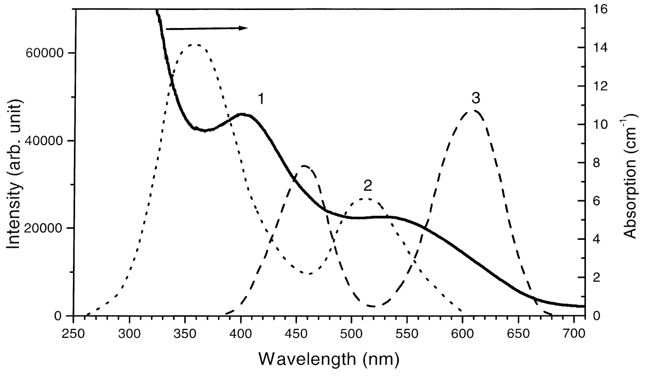

Fig. 3. Absorption spectrum of the as-grown $LaGaO_3$ crystal (line 1). Excitation spectrum of the Cr^{3+} photoluminescence (line 3) excitation spectrum of the recombination center associated with TSL (line 2).

The $LaGaO_3$ as grown crystals exhibit strong photochromic effects [8,13]. Some of those processes are stable at room temperature (i.e. light-induced changes of absorption are permanent or quasi-permanent at room temperature), and the others are transient. Lowering of the temperature stabilizes the transient absorption changes, making them permanent at low temperatures. The absorption changes, induced in the oxidized crystals by the 488-nm argon-ion laser line at $T=100$ K, are presented in Fig. 4. The bleaching of the crystal near 450 nm and increase in absorption with a maximum at 700 nm are simultaneously observed under the influence of such illumination. There is also a reverse process possible: the illumination of the crystal (previously illuminated in the 450-nm band) by the light with wavelength in the range of the 700-nm band decreases the intensity of this band and increases the absorption in the 450-nm band. The light-induced absorption changes decay with two-exponential type of decay kinetics. The temperature dependencies of the decay times are presented in the inset in Fig. 4 as the Arrhenius plot. The decay times are exponentially dependent on temperature:

$$\tau^{-1} = \tau_0^{-1} \cdot \exp\left(-\frac{\Delta E}{kT} \right) \quad (3)$$

where ΔE is the activation energy and k is the Boltzman constant. The activation energies of both components of the decay kinetics are equal to 0.11 and 0.16 eV.

4. Discussion of results

The regular Cr^{3+} ions are supposed to substitute for Ga^{3+} ions in the $LaGaO_3$ crystal. Therefore they experience a crystal field with a slightly distorted octahedral symmetry. In accordance with the crystal field theory [14], the excitation bands of the Cr^{3+} ions with peaks at 610 and 460 nm are associated with spin-allowed transitions between the $^4A_2$ ground level and the $^4T_2$ and $^4T_1$ excited levels, respectively. The Cr^{3+} luminescence occurs between the ^2E excited state and the ground state. The fit of the crystal field theory to the spectral positions of these levels yields the values of the Racah parameters for the isolated Cr^{3+} ions. They are equal to: $B=563$ cm^{-1}, $C=3151$ cm^{-1} and $Dq=1639$ cm^{-1}. Estimated this way, the Dq value is smaller than previously obtained by Ryba-Romanowski et al. [12]. However, it means that the isolated Cr^{3+} ions experience so-called strong crystal field (i.e. the ^2E level is a first excited state of the ion), in agreement with Ryba-Romanowski et al.

The TSL process in the $LaGaO_3$ crystal with a residual concentration of Cr^{3+} ions is associated with luminescence of an unknown defect. It emits light in a spectral range different to isolated Cr^{3+} ions in the $LaGaO_3$ host (Fig. 2). Moreover, its excitation spectrum differs strongly from the excitation spectrum of Cr^{3+} ions. The nature of the defects, which emit at 710 nm remains unknown. Possibly it is associated with Cr^{3+} occupying the La^{3+} position or with Cr^{3+} in the regular gallium position perturbed by a neighboring defect. The excitation spectrum of this luminescence with two broad bands resembles very much the Cr^{3+} excitation spectrum, although these bands are localized at different spectral regions than those for Cr^{3+} ions. Crystal-field symmetry of La^{3+} is different from Ga^{3+} ions, as well as their coordination numbers, equal to six for Ga and probably nine or 10 for La [15]. Therefore the position of the energy levels of Cr^{3+} ions substituting for La^{3+} cannot be calculated using the classical crystal-field theory of Tanabe-Sugano. Indeed, an attempt to fit this theory to the observed spectra gives unreasonable values for Racah parameters. A similar situation can occur if the Cr^{3+} substitutes for Ga site and is perturbed by a neighboring defect.

Luminescence decay times of the emission associated with the TSL recombination center are about 5–6 times shorter than the decay times of Cr^{3+} luminescence. This is another feature which distinguishes this luminescence from the luminescence of regular chromium ions in the $LaGaO_3$ crystals intentionally doped with Cr. However the temperature dependence of the luminescence decay times of this additional luminescence also resembles the temperature dependence of the Cr^{3+} emission [12].

Several trapping levels have been identified in the $LaGaO_3$ crystals in the TSL experiment (Fig. 1). They have activation energies in the range between 0.1 and 0.9 eV and different relative concentrations. The trap, denoted B, is a dominant one in both as-grown and oxidized samples. This center is relatively weakly affected by the annealing in oxygen. The traps denoted as C and D are removed from the crystals by the oxidizing process. Previously we have established that the annealing in oxygen atmosphere induces electrical hole transport in the examined crystals. It seems probable that the traps C and D are the electron traps, which are depopulated by incorporation of oxygen to the crystal, which act as acceptors.

The activation energies of the absorption decay kinetics in both light-induced bands are in a good agreement with the activation energies of traps A and B. Especially important is the trap B, since it is the dominant trap level in the crystals. Therefore we associate the A and B TSL peaks with the process of thermal relaxation of the defects responsible for the photochromic effect in the 450- and 700-nm bands. The holes photoexcited from deep photochromic centers are captured by the other deep centers and by shallow traps. Photoionization and retrapping of charges by deep centers result in changes of absorption in the 450- and 700-nm bands. The thermal release of holes from the shallow traps restore the population of holes on the deep photochromic centers. The excess of energy after recapture of hole by the deep center is transferred to the defect, which emits light in the TSL process. This way the activation energies found from the TSL experiment are equal to the value of the thermal energy barrier calculated from the temperature dependence of the decay times of the additional absorption of the photochromic centers. The photochromic processes and the main channels of excitation and recombination of the photochromic defects and a mechanism of the TSL are schematically depicted in Fig. 5.

In the crystals with a very small amount of Cr^{3+} ions, the TSL process preferentially proceeds through the defect, which emits light with a spectral maximum at 712 nm. Most probably this defect is located close to the traps involved in the TSL process. An increase in concentration of chromium ions in the crystals reduces the average distance between the defects active in the TSL process and the Cr^{3+} ions, substituting regular Ga positions in the host. Therefore the relaxation energy can also be transferred to them. This is the reason that, in the crystals with a high concentration of Cr^{3+}, the typical luminescence of Cr^{3+} ions is also observed in the TSL experiments.

5. Conclusions

The TSL and induced absorption experiments allow identification of the relaxation process of the photochromic effect in as-grown $LaGaO_3$ crystals. Low values of the energy barriers which govern the relaxation process make this photochromic effect stable only at low temperatures. Other photochromic effects are also observed in these crystals, which become stable at much higher temperatures

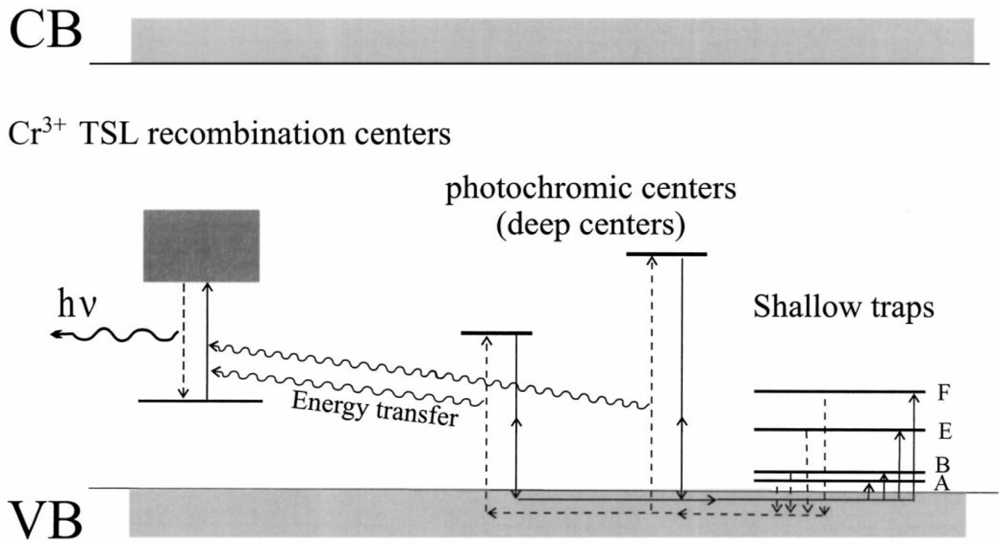

Fig. 5. The mechanism of photochromic processes, the excitation and relaxation channels of deep centers in oxidized $LaGaO_3$ crystals and the mechanism of TSL (see text).

[8]. It has been shown that in crystals with a residual concentration of chromium, the emitting defect in the TSL process is different from typical isolated Cr^{3+} ion in this host. Additional studies are necessary in order to identify fully the defect structure of $LaGaO_3$ crystals.

Acknowledgements

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