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Crystal growth and optical properties of Co^{2+} doped $SrLaGa_3O_7$

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ABSTRACT

Cobalt doped $SrLaGa_3O_7$ single crystals have been grown by the Czochralski method in a nitrogen atmosphere and by a floating zone method with optical heating in air. Starting concentrations of Co in the melt were: 0.15, 0.3, 2 and 3 mol.% with respect to Ga by the Czochralski method whereas 2 and 4 mol.% by the floating zone method. We have presented absorption spectra as well as EPR spectra related to octahedrally coordinated Co^{2+} ion in $SrLaGa_3O_7$. It show EPR spectra with a spin of $S=1/2$, $g_{\|}=2.26\pm0.04$, $g_{\perp}=4.7\pm0.2$ and tree different octahedral positions in SLGO lattice.

Keywords: crystal growth, Electron Spin Resonance, absorption spectra, gallate crystals, thermal annealing.

1. INTRODUCTION

$SrLaGa_3O_7$ (SLGO) belongs to the family of binary gallates of alkaline and rare earth metals. Crystal of these compounds have the tetragonal gehlenite ($Ca_2ASl_2SiO_7$) structure (space group: $P\text{-}42_1m_1$, D^3_{2d}). Unit cell parameters of SLGO crystals are: $a = 0.8058$ nm and $c = 0.5333$ nm [1].

Single crystals of gehlenites such as $BaLaGa_3O_7$ (BLGO) [1], $SrLaGa_3O_7$ (SLGO) [2, 3] and $SrGdGa_3O_7$ (SGGO) were manufactured for potential laser and display applications as matrix materials. They were doped with neodymium [4], praseodymium [5] and chromium [6]. Although SLGO crystals doped with various rare-earth ions have been investigated [2-5, 7-9], there is no detailed report on the optical properties of SLGO doped with Co^{2+} ions.

In the present paper the behaviour of Co ion intentionally introduced into the crystal lattice is investigated by means of optical and EPR techniques.

2. EXPERIMENTAL

2.1. Single crystal growth of $SLGO:Co^{2+}$

Single crystals of $SrLaGa_3O_7$ doped with cobalt (SLGO:Co) have been grown using the Czochralski method in a nitrogen atmosphere and the floating zone method with optical heating in air. Starting compositions of SLGO matrix slightly differ (about 0.8 mol.%) from the stoichiometric one in the direction to $SrGa_2O_4$ rich. Starting concentrations of Co in the melt were: 0.15, 0.3, 2 and 3 mol.% with respect to Ga in the Czochralski method whereas 2 and 4 mol.% in the floating zone method. 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.%.

Single crystals obtained by the Czochralski method were pulled from a 40 mm diameter iridium crucible in nitrogen atmosphere containing 1 vol.% of oxygen in the <001> direction on oriented seed crystals. The pulling rate was decreased in the range from 2.2 mm/h to 1 mm/h as the cobalt concentration in the melt was increased.

High purity carbonate, $SrCO_3$ (4N5) and oxides La_2O_3 (5N), Ga_2O_3 (5N) and Co_3O_4 (3N) were used as starting materials. They were annealed or dried before weighing. Starting melt composition was calculated on the basis of congruent melting composition $Sr_{1.04}La_{0.935}Ga_{3.02}O_{7-\delta}$. Concentrations of cobalt admixture in starting melts with reference to gallium were equal to 0.15 mol.% (P1), 0.3 mol.% (P2), 2 mol.% (P3) and 3 mol.% (P4). A convex crystal-melt interface was kept during the whole crystal growth process. Single crystals with the diameter of 20 mm and length up to 60 mm were obtained.

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They had a blue color the intensity of which increased with increasing dopant concentration. In the core region a precipitation extending along the crystal growth direction with a diameter of around 1 mm appeared in the crystal with the highest cobalt concentration (P4). Such precipitation's were not observed in crystals with lower dopant concentrations (P1-P3).

2.2. Absorption measurements

To study of optical properties of the SLGO:Co 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 - 25 000 nm using LAMBDA-900 PERKIN-ELMER and FTIR 1725 PERKIN-ELMER spectrophotometers. We have not noticed the emission related to Co in the visible and near infrared region. In this paper we present the absorption spectra of P3 sample. Changes in the absorption of P3 sample were also investigated after annealing treatment at 1050°C in the air for 16h.

2.3. ESR measurements

The samples for measurement had dimension of 2.5*2.5*2 mm^3. The experiments were performed with X-band spectrometer for frequency f = 9.25 GHz. During measurements the samples were mounted in a helium gas-flow Oxford Instruments cryostat. The samples temperature was varied in the range 4K to 13 K. The samples were glued to a rotating sample holder for the measurements of the angular variation of the EPR spectra. In this paper we present the ESR spectra of both P1 and P3 samples.

3. RESULTS

3.1. Absorption measurements

The octahedral crystal field acting on Co^{2+} ion substituting Sr^{2+} splits the sevenfold degenerate ^4F state into an orbital triplet $^4T_1$, followed by another orbital triplet $^4T_2$ and an orbital singlet $^4A_2$ [10]. The next higher state of the free Co^{2+} ion has the $^4T_1(^4P)$ configuration. The spin-orbit interaction and low symmetry field split the twelve fold degenerate $^4T_1$ level into a number of Kramer's doublets. Co^{2+} in the octahedral field has been investigated in various lattice long time ago [11]. Thus still there are many questions that are not clear and therefore have to be discussed. Especially it concerns the spin-orbit and electron – lattice interactions, the effects that are responsible for the specific absorption band shape.

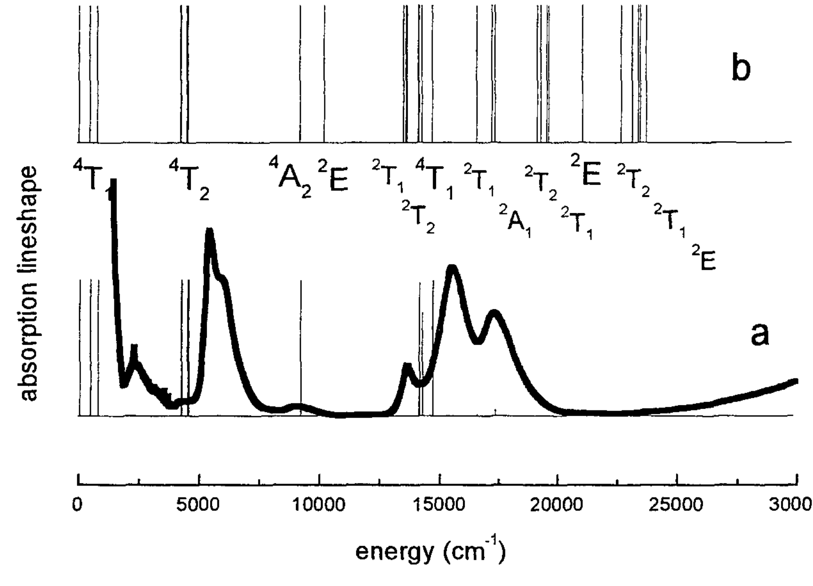

Fig. 1. Absorption line shape of P3 crystal.

Absorption line shape of the $SrLaGa_3O_7$:Co is presented in Fig.1.a. The line shape has been obtained from the absorption spectrum by dividing the absorption by photon energy [12]. The main features of spectrum consist of a double band in the IR region (5000-7500 cm^{-1}) and triple band in the visible region (12500- 20000 cm^{-1}) . The latter absorption band is responsible for blue color of the sample. We notice also the strong absorption in the far IR, and in the UV region (not indicated in figure).

One can analyze the spectrum of Co^{2+} (octahedrally coordinated $3d^7$ system) using crystal field approach [13], that describes the energetic structure of the ion by the crystal field strength parameter 10Dq, the Racah parameters B and C, and the spin-orbit coupling ζ. In Fig 1.b we present the energetic structure of octahedrally coordinated Co^{2+}, which was calculated for 10Dq = 4750 cm^{-1}, B = 720 cm^{-1}, C = 3170 cm^{-1} and spin – orbit coupling constant ζ = 400cm^{-1}. It seems that values of parameters listed above reproduce quite well the energy of $^4T_1 \rightarrow ^4A_2$ absorption band. On the other hand one can see that calculated energy of the $^4T_2$ multiplet is smaller than the energy of respective $^4T_1 \rightarrow ^4T_2$ absorption band. Up to some extend the situation is similar as far as the $^4T_1 \rightarrow ^4T_1$ transition is considered. Such a deviation is attributed to the strong Jahn-Teller coupling of the ground state. It was discussed elsewhere [14] that for such a system the real crystal field strength 10Dq can be different than the energy of absorption band.

One notices that the ground state of the system is well defined spin – orbit and Jahn-Teller splitted the $^4T_1$ multiplet. Considering the relative intensities of the absorption bands our spectra are consistent with the spin-selection rule that allows only the quartet – quartet transitions and forbid the transitions from the ground state to the excited doublets. In Fig. 1.a the solid vertical line heights are proportional to the percentage of quartet in given state. It is seen that one well reproduce the transitions from the ground state to the $^4T_2$ and $^4T_1$ states. Also the strength and position of the spin – allowed $^4T_1 \rightarrow ^4A_2$ transition seems to be well fitted. In fact the triple structure between 12500 cm^{-1} and 20000 cm^{-1} is related to the mixed states: $^4T_1$ quartet and $^2T_1$, $^2T_2$, $^2T_1$ and $^2A_1$ doublets. The strong spin – orbit coupling that interacts together with the strong Jahn-Teller effect produces the specific feature of the absorption lineshape. Thus it is difficult to attribute the absorption peaks to the specific crystal field states unambiguously.

3.2. Additional absorption after annealing treatment. Co^{3+} absorption

Fig. 2. presents absorption of P3 single crystal before (1) and after (2) annealing in oxygen for 16 h in the air. As it can be seen additional absorption band centered at about 1200 nm arises in the second case, which lead to decrease in the intensity of Co^{2+} absorption. This band may be connected with $^5T_2 \rightarrow ^5E$ transition of Co^{3+} ion in octahedral coordination.

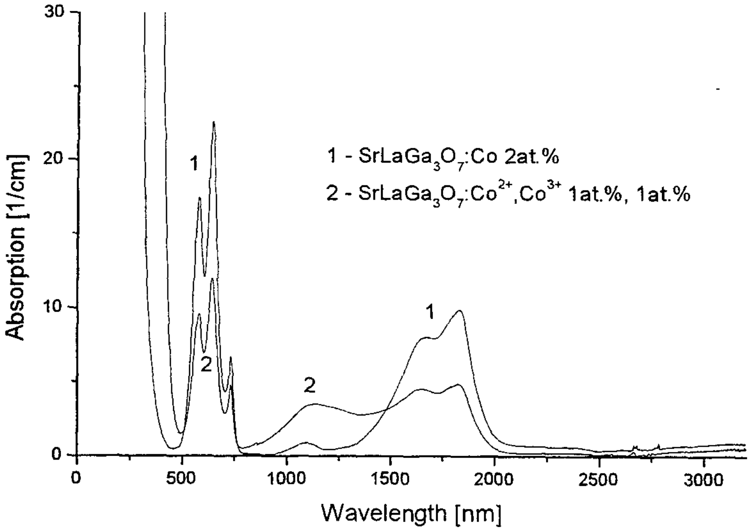

Fig. 2. Absorption of P3 crystal before (1) and after (2) annealing in the air for 16 h.

If we assume that annealing leads to ionization of Co^{2+} at octahedral positions of Sr^{2+} then at first approximation 10Dq for Co^{3+} system should be equal to 10Dq of Co^{2+} one. But obtaining due to ionization Co^{3+} ions have got smaller ionic radii (0.525 as compare to 0.65 of Co^{2+} [15]) and the strength of Coulomb interaction between central ion and ligands is much more greater, so 10Dq is also greater, about 10Dq = 6606 cm^{-1}. Moreover, one can take into account also that in the $^5T_2$

ground state there arises strong lattice relaxation. So additional absorption at about 1200 nm may be correlated to $^5T_2 \rightarrow {}^5E$ transition of Co^{3+} ion.

3.3. ESR spectra and their analysis

The ESR spectra were observed at temperatures from 4.2K to 12.4 K. No ESR lines that could be attributed to Co^{2+} pairs was observed. The spectrum consists of eight hyperfine structure components due to Co^{59} nuclear spin I=7/2. Fig. 3 shows typical ESR spectra of Co^{2+} for the magnetic fields applied perpendicular and parallel to the c-axis direction and for two applied concentrations of Co^{2+} ions 0.15at.% and 2at.%. The group of the observed 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:

$$\hat{H} = g_{\parallel}\mu_B H_Z \hat{S}_Z + g_{\perp}\mu_B (H_X \hat{S}_X + H_Y \hat{S}_Y) \qquad (1)$$

where: μ_β – Bohr magneton, $g_{\parallel}=2.26\pm0.04$, $g_{\perp}=4.7\pm0.2$, H – magnetic field and S – electron spin. The obtained ESR data do not indicate presence of Co^{3+} ions.

Fig. 4. presents angle dependencies of ESR lines. As it is seen there are tree different lines distinguishable corresponding to the tree octahedral nonequivalent positions of Co^{2+} ions in SLGO lattice one of them being Sr 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.

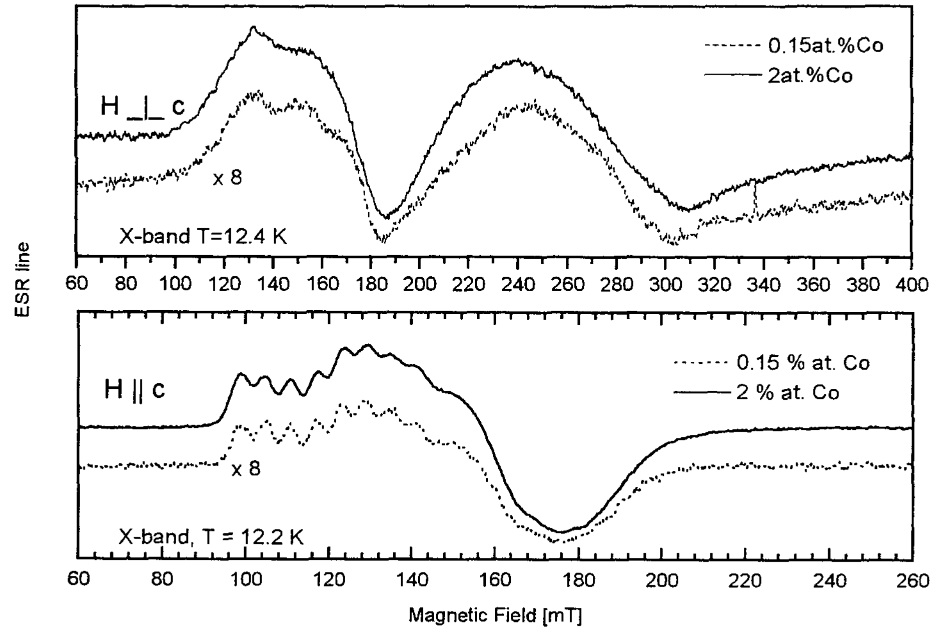

Fig. 3. Typical ESR lines of $SrLaGa_3O_7$:Co single crystal for two cases H⊥c and H||c and two values of Co^{2+} concentration 0.15at.% and 2at.%.

Intensity of ESR lines changes after annealing of the crystal in the air in such a way that relative intensity of ESR line is smaller one. This confirms supposition about ionization process during annealing treatment of SLGO:Co sample.

4.CONCLUSIONS

Analysis of the absorption spectrum of Co doped $SrLaGa_3O_7$ in the framework of the crystal field approach and EPR measurements allow to conclude that we deal with octahedrally coordinated Co^{2+} ions, that replace the Sr in the lattice.

Analysis of the EPR spectrum confirm results obtained by optical measurements that there arise only Co^{2+} ions in SLGO:Co single crystals and indicate tree different octahedral positions of the ions one of which is Sr^{2+}.

Annealing at 1050°C in the air for 16h may perform about 50% Co^{2+} ions to Co^{3+} state. The coordination of Co^{3+} ions seems to be also octahedral.

It may be supposed that the quality (absence of the precipitation in the core region) of highly doped crystals will considerably improve if the above fact will be taken into account when calculating the starting composition of the melt. This will make an optimization of the starting melt composition possible.

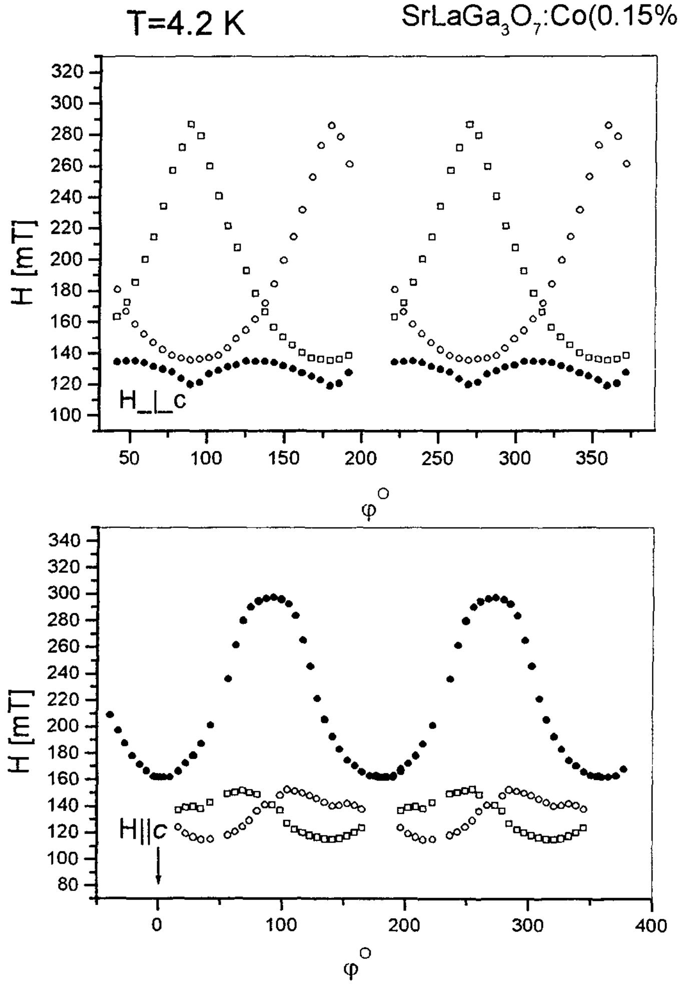

Fig. 4. Angular dependencies of ESR lines of SLGO:Co (P3) single crystal for two perpendicular directions.

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