



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Optical Materials 24 (2003) 151–162

www.elsevier.com/locate/optmat

The presence of different oxidation states of cations in optical hosts on the base of $\text{Co}:\text{SrLaGa}_3\text{O}_7$

Sławomir M. Kaczmarek^a, Georges Boulon^{b,*}^a *Institute of Physics, University of Technology, Al. Piastów 48, 70-310 Szczecin, ZSO 22, Gwiazdzista 35, Warsaw, Poland*^b *Laboratoire de Physico-Chimie des Matériaux Luminescents, Université Claude Bernard Lyon 1, UMR CNRS 5620, Bat. A. Kastler, 10 rue Ampère, 69622 La Doue Villeurbanne, France*

Received 8 December 2002; accepted 24 February 2003

Abstract

Absorption, electron spin resonance (ESR) and RBS spectra were analyzed with the aim to define of oxidation states and sites of cobalt ions in gehlenite structure of $\text{SrLaGa}_3\text{O}_7$ single crystal. It was stated that cobalt $2+$ substitute octahedral sites, which is rather not expected result. ESR measurements have given values of g -factor for Co^{2+} ion equal to $g_{\parallel} = 2.26 \pm 0.04$, $g_{\perp} = 4.7 \pm 0.2$. $3+$ state of Co^{2+} ion in $\text{SrLaGa}_3\text{O}_7$ lattice one can obtain by irradiation it with γ -rays, electrons, protons or annealing at oxidizing atmosphere. We observed ${}^5\text{T}_2-{}^5\text{E}$ Co^{3+} transition band peaked at about 1200 nm. We observed also that color centers, which appeared after the irradiations, shift the short-wave absorption edge towards the longer wavelengths by a few hundreds nm. The changes are attributed to the lattice Ga^{2+} centers which are formed according to the reaction $\text{Ga}^{3+} + e^- \rightarrow \text{Ga}^{2+}$ with a spin of $S = 1/2$, $g_{\parallel} = 1.9838(5)$ and $g_{\perp} = 2.0453(5)$. Co-doping with vanadium reveals in higher radiation hardness of $\text{Co}:\text{SrLaGa}_3\text{O}_7$ crystal.

© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Detailed knowledge of the nature and number of activator sites in crystals doped with rare-earth and transition metal ions is of paramount importance in the design of luminescent devices and lasers based on these materials.

Crystals $\text{SrLaGa}_3\text{O}_7$ have the tetragonal gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) structure, space group $\text{P42}_1\text{m}$, D_{2d}^3 . The unit cell parameters are $a = 0.8058$ nm

and $c = 0.5333$ nm [1]. Gehlenites such as $\text{BaLaGa}_3\text{O}_7$ (BLGO) [1], $\text{SrLaGa}_3\text{O}_7$ (SLGO) [2,3] and $\text{SrGdGa}_3\text{O}_7$ (SGGO) were manufactured as matrix materials for potential laser and display applications.

The crystal is slightly birefringent with refractive indices practically constant in the transparency region, $n_{\perp} = 1.845$ and $n_{\parallel} = 1.850$ [4]. The extraordinary value of nonlinear refractive index $n_2 = (6.8 \pm 1) \times 10^{-20}$ m^2/W . The value show the crystal reveal promise as host for mode-locked lasers based on the Kerr-lens effect [5].

It has been found [6,7] that the Co^{2+} ions substitute octahedrally coordinated Sr^{2+} in the material. According to the crystal field theory energies

* Corresponding author. Fax: +33-4-72-43-11-30.

E-mail address: georges.boulon@pctl.univ-lyon1.fr (G. Boulon).

of the Co^{2+} system in octahedral symmetry depend on three parameters, the crystal field strength $10 Dq$ and two Racah parameters B and C . For $Dq/B < 2.1$ the ground state is the spin quartet 4T_1 as can be seen in Fig. 1a. In our previous paper

[6] where we have presented the absorption spectra of the $\text{SrLaGa}_3\text{O}_7:\text{Co}^{2+}$, we have estimated the quantity of $10 Dq$ and Racah parameters B and C ($10Dq = 4750 \text{ cm}^{-1}$, $B = 720 \text{ cm}^{-1}$ and $C = 3170 \text{ cm}^{-1}$). In octahedral coordination 4T_1 state splits

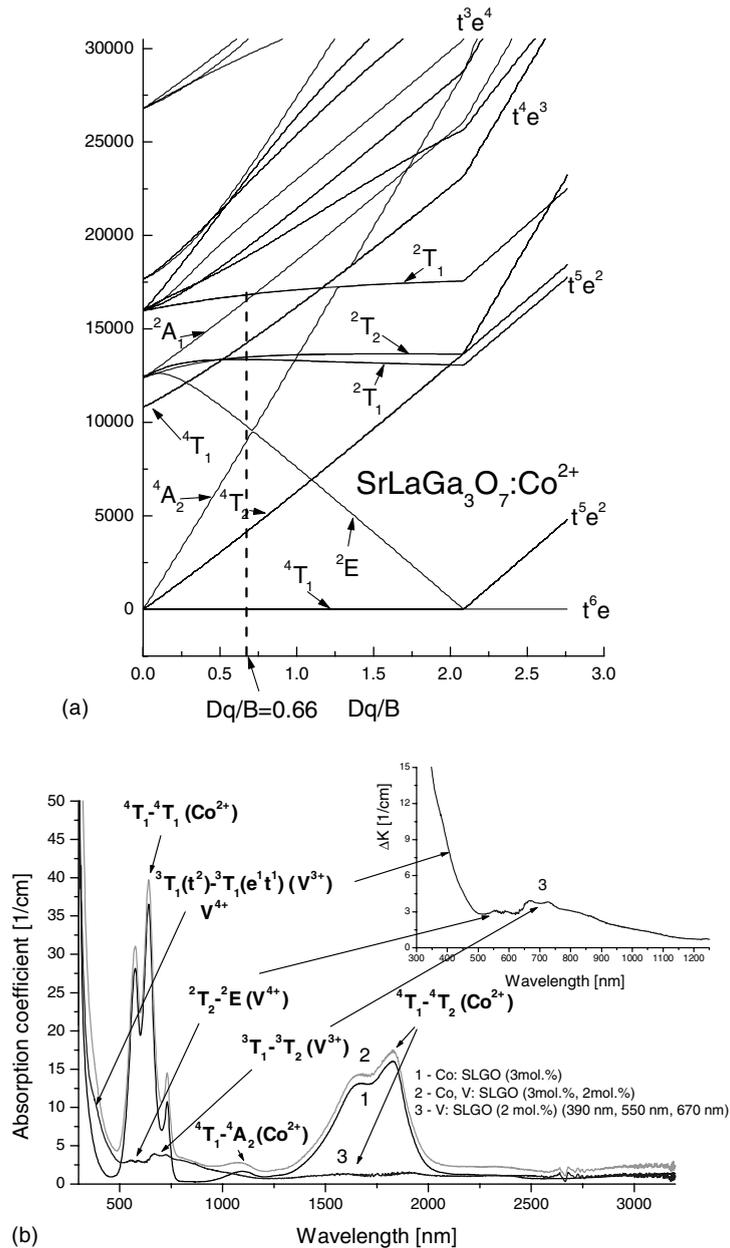


Fig. 1. (a) Tanabe–Sugano diagram of the Co^{2+} transition metal ion in $\text{SrLaGa}_3\text{O}_7$; (b) room temperature absorption spectra of Co:SLGO (1), Co, V:SLGO (2) and extracted differential spectrum of V:SLGO (3).

into 4T_1 , 4T_2 and 4A_2 states. The 4T_1 ground state is split by Jahn–Teller effect. The first excited state is 4T_2 energetically well separated from others. In the case of 4T_1 (F)– 4T_2 (F) transition it has been found that the Jahn–Teller effect in the 4T_1 ground state is responsible for its specific shape (double band) as well as for the fact that the bands are shifted with respect to the energy calculated in the framework of the crystal field model. The Jahn–Teller stabilisation energy has been estimated to be 507 cm^{-1} .

The excited 4T_1 electronic manifold is close to 2T_1 , 2T_2 , 2T_1 and 2A_1 doublets. Since all these states are mixed by the spin–orbit interaction one expects that excited electronic manifolds are rather complicated. In paper [7], the special attention was paid to the analysis of the structure of absorption band related to the 4T_1 (4F)– 4T_1 (4P) transition. The electronic configuration of 4T_1 (4F) ground state is t^6e while electronic configuration of 4T_1 (4P) excited state is t^5e^2 . This band is characterized by triple structure which some people assign to mixed Co^{2+} and Co^{3+} presence while in fact it is connected with the mixing of the above-mentioned excited states of Co^{2+} . Three line shapes of the 4T_1 – 4T_1 transition was related to the existence of Fano anti-resonance between the homogeneously broadened Jahn–Teller split 4T_1 state and sharp doublet 2T_1 , 2T_2 and 2T_1 states.

In this paper we analyze co-doping of the crystal with Co and V with the aim of improve of the charge compensation and improve of Co^{2+} incorporation. Moreover, we try to check whether is it possible to create Co^{3+} state in $\text{SrLaGa}_3\text{O}_7$ single crystal by some kind of treatment as e.g. annealing in the air and in oxygen and/or ionizing radiation by electrons, protons and γ quanta.

2. Experimental

2.1. Single crystal growth of Co:SLGO and Co, V:SLGO

Crystal growth by the Czochralski method and the crystal structure of these crystals have been reported in several works [1–3]. Pure single crystals

of $\text{SrLaGa}_3\text{O}_7$ and doped with cobalt and vanadium have been grown in the Institute of Physics Polish Academy of Sciences in Warsaw, using the Czochralski method in a nitrogen atmosphere and the floating zone method with optical heating in the air. High purity carbonate, SrCO_3 (4N5) and oxides La_2O_3 (5N), Ga_2O_3 (5N), Co_3O_4 (3N) and V_2O_5 (4N) were used as starting materials. Crystals were pulled from a 40 mm diameter iridium crucible in nitrogen atmosphere containing 1 vol.% of oxygen in the $\langle 001 \rangle$ direction on oriented seed crystals. The pulling rate was in the range 2–1 mm/h as the cobalt concentration in the melt was increased and V added. Starting concentrations of Co in the melt were: for Co:SLGO crystals–0.15 mol.% while for Co-V mixed crystal 3 mol.% of Co and 0.1 mol.% of V with respect to Ga. The floating zone method was employed in order to determine the maximum dopant concentration at which obtained crystals are still transparent. Since the crystal obtained by the floating zone method from the melt containing 4 mol.% of Co was nontransparent, we decided to limit the dopant concentration for the Czochralski method to 3 mol.%. Co-doping with vanadium using Czochralski method, due to charge compensation, was able up to 2 mol.% of V and 3 mol.% of Co.

Pure SLGO crystals were transparent, Co:SLGO crystals had a blue color the intensity of which increased with increasing dopant concentration, while V co-doping revealed in yellow admixing of the blue color of the crystal.

2.2. Annealing and irradiation treatments: spectroscopic measurements

Annealing was performed for three types: annealing in the air at 700 K for 3 h to remove color centers induced by γ -irradiation, annealing in the air at 1373 K for 16 h of “as-grown” Co:SLGO crystal to ionize Co^{2+} to Co^{3+} , and, annealing in the oxygen at 1323 K for 16 h of the crystal previously annealed in the air and the crystal previously irradiated with protons to prolongation the previous changes. Gamma doses up to 10^6 Gy from ${}^{60}\text{Co}$ source (1.25 MeV), electron fluencies up to 10^{17} el/cm² (1 MeV) from Van de Graaff

accelerator and protons fluencies up to 2×10^{14} from C-30 cyclotron (21 MeV) were used.

To study of optical properties of the Co:SLGO and Co, V:SLGO single crystals, polished in both sides, parallel-plate samples of thickness from 0.3 to 1 mm were prepared. The absorption spectra were taken at 300 K in the spectral range between 190 and 25 000 nm using LAMBDA-900 Perkin–Elmer and FTIR 1725 Perkin–Elmer spectrophotometers. Values of the additional absorption (ΔK factors) caused by the irradiation and annealing were calculated from the formula

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

where λ stands for wavelength, d for the sample thickness, T_1 and T_2 for transmission of the sample before and after given type of treatment, respectively.

2.3. ESR investigations

The samples, typically of $3.5 \times 3.5 \times 2$ mm, were measured in a BRUKER ESP-300 ESR spectrometer (X-band). The spectrometer was equipped with helium flow cryostat type ESR-900 Oxford Instruments. The ESR lines were observed before and after gamma exposure of 10^5 Gy dose in the temperature range from 4 to 300 K and microwave power from 0.002 to 200 mW. Moreover, the above investigations were performed for crystals annealed in the air at 700 K for 3 h.

2.4. RBS investigations

RBS/channeling experiments with He^+ ions were carried out in the 1 MeV Van de Graaff accelerator of the Institute of Nuclear Chemistry and Techniques in Warsaw at 300 K. The He^+ beam current was in the order of $I < 8$ nA with a typical energy of 1.7 MeV. The angle of the detector position was equal to $\Theta = 170^\circ$, charge was $Q = 20$ μC . We have registered RBS spectra of “random” type (for samples disorientation $-8^\circ < \beta < 8^\circ$) and “aligned” spectra for oriented samples.

3. Results and discussion

3.1. Crystal structure

The melilite structure can be described as formed by layers of large polyhedra (Thomson cubes) alternating along the c -axis, forming five-fold rings. These large sites have a very distorted square antiprism configuration, known as Thomson cubes. In the $\text{SrLaGa}_3\text{O}_7$ structure the Thomson cubes are filled statistically by Sr^{2+} ions and La^{3+} ions in the ratio 1:1 [8]. So, 4e site of C_s symmetry is equally occupied by Sr or La atoms but also by Ga ions.

In this structure Ga atoms occupy two crystallographically different positions. The Ga(1) (T_1 -type tetrahedron) atom with the symmetry S_4 is surrounded by four oxygen atoms at a distance of 1.837 Å in $\text{BaLaGa}_3\text{O}_7$ (BLGO). Type T_1 tetrahedra contain a half of the B-coordinated Ga ions. The type Ga(2) (T_2 -type tetrahedron) atom occupies a site of the m symmetry and is coordinated by two oxygen atoms equidistant at 1.859 Å and by two others at 1.833 Å and 1.791 Å in BLGO [1]. The type T_2 tetrahedra contain the other half of the B-coordinated Ga ions and all of the C-coordinated Ga ions. The T_2 tetrahedra are distorted and are linked to each other at one corner forming pairs of pyramids having one vertex along the optical axis. These tetrahedral are subjected to a dominant C_{3v} distortion. A weaker perturbation reduces the local symmetry to C_s [8].

3.2. Absorption measurements

In Fig. 1b, one can see absorption spectra of the obtained crystals: Co:SLGO (3 wt.%) and Co, V:SLGO (3 wt.%, 2 wt.%). We observed the fundamental absorption edge (FAE) of the crystal being dependent on the dopant concentration. For concentrations of Co ions changing from 0.15 up to 3 mol.% the value of the FAE changed from 260 to 295 nm. In the case of Co, V:SLGO (3 mol.%, 2 mol.%) crystal it was equal about 300 nm.

The main features of the absorption spectra of Co:SLGO and Co, V:SLGO consist of some octahedrally coordinated, Co^{2+} related absorption bands: double band in the IR region (5000–7500

cm^{-1} - ${}^4\text{T}_1$ - ${}^4\text{T}_2$ single-electronic spin allowed transition), a triple band in the visible region (12500–20000 cm^{-1} - ${}^4\text{T}_1(\text{F})$ - ${}^4\text{T}_1(\text{P})$ single-electronic spin allowed transition), and a small bump between them related to double-electronic spin allowed ${}^4\text{T}_1$ - ${}^4\text{A}_2$ transition.

The shape of the absorption spectrum is somewhat only dependent on the V presence. As regard to vanadium co-doping (see curve 3, being only extracted differential spectrum of V:SLGO crystal), three bands peaked at about 390, 550 and 670 nm indicate clearly that vanadium is incorporated in more than one valency state. The ground state of trivalent vanadium is ${}^3\text{T}_1$ and two strong absorption bands associated with allowed transitions to the ${}^3\text{T}_2$ and ${}^3\text{T}_1$ excited states are expected in visible. Tetravalence vanadium is iso-electronic to Ti^{3+} and has d^1 electronic configuration. Its free ion ground state ${}^2\text{D}$ splits in octahedral field into the ${}^2\text{T}_2$ ground state and a single excited the ${}^2\text{E}$ state. Corresponding absorption appears in the blue-green region and may form a double band associated with a Jahn–Teller distortion [9].

We assume that the absorption spectra presented in Fig. 1b are due to V^{3+} (${}^3\text{T}_1$ - ${}^3\text{T}_1$ and ${}^3\text{T}_1$ - ${}^3\text{T}_2$, 390 nm and 670 nm, respectively) and V^{4+} (${}^2\text{T}_2$ - ${}^2\text{E}$, 550 nm). Since the bands are shifted towards larger wavelengths as compare to e.g. V:LaGaO₃ [10], we suppose that vanadium ions are placed in octahedral sites with a weaker crystal field, as e.g. strongly distorted Ga(2) sites of C_s symmetry. Photoluminescence measurements have not shown any emission from both vanadium and cobalt ions up to 1700 nm. Vanadium emission may not be observed due to the strong absorption of Co^{2+} , while Co^{2+} emission is expected to arise in the middle infrared range (about 4 μm).

The absorption spectra of Co^{3+} in octahedral coordination depends on the strength of the crystal field. In a weak crystal field the ground state is the ${}^5\text{T}_2$ quintet and the corresponding spectrum would then consist of one band associated with the allowed ${}^5\text{T}_2$ - ${}^5\text{E}$ transition. In a strong crystal field the ground state is the nonmagnetic ${}^1\text{A}_1$ state and two absorption bands in the visible, associated with allowed ${}^1\text{A}_1$ - ${}^1\text{T}_1$ and ${}^1\text{A}_1$ - ${}^1\text{T}_2$ transitions are expected to appear [11]. To obtain some kind of Co^{3+} absorption we performed annealing of the

Co:SLGO crystal in the air for 16 h, in oxygen for 16 h and also underwent the crystal to different type of ionizing radiation.

Fig. 2 presents absorption spectrum of “as-grown” (a) and additional absorption spectra (b)–(d) of Co:SLGO (2 mol.%) single crystal after γ -irradiation with a dose of 10^5 – 10^6 Gy (b), annealing in the air for 16 h and additional annealing of the same sample in oxygen for subsequent 16 h (c) and irradiation with 1 MeV electrons with a fluency of 10^{17} el/cm² (d). All these treatments were performed for different samples of the same thickness and Co concentration. As one can see three main features one can distinguish: strong additional absorption in the range of the FAE, negative additional absorption (bleaching) in the range of ${}^4\text{T}_1$ - ${}^4\text{T}_1$ and ${}^4\text{T}_1$ - ${}^4\text{T}_2$ transitions, and, proportional to a gamma quanta dose and a time of annealing in the air and oxygen, positive additional absorption with a maximum at about 1200 nm. Changes in the range of ${}^4\text{T}_1$ - ${}^4\text{A}_2$ transition (1098 nm) are nondistinguishable due to strong changes in the absorption near 1200 nm band.

When one irradiate of the crystal with protons and next anneal in oxygen, we can observe the same changes as above mentioned. The results of the experiment are presented in Fig. 3, where one can compare additional absorption bands after proton irradiation with a fluency of 2×10^{14} prot/cm² (b) and subsequent annealing of the same sample in oxygen for 16 h (c) with an absorption of “as-grown” Co:SLGO crystal (a).

So, from Figs. 2 and 3 we can conclude, that independently on the kind of the treatment: irradiation, annealing, all the changes are assigned to the Co valency change (ionizing of Co^{2+} to Co^{3+}) and the second type of valency change, namely $\text{Ga}^{3+} \rightarrow \text{Ga}^{2+}$ [12], associated with strong additional absorption in the range of the FAE. The latter conclusion can be explained by means of the following process: Ga^{3+} ion captures the electron which was knocked out from O^{2-} ion by γ or proton irradiation and in a consequence, Ga^{2+} paramagnetic center is formed with a spin value equal to $S = 1/2$. The process can be illustrated by the following reactions: $\text{O}^{2-} + \gamma \rightarrow \text{O}^{1-} + e^-$; $\text{Ga}^{3+} + e^- \rightarrow \text{Ga}^{2+}$. Fig. 4 shows complexes of $(\text{Ga}-\text{O})^{1-}$ in SLGO structure after different types

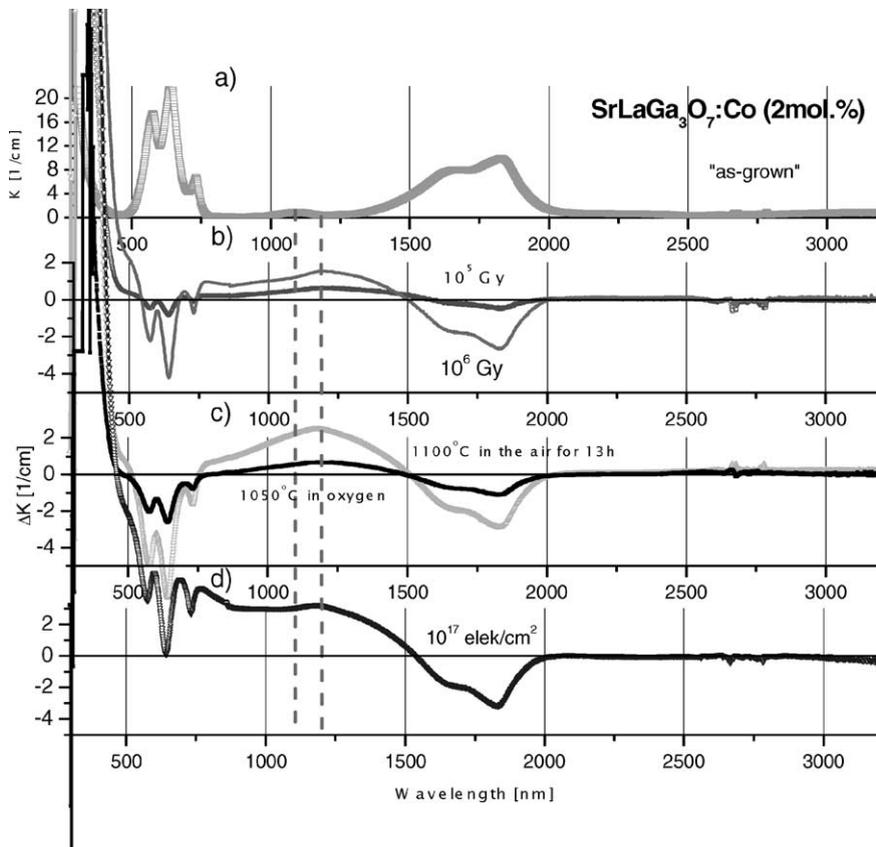


Fig. 2. Absorption (a) and additional absorption (b)–(d) of Co:SLGO (2 mol.%) single crystal after γ -irradiation with a dose of 10^5 and 10^6 Gy (b), annealing in the air and subsequent annealing in oxygen (c) and irradiation with 1 MeV electrons with a fluency of 10^{17} el/cm².

of the treatment. In paper [12], we have shown that this kind of radiation defect does not depend on the kind of doping of the SLGO crystal.

If we compare transmission of the Co:SLGO (2 mol.%) “as-grown” single crystal with transmissions of the crystal after different kind of the treatments described in Fig. 2, then one can conclude that this kind of the radiation defect shifts FAE towards longer wavelengths proportionally to γ -, proton, electron dose/fluency and time of annealing in the air or oxygen. The wavelength for which the transmission value reach the level of 0.001 was taken as a short-wave absorption edge. As seen from Fig. 5a and b, this edge became shifted with the increase of the γ -irradiation dose towards the longer wavelengths. The quantity of

this shifting one can define radiation hardness of a given crystal. In Fig. 5 we compare two investigated crystals: Co:SLGO (3 mol.%) (a) and Co, V:SLGO (3 mol.%, 2 mol.%) (b). As one can see higher radiation hardness reveals vanadium co-doped Co:SLGO single crystal. It is obviously expected result because the co-doped with vanadium crystal reveal higher charge balance then Co:SLGO one.

Also values of additional absorption of Co, V:SLGO after mentioned above treatments are much lower (two times) as compare to Co:SLGO crystal. So, one can state, co-doping with vanadium increase radiation hardness of the crystal.

Time quenching measurements performed for the above mentioned radiation defect obtained

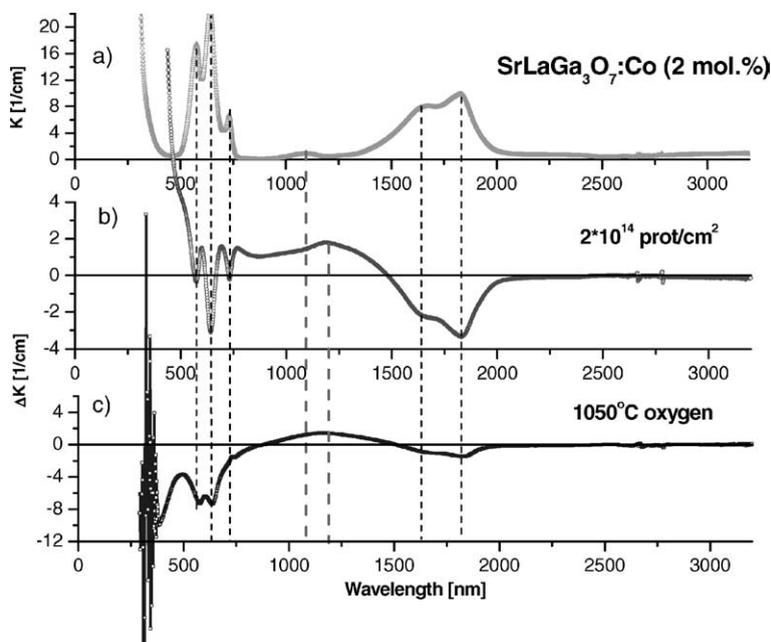


Fig. 3. Absorption of “as-grown” (a) and additional absorption of Co:SLGO (2 mol.%) after proton irradiation with a fluency of 2×10^{14} prot/cm² (b) and subsequent annealing of the same sample in oxygen for 16 h (c).

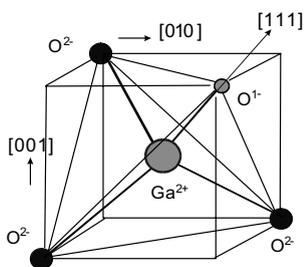


Fig. 4. Complexes of $(\text{Ga-O})^{1-}$ arising in SLGO structure (T_1 tetrahedron) after γ -, proton, electron irradiation or annealing in the air or oxygen.

after 10^5 Gy irradiation have shown that the value of the time is as high as 400 h.

To perform analysis of the valency states of Co in SLGO crystals we can compare absorption and changes in the absorption after annealing in oxygen with corresponding absorption spectrum of Co in other host, e.g. $\text{Li}_2\text{B}_4\text{O}_7$. It is presented in Fig. 6.

In Fig. 6 one can see absorption of Co: $\text{Li}_2\text{B}_4\text{O}_7$ glass obtained in the oxidizing atmosphere (pos-

sible presence of Co^{3+} and Co^{2+} states) (1), absorption of Co:SLGO (2 mol.%) (2), absorption of Co:SLGO (2 mol.%) after annealing in the air for 16 h (3) and additional absorption of the crystal after this annealing. One can observe characteristic bleaching reported previously for Co^{2+} absorption bands and additional absorption band peaked at about 1200 nm (curve 4) which we assign to Co^{3+} absorption. Because the band is single one we conclude that it is attributed to ${}^5T_2 \rightarrow {}^5E$ transition of Co^{3+} in octahedral weak field position. Moreover, using annealing in oxygen as the best effective ionization process one can not obtain more ionized Co ions than a half of all.

When we take into account that two main positions in the SLGO lattice preferred by Co^{2+} ions are Sr^{2+} and La^{3+} , then we can conclude that the only one of the positions is preferred for Co^{3+} creating, and, it seems that this is La^{3+} position. It explains the fact that total quantity of Co^{3+} ions may be only a half of all cobalt ions (in the SrLa-Ga₃O₇ structure the Thomson cubes are filled statistically by Sr^{2+} ions and La^{3+} ions in the ratio 1:1). So, Co^{3+} :SLGO crystal one can obtain after

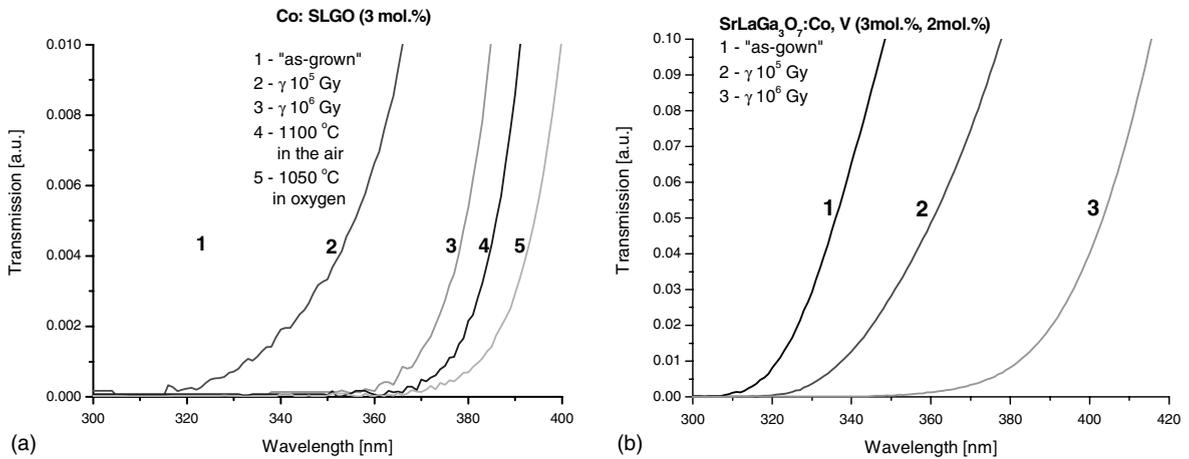


Fig. 5. (a) Change in the position of FAE of Co:SLGO (3 mol.%) after different types of treatments: (1) "as-grown"; (2) γ 10^5 Gy; (3) γ 10^6 Gy; (4) 1100 °C in the air; (5) 1050 °C in oxygen. (b) Change in the position of FAE of Co, V:SLGO (3 mol.%, 2 mol.%) after different types of treatments: (1) "as-grown"; (2) γ 10^5 Gy; (3) γ 10^6 Gy.

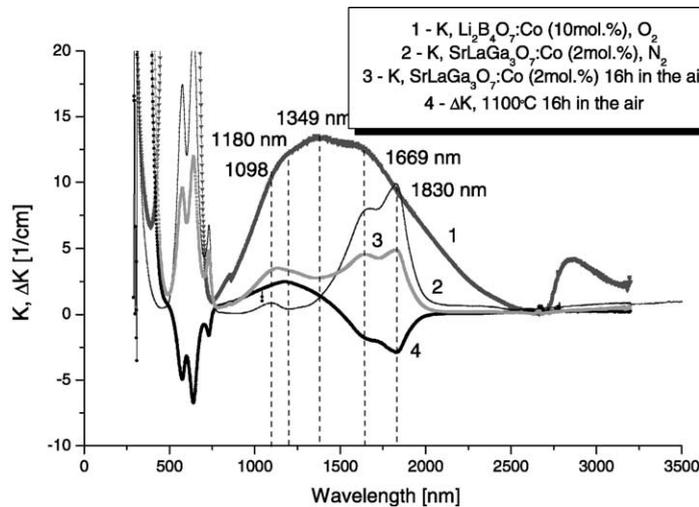


Fig. 6. Comparison of the absorption between "as-grown" Co:Li₂B₄O₇ (10 mol.%) (1), "as-grown" Co:SLGO (2 mol.%) (2), Co:SLGO (2 mol.%) after annealing in the air for 16 h (3) and additional absorption after this annealing (4).

some kind of ionizing treatment including annealing in the air and in oxygen.

3.3. ESR spectra and their analysis

The ESR spectra were observed at temperatures from 4.2 to 12.4 K. No ESR lines that could be

attributed to Co²⁺ pairs were observed. The spectrum consists of eight hyperfine structure components due to Co⁵⁹ nuclear spin $I = 7/2$. Fig. 7 shows typical ESR spectra of Co²⁺ for the magnetic fields applied perpendicular and parallel to the c -axis direction and for concentration of Co²⁺ ions 2 mol.%. The group of the observed

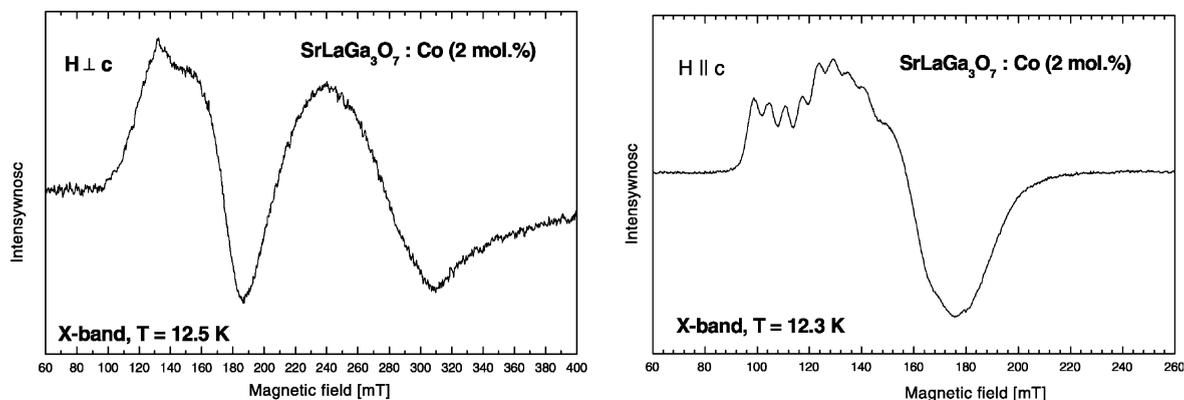


Fig. 7. Typical ESR lines of Co:SLGO single crystal for two cases $H_{\perp c}$ and $H_{\parallel c}$ and Co^{2+} concentration 2 mol.%.

lines is interpreted as a consequence of the transition between the lowest Kramers doublet ($M_s = \pm 1/2$) levels.

The observed resonance signal is very anisotropic. The positions of experimental lines can be described by the spin–Hamiltonian of tetragonal symmetry with an effective spin $S = 1/2$:

$$\hat{H} = g_{\parallel} \mu_B H_Z \hat{S}_Z + g_{\perp} \mu_B (H_X \hat{S}_X + H_Y \hat{S}_Y) \quad (2)$$

where μ_B —Bohr magneton, $g_{\parallel} = 2.26 \pm 0.04$, $g_{\perp} = 4.7 \pm 0.2$, H —magnetic field and S —electron spin. The obtained ESR data do not indicate presence of Co^{3+} ions.

The intensity of ESR lines changes after annealing of the crystal in the air and after ionization using γ -quanta, protons or electrons in such a way that relative intensity of ESR line is smaller one. This confirms supposition about ionization process during annealing treatment of Co:SLGO sample.

Fig. 8 presents angle dependencies of ESR lines. As it is seen there are three different lines distinguishable corresponding to the three octahedral nonequivalent positions of Co^{2+} ions in SLGO lattice two of them being Sr and La positions. It is possible that some of Co^{2+} ions locates at tetrahedral Ga^{3+} positions (for this case fine structure from $3/2$ spin should be observed and g -factor should be equal to about 2). But we observed only a weak one signal in the range of $g = 2$. Bearing in the mind that some of Ga(2) positions may take C_s

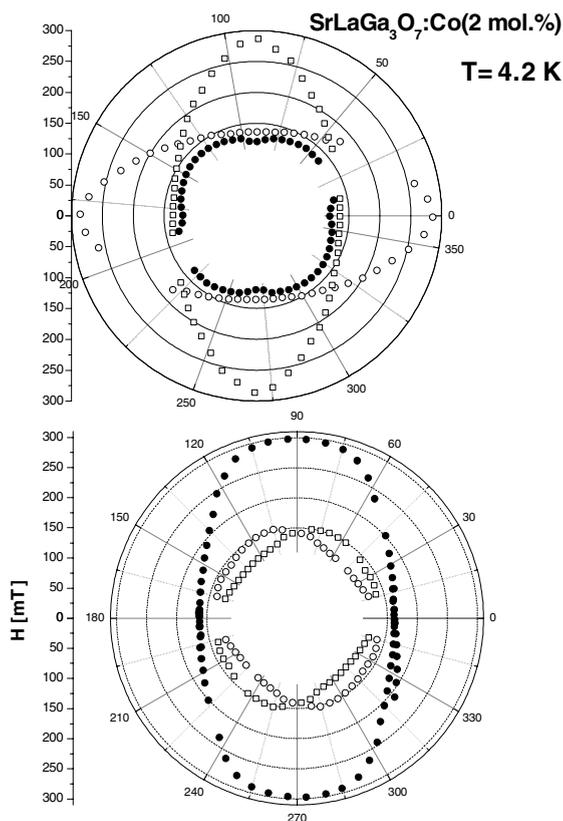


Fig. 8. Angular dependencies of ESR lines of Co:SLGO single crystal for two perpendicular directions.

symmetry, all the three lines seen in the angle dependence are now described.

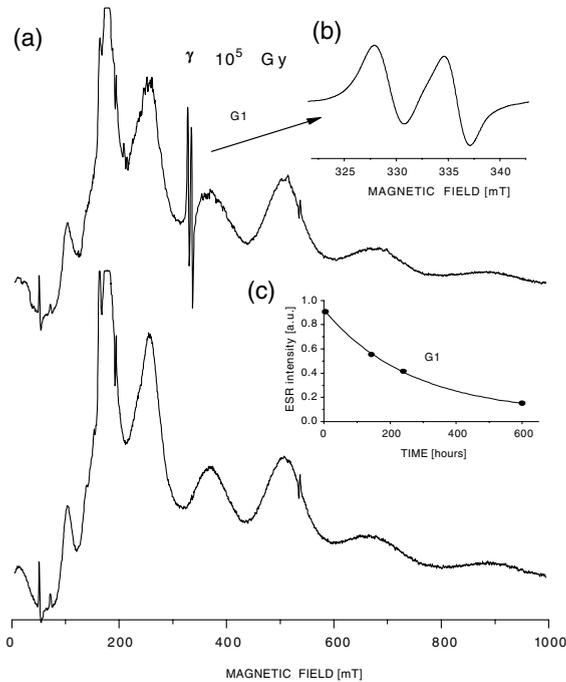


Fig. 9. ESR spectrum for SLGO crystal before and after γ -irradiation with the dose of 10^5 Gy: (a) ESR spectra before and after γ -exposure; (b) G1 defect in SLGO crystal and (c) time quenching of G1 defect. Fitting was performed for the curve: $y = y_0 + A_1 * \exp(-(x - x_0)/\tau)$, where $x_0 = 0$, $y_0 = 0.06245$, $\tau = 264\text{h}$, $A_1 = 0.86$ and $\chi_{\text{sqf}} = 7.516 \times 10^{-5}$.

ESR measurements revealed also that after 10^5 Gy γ exposure of SLGO undoped and Co doped (2 mol.%) crystal an anisotropic spectrum is observed. This spectrum has two lines with linewidth $\Delta H_{\text{pp}} = 3$ mT, marked as G1 in Fig. 9. From angular dependencies registered for the paramagnetic radiation defect introduced to the crystal by γ -, proton, electron or annealing treatments we obtained $g_{\parallel} = 1.9838(5)$ and $g_{\perp} = 2.0453(5)$ [12].

After annealing the crystals in the air at 700 K for three hours mentioned above lines disappear. Time quenching value of the paramagnetic center (Fig. 9c) very well correspond to time quenching value of the strong additional absorption band in the range of FAE we described in optical investigations. So, one can conclude that the paramagnetic defect is responsible for the shifting of the FAE of Co:SLGO single crystal towards larger wavelengths with increase of a dose/fluency and a time of annealing treatment.

3.4. RBS spectra and their analysis

We have performed irradiation of the crystals with α -particles registering RBS-spectra. Typical random and aligned spectra are presented in Fig. 10. As one can see only La, Sr and Ga ions are

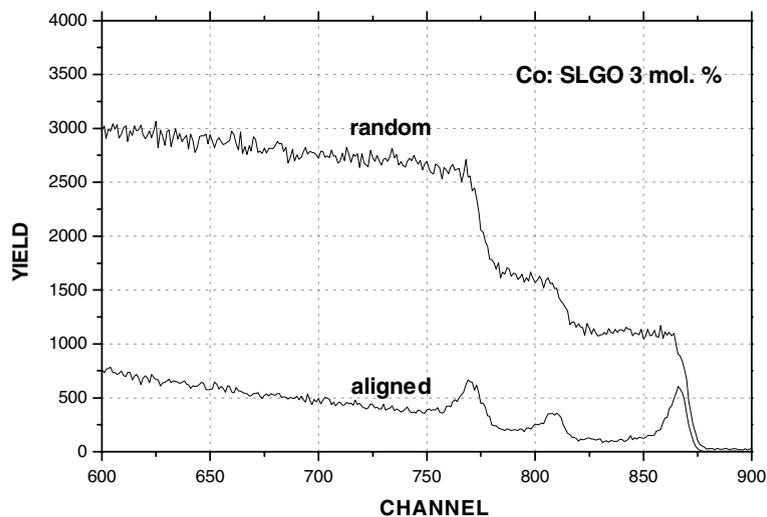


Fig. 10. Random and aligned spectra of Co:SLGO (3 mol.%).

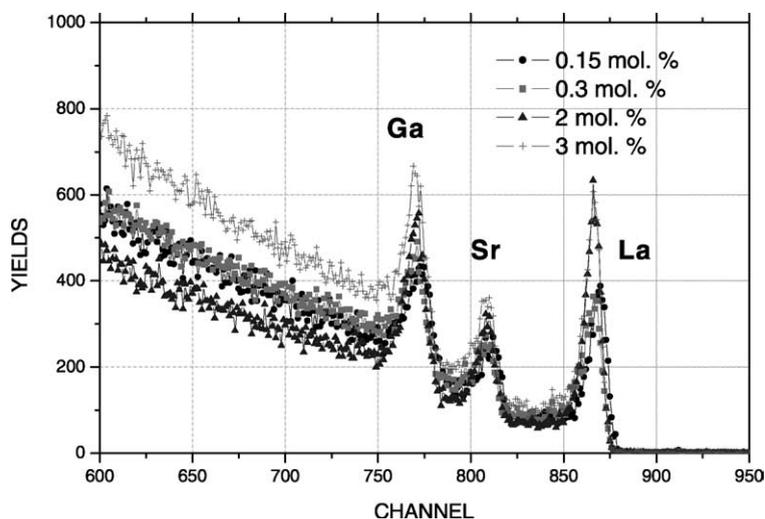


Fig. 11. Aligned spectra of all obtained crystals.

present in channels of the crystal. There is not seen cobalt ions. So, one can conclude, cobalt ions are incorporated mainly at site positions.

Fig. 11 shows aligned spectra of all obtained Co:SLGO crystals (concentrations from 0.15 to 3 mol.%). As one can see, for low concentrations of Co ions, Sr and La sites are substituted by Co equivalently. The situation changes for highly (more than 2 mol.%) doped crystals when almost twice increase is observed in the quantity of La ions in the channels. There is also observed increase in the presence of Ga ions in the channels with Co concentration. So, one can state that positions of Co ions in the SLGO lattice strongly depend on the concentration of Co and Sr, and, La positions stay nonequivalent in the case of high doping.

4. Conclusions

The main features of the absorption spectra of Co:SLGO and Co, V:SLGO consist of some octahedrally coordinated, Co^{2+} related absorption bands: double band in the IR region ($5000\text{--}7500\text{ cm}^{-1}$ ${}^4\text{T}_1\text{--}{}^4\text{T}_2$ single-electronic spin allowed transition), a triple band in the visible region ($12500\text{--}20000\text{ cm}^{-1}$ ${}^4\text{T}_1(\text{F})\text{--}{}^4\text{T}_1(\text{P})$ single-electronic spin allowed transition), and a small bump between

them related to double-electronic spin allowed ${}^4\text{T}_1\text{--}{}^4\text{A}_2$ transition.

The shape of the absorption spectrum of Co, V:SLGO single crystal is somewhat only dependent on the V presence. As regard to vanadium co-doping, three bands peaked at about 390, 550 and 670 nm indicate clearly that vanadium is incorporated in more than one valency state. We assigned 390 and 670 nm bands to V^{3+} and 550 nm band to V^{4+} .

$3+$ state of Co one can obtain by irradiation of Co:SLGO single crystal with γ -rays, electrons, protons or annealing at oxidizing atmosphere. We observed ${}^5\text{T}_2\text{--}{}^5\text{E}$ Co^{3+} transition band peaked at about 1200 nm and simultaneous decrease in the absorption (bleaching) in the range of ${}^4\text{T}_1\text{--}{}^4\text{T}_2$ and ${}^4\text{T}_1\text{--}{}^4\text{T}_1$ transitions of Co^{2+} . This band correspond to weak field octahedral position of Co^{3+} ion.

ESR measurements have given values of g -factor for Co^{2+} ion equal to $g_{\parallel} = 2.26 \pm 0.04$, $g_{\perp} = 4.7 \pm 0.2$. RBS spectra have shown that Co^{2+} ions substitute mainly at site positions of Sr and La. Moreover, it was found that positions of Co ions in the SLGO lattice strongly depend on the concentration of Co. Sr, and, La positions stay nonequivalent in the case of high Co doping.

After annealing in the air, in oxygen and after irradiation with γ -quanta up to 10^6 Gy, protons

2×10^{14} protons/cm² and 1 MeV electrons of 10^{17} el./cm² fluency, in the Co:SLGO and Co, V:SLGO crystals, there arises also color centers which shifts FAE towards longer wavelengths by a few hundreds nanometer. The changes are attributed to the lattice Ga²⁺ centers which are formed according to the reaction $\text{Ga}^{3+} + e^{-} \rightarrow \text{Ga}^{2+}$ with a spin of $S = 1/2$, $g_{\parallel} = 1.9838(5)$ and $g_{\perp} = 2.0453(5)$.

Co-doping with vanadium reveals in higher radiation hardness of Co:SrLaGa₃O₇ crystal.

Annealing of the gammas and protons irradiated crystal with doses up to 10^6 Gy and 10^{13} – 10^{14} particles/cm², respectively, at 700 K for 3 h, causes disappearance of the produced color centers.

The above results can be explained as follows. For given growth conditions (e.g. growth method, purity of the starting material, growth atmosphere and technological parameters) some definite subsystem of point defects appears in the crystal (e.g. doping ions, vacancies or interstitial defects). At the end of the growth process it is electrically balanced and is left in a metastable state. Some external factors, like irradiation or thermal processing, may lead to the transition of this subsystem from one metastable state to another. During this transition point defects may change their charge state.

Acknowledgements

We would like to acknowledge to Prof. M. Berkowski from the Institute of Physics, Polish Academy of Sciences for SLGO and Co, V:SLGO crystals, to Dr. P. Aleshkevich, from the same institute for ESR measurements, to Dr. M. Kwasny from the Institute of Optoelectronics MUT for spectroscopy measurements and to Dr. Warchol

from the Institute of Nuclear Chemistry and Techniques in Warsaw for RBS measurements.

References

- [1] M. Berkowski, M.T. Borowiec, K. Pataj, W. Piekarczyk, W. Wardzyński, *Physica* 123B (1984) 215–219.
- [2] A.A. Kamiński, E.L. Belokoneva, B.V. Mill, S.E. Sarkisov, K. Kurbanov, Crystal structure, absorption, luminescence properties, and stimulated emission of Ga gehlenite (Ca_{2-x}NdGaSi_{1-x}O₇), *Phys. Stat. Sol. (a)* 97 (1986) 279–290.
- [3] I. Pracka, W. Giersz, M. Świrkowicz, A. Pajęczkowska, S.M. Kaczmarek, Z. Mierczyk, K. Kopczyński, The Czochralski growth of SrLaGa₃O₇ single crystals and their optical and lasing properties, *Mater. Sci. Eng. B* 26 (1994) 201–206.
- [4] W.R. Romanowski, S. Gołąb, D. Dominiak-Dzik, W.A. Pisarski, M. Berkowski, J. Fink-Finowicki, Growth and spectroscopy of chromium doped SrXGa₃O₇ (X = La, Gd) crystals, *Spectrochim. Acta A* 54 (1988) 2071.
- [5] Z. Burshtein, Y. Kostoulas, H.M. van Driel, Determination of the nonlinear refractive indices of Ca₂Ga₂SiO₇ and SrLaGa₃O₇ with intense femtosecond optical pulses, *J. Opt. Soc. Am. B* 14 (10) (1997) 2477.
- [6] M. Grinberg, S. Kaczmarek, M. Berkowski, T. Tsuboi, *J. Phys. Cond. Mater.* 13 (2001) 743–752.
- [7] M. Grinberg, T. Tsuboi, M. Berkowski, S.M. Kaczmarek, *J. Alloys Compd.* 134 (1–2) (2002) 170–173.
- [8] M.A. Scott, D.L. Russell, B. Henderson, T.P.J. Han, H.G. Gallagher, Crystal growth and optical characterization of novel 3d² ion laser hosts, *J. Cryst. Growth* 183 (1998) 366–376.
- [9] J.P. Meyn, T. Danger, K. Peterman, G. Huber, *J. Lumin.* 55 (1993) 55.
- [10] W.R. Romanowski, S. Gołąb, G. Dominiak-Dzik, M. Berkowski, Optical spectra of a LaGaO₃ crystal singly doped with chromium, vanadium and cobalt, *J. Alloys Compd.* 288 (1999) 262–268.
- [11] D.S. McClure, *J. Chem. Phys.* 36 (1962) 2757.
- [12] S.M. Kaczmarek, R. Jabłoński, I. Pracka, G. Boulon, T. Lukasiewicz, Z. Moroz, S. Warchoń, Radiation defects in SrLaGa₃O₇ crystals doped with rare-earth elements, *Nucl. Instrum. Methods B* 142 (1998) 515–522.