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Recharging Processes of Chromium Ions in Cr:SrGdGa₃O₇ and Cr:SrLaGa₃O₇ Single Crystals

Growth and recharging processes of chromium ions in SrGdGa₃O₇ and SrLaGa₃O₇ single crystals incorporated during growth or doping by diffusion (only for SrLaGa₃O₇ crystal) were analyzed. The annealing at 1000°C in air and ionizing with gamma rays (doses from 10³ to 10⁵ Gy) and protons (10¹⁴ cm⁻² only for SrGdGa₃O₇ crystal) were performed. Different kinds of chromium ions valency, from two to four, were found. Electron spin resonance measurements in the temperature range 5-300K with the use of Bruker spectrometer were also done.

Keywords: additional absorption, gamma exposure, proton irradiation, electron spin resonance

1. Introduction

Cr³⁺:SrGdGa₃O₇ crystals (Cr:SGGO) and Cr³⁺:SrLaGa₃O₇ crystals (Cr:SLGO) belongs to the family of alkaline and rare-earth gallates, which are described by general formula ABC₃O₇. They have the tetragonal gehlenite (Ca₂Al₂SiO₇) structure (space group P4₂m, D_{2d}³). Unit cell parameters of SLGO and SGGO are: a=0.8058 nm, c=0.5333 nm and a=0.79868 nm, c=0.5255 nm, respectively. These crystals can be doped by any of rare-earth elements (Ce to Eu instead of La and Tb to Lu instead of Gd). In addition, a part of Ga ions can be replaced by Cr ions. Bivalent Sr ions and trivalent rare-earth ions occupy equivalent crystallographic positions with stochastic distribution, therefore these materials exhibit some glass-like proper-ties. However, they show high thermal conductivity and other features characteristic for ordered crystals. Thus, this class of materials is very interesting for both basic research and laser technology (SCOTT et al.).

Some of the members of the family of compounds Nd³⁺: BaLaGa₃O₇ (Nd: BLGO) and Nd³⁺: SrLaGa₃O₇ (Nd: SLGO) were investigated elsewhere (RYBA-ROMANOWSKI et al. 1987, 1988, KACZMAREK et al.). Measurements of spectral and lasing characteristics of Nd:SGGO crystals doped with 1.2 at. % of Nd³⁺ and Cr:SLGO crystals doped with 0.1 at. % of Cr³⁺ were presented in (HANSON et al., HOFFMAN et al., DEMOS et al.). Spectroscopic characteristics (absorption at 300K and 77K) of Cr:SGGO and Cr:SLGO single crystals has been presented in (RYBA-ROMANOWSKI et al. 1997). It was found, that the color of the crystals is associated mainly with the absorption of Cr⁴⁺ ions that substitutes Ga³⁺ ions and structural defects resulting from stoichiometry deviations.

In the present paper changes in the valency of chromium ions in Cr:SLGO and Cr:SGGO single crystals under ionizing radiation and thermal annealing treatments are investigated.

2. Experimental

2.1. Crystal growth

Chromium doped SLGO and SGGO single crystals have been grown by the Czochralski method in an atmosphere of nitrogen with an admixture of 1% oxygen. Starting

concentrations of Cr in the melt were 0.05, 0.1 and 0.25 at. % with respect to Ga. Crystals with 18 mm diameter were pulled from a 40 mm diameter iridium crucible on <001> oriented seeds. The pulling rate ranged from 1.5 to 4 mm/h. Con-vox crystal - melt interface was kept during the whole crystal growth process.

Chemical composition of both crystals slightly differs (0.7 - 1.2 at. %) from stoichiometric one and therefore, they may be treated as solid solutions of gehlenites and SrGa_2O_4 . Uniform distribution of Sr, La/Gd and Ga along crystal growth direction has been confirmed by Electron Probe Microanalysis method. This fact implies that the starting melt composition was properly chosen and did not change during the crystal growth process. Chromium doped crystals are diachronic with blue color. The color intensity is correlated with Cr concentration.

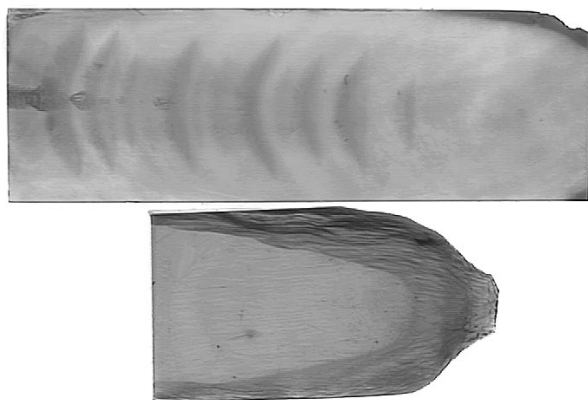


Fig. 1: Cr:SLGO single crystal as compared to Cr:SGGO single crystal

Fig. 1 present photos of the two investigated crystals with Cr concentration equal to 0.25 at. %. It can be seen, that Cr:SLGO crystal show non-homogeneity in Cr distribution along the crystal. Homogeneous Cr distribution was obtained for all SGGO crystals but in the SLGO only for 0.05 and 0.1 at. % Cr concentrations.

2.2 Diffusion process

SLGO plates embedded in the powdered Cr_2O_3 were heated in air at two temperatures: at 900°C for 20h and at 1000°C for 30h. After each diffusion process plates were irradiated by gamma's with a dose of 10^5 Gy.

2.3. Spectroscopic investigations of annealed and irradiated samples

Both sides polished samples 1-2 mm thick were optically investigated before and after the next treatments: γ -irradiation with doses 10^3 - 10^5 Gy from ^{60}Co source, proton irradiation's with an energy of 21 MeV and a fluency of 10^{14} cm^{-2} from C-30 cyclotron and thermal annealing at 1000°C in air for 3h. Eight samples of SGGO crystal were investigated: SRGD1...SRGD6, SGGOCR1 and SGGOCR2 and two of SLGO. The absorption spectra at 300K and 77K were measured using LAMBDA-2 Perkin-Elmer spectrometer. Additional absorption (AA) bands induced by gamma's, protons and annealing were defined as follows:

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

where: d is the thickness of the sample, T_1 , T_2 are the transmissions of the sample before and after irradiation or annealing, respectively.

2.4. ESR measurements

Electron spin resonance (ESR) spectra were recorded at 9.4 GHz, at temperature range from 4 K to 300 K using BRUKER ESP -300 X-band spectrometer.

3. Results and discussion

3.1. Cr:SGGO crystals

Fig. 2 presents ESR spectra for two positions of magnetic field vector with respect to c -axis of the Cr:SGGO crystal for microwave power $P=0.2$ mW and at a temperature of $T=5$ K. The width of the ESR spectra for Gd is about 450 mT and therefore chromium lines are not observed. Fig. 3 shows change in ESR signal amplitude v.s. temperature, from 5K to 300K. No lattice relaxation and pair of ions interaction is observed. For so great concentration of Gd^{3+} ions, by our opinion, the strong interaction between pairs of Gd^{3+} ions should exist.

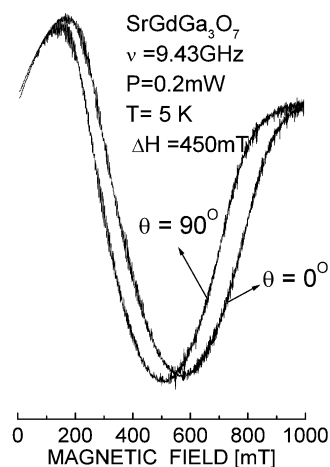


Fig. 2: ESR signal from Cr:SGGO crystal at 5K for two orientation of magnetic field with respect to c -axis: 90° and 0°

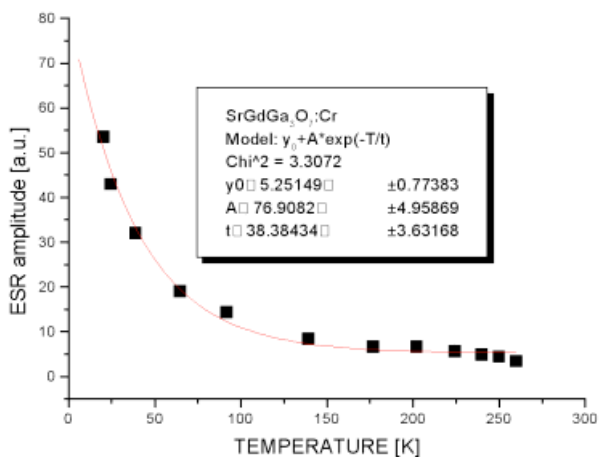


Fig. 3: Temperature dependence of ESR signal for Cr:SGGO crystal in the range of 5-300 K

In Fig. 4a absorption spectra for six investigated crystal samples are depicted. Fundamental optical absorption edge (FAE) begins at 250 nm and shifts towards the longwave direction by about 10 nm with an increase of Cr^{3+} concentration from 0.05 to 0.1 at. %. Clear bands can be distinguished, at: 253, 274, 306, 311, 450, 548, 600, 706 and 775 nm in UV and VIS region of absorption spectrum. The bands with maxima: 274, 306 and 311 are connected with Gd^{3+} ion in position of Ga^{3+} . Bands with maxima at: 548 and 600 nm one can be treated as transition inside Cr^{3+} ions, while 706 and 775 nm bands as transitions inside Cr^{4+} ions. The band at 253 nm is probably associated with non-controlled ions, e.g. Fe^{3+} , coming from Cr_2O_3 oxide, while the band at 450 nm with Cr^{2+} ions. The above assumption is confirmed by irradiation and annealing treatments of the investigated crystals, according to results

presented in Figs 4b, c. After γ -irradiation at 300 K at least three AA bands can be distinguished.

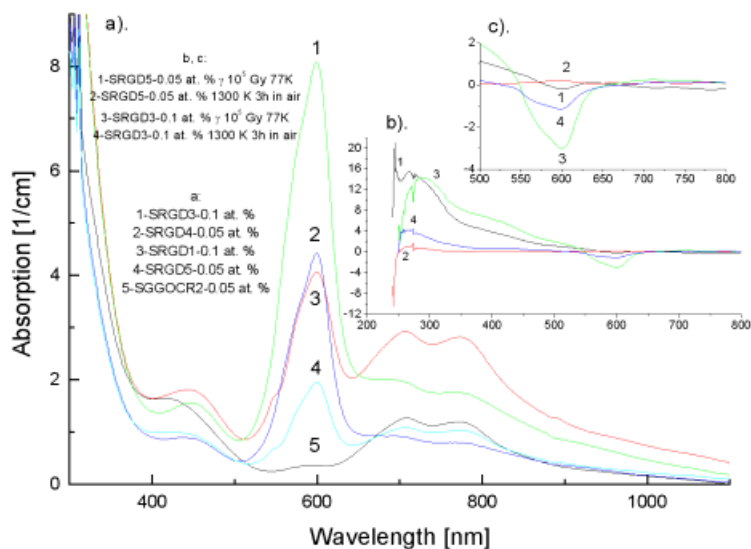


Fig. 4: Absorption (a) and AA (b, c) in Cr:SGGO single crystal after γ -irradiation with doses 10^3 - 10^5 Gy

The first one (about 16 cm^{-1} in intensity), in dependence on Cr concentration, is centered near 270 nm or 290 nm centered, for 0.05 and 0.1 at. %, respectively. This band is probably associated with $\text{Ga}^{3+} \rightarrow \text{Ga}^{2+}$ reaction, which leads to paramagnetic defect of G1 type, observed earlier for SLGO single crystal by Kaczmarek et al.

Second band, at 364 nm, in our opinion, is associated with oxide vacancies. Relative intensity of the two maxima clearly depends on dose value. With an increase of a dose from 10^3 to 10^5 Gy, intensity of the first maximum increases while that of the second diminishes. Similar results for Nd:SLGO single crystal were earlier obtained by Kaczmarek et al. Third band, at 600 nm, with values of AA < 0 correspond to a decrease in Cr^{3+} concentration.

Moreover, the wide AA bands with maxima at 706 and 775 nm are observed. They can be connected with a change in Cr^{4+} concentration. The γ -irradiation, performed at 77K does not introduce additional AA bands. Also an increase in AA intensity with respect to γ -irradiation at 300K is not observed. Accordingly to Fig. 4b, c annealing of Cr:SGGO crystals in air for 3h at 1000°C gives at least two AA bands, first at 270 nm and second at 600 nm. The second band can be connected with a change in Cr^{3+} concentration and effectively in Cr valency. For all the treatments changes near 450 nm band is also seen.

Among six investigated samples there are three the most characteristic: SRGD3 (0.1 at. % Cr; 8 cm^{-1} at 600 nm), SRGD6 (0.05 at. % Cr; 4 cm^{-1} at 600 nm) and SRGD5 (< 0.05 at. % Cr; 1.8 cm^{-1} at 600 nm). For SGDR3 specimen a decrease in Cr^{3+} concentration after both annealing and irradiation is observed which suggests that the main mechanism of valency change in chromium is ionization process of the type: $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$. So, in SRGD3 sample Cr^{3+} and Cr^{4+} ions may be present. For SRGD6 sample Cr^{3+} concentration increases after γ -irradiation which means that $\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$ reaction takes place, probably due to Compton effect. So, in SRGD6 sample Cr^{3+} and Cr^{4+} ions can be also present. For SRGD5 crystal an increase in Cr^{3+} and Cr^{4+} concentration after annealing process at 1000°C is observed which suggests the presence of Cr^{2+} ions and Cr^{3+} ions in the crystals. An ionization with gamma's leads to an opposite effect: $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$. So, in SRGD5 sample Cr^{3+} and Cr^{2+} ions should be present.

In Fig. 5 changes in absorption spectrum of Cr:SGGO crystal after γ -irradiation with doses of 10^3 and 10^5 Gy and protons with fluency of 10^{14} cm⁻² are presented. It can be seen from Fig. 5a that change in valency of chromium ions depend on value of dose and is greater for higher dose. After a time interval of 0.5 year from γ -irradiation with a dose of 10^5 Gy, intensity of AA bands is of the same order of magnitude as intensity of AA immediately after γ -irradiation with a dose of 10^3 Gy.

Moreover, in the range of 600 nm band no changes are observed, which means that recharging of chromium ions due to ionization is stable in time.

Fig. 5b show changes in absorption of Cr:SGGO crystal after proton irradiation. The changes are similar as for γ -irradiation.

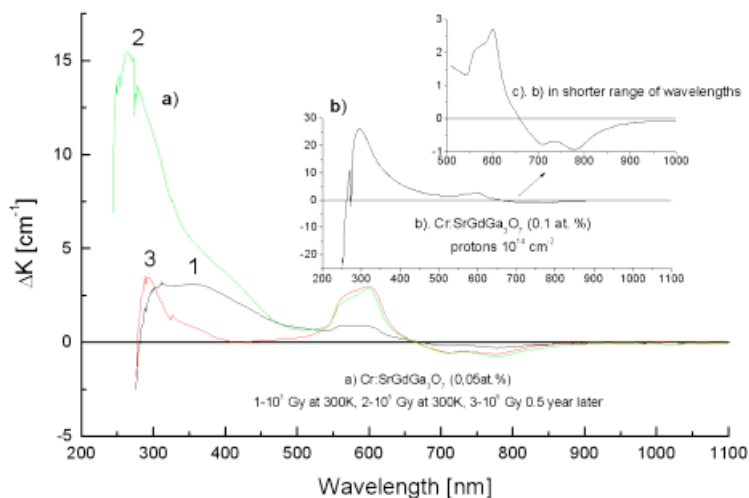


Fig. 5: AA bands in Cr:SGGO crystal for different doses of γ -irradiation and after relaxation in time for 0.5 year at 300K (a) and protons with a fluency of 10^{14} cm⁻² and energy of 21 MeV (b, c)

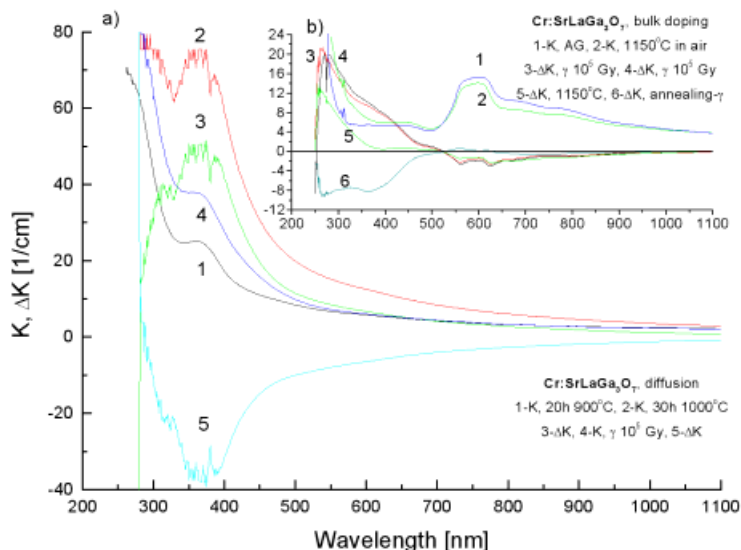


Fig. 6: Absorption and additional absorption in Cr:SLGO crystals doped during diffusion (a) and during growth (b)

3.2. Cr:SLGO crystals

ESR measurements did not show any Cr lines in these crystals, which was an unexpected effect. High level of defective structure of the crystals can be a possible explanation of this phenomenon.

Fig. 6 illustrates changes in valency of Cr ions in SLGO single crystal doped during growth as compared to SLGO specimens with Cr introduced by diffusion. According to Fig. 6a, during a diffusion process, Cr ions substitute mainly positions that give absorption characteristic for oxide vacancies (AA band at 364 nm). An increase of diffusion temperature leads to an increase in Cr concentration. Changes over 364 nm band after ionizing radiation process with gamma's are associated mainly with valency changes of Cr ions (also the band at ~280 nm is seen) and means that recharging process of the type: $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$ (ionization process) takes place. Excitation of the band with a wavelength of 355 nm gives emission at 458, 487 and 580 nm.

From Fig. 6b it is evident that for „as grown” Cr:SLGO crystal the same effect as for diffusive doping is observed, because annealing and irradiation processes give the same result: a decrease of Cr^{3+} concentration. Moreover, in contrary to Cr:SGGO crystal, the band at 364 nm is higher, which means stronger defective structure of Cr:SLGO lattice as compared to Cr:SGGO crystal (more oxide vacancies). This observation is in agreement with an earlier one describing difficulties in obtaining homogeneous distribution of Cr ions in the case of higher doping (0.25 at. %). Cr:SLGO crystal, for which results of investigations are presented in Fig. 6b was firstly γ -irradiated with a dose of 10^5 Gy, then annealed at 400°C, next again irradiated with the same dose and finally annealed for 17h in air at 1150°C. Curves 4 and 5 clearly show that the crystal is stable with respect to γ -irradiation.

Similarly as for Cr:SGGO crystals, bands at 548 and 600 nm are electron transition bands inside Cr^{3+} ion and bands at 706 and 775 nm are electron transition bands in Cr^{4+} ion. So, in „as grown” Cr:SLGO crystals Cr^{3+} and Cr^{4+} are simultaneously observed in optical absorption spectrum.

In Fig. 7 conductivity vs. temperature function is presented for Cr:SGGO, Cr:SLGO, Cr:SLGO (diffusion) as compared to Nd:SLGO and pure SLGO crystals. The band gap value calculated from the slopes of the presented curves is equal to about 2.4 eV. It can be seen that more defective structure shows Cr:SLGO crystal. Moreover, it is seen also that Cr:SGGO crystal show small dopant conduction.

4. Conclusions

In crystals grown at a relatively high pulling rate the fluctuations of chromium content were visible. To obtain crystals with uniform distribution of Cr it is necessary to pull them at a sufficiently low rate (below a certain critical value dependent on Cr content), <1.5 mm/h.

In the investigated Cr:SGGO crystals the presence of Cr^{2+} , Cr^{3+} and Cr^{4+} ions were detected. Their concentration depend on initial concentration of Cr^{3+} ions in the melt. Changes in absorption after annealing or ionizing treatments depends also on this initial concentration. For greater values of Cr^{3+} concentration $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$ reaction (ionization) during annealing and irradiation treatments are preferred. For lower values of Cr^{3+} concentration $\text{Cr}^{2+} \rightarrow \text{Cr}^{3+}$ reaction during annealing and $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ during irradiation are preferred. So, for greater Cr^{3+} concentration Cr^{3+} and Cr^{4+} ions are present in Cr:SGGO lattice, whereas for lower initial concentration of Cr^{3+} ions, Cr^{3+} and Cr^{2+} ions are seen in optical absorption spectrum.

In Cr:SLGO crystals transitions in Cr^{3+} and Cr^{4+} ions are seen in absorption spectrum.

After thermal or ionizing treatments ionization takes place as a result of reaction: $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$. The same phenomenon is observed for Cr:SLGO crystals doped by diffusion process. Cr ions locate mainly in lattice sites characteristic for oxide vacancies, formed in the crystal during growth process.

The structure of Cr:SLGO crystal is more defected than Cr:SGGO one. Probably, it is a reason why less Cr ions can be introduced into this crystal.

Absorption spectrum of Cr:SGGO crystal shows bands characteristic for Cr^{3+} ions also as opposite to previous investigations, where Cr^{4+} bands only were detected [8].

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References

- DEMOS, S.G., PETRICEVIC, V., ALFANO, R.R.: Phys. Rev. **B52**, (1995) 544
HANSON, F., DICK, D., VERDUN, H.R., KOKTA, M.: J. Opt. Soc. Am. **B8**(8) (1991) 1668
HOFFMAN, K.R., JIA, W.: Phys. Rev. **B49** (1993) 15505
KACZMAREK, S.M., KOPCZYNSKI, K., MIERCZYK, Z.: Proc. of SPIE, **2202** (1995) 182
RYBA-ROMANOWSKI, W., GOLAB, S., DOMINIAK-DZIK, G., PISARSKI, W.A., BERKOWSKI, M., FINK-FINOWICKI, J.: Proc. of Excited States Conference, Duszniki Zdr., 1997
RYBA-ROMANOWSKI, W., GUTOWSKA, M.U., PIEKARCZYK, W., BERKOWSKI, M., MAZUREK, Z., JEZOWSKA-TRZEBIATOWSKA, B.: J. of Luminescence, **36** (1987) 369
RYBA-ROMANOWSKI, W., JEZOWSKA-TRZEBIATOWSKA, B., PIEKARCZYK, W., BERKOWSKI, M.: J. Phys. Chem. Solids, **49** (2) (1988) 199
SCOTT, M.A. RUSSELL, D.L., HENDERSON, B., HAN, T.P.J., GALLAGHER, H.H.: J. of Crystal Growth, **183** (1998) 366

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