

# INVESTIGATION OF COLOUR CENTRES IN SrLaAlO<sub>4</sub> AND SrLaGaO<sub>4</sub> SINGLE CRYSTALS

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Absorption spectra of SrLaAlO<sub>4</sub> and SrLaGaO<sub>4</sub> single crystals are investigated as well as their changes after irradiation by  $\gamma$ -quanta (<sup>60</sup>Co source). Both crystals reveal a similar behaviour that is caused, as it seems, by the same nature of colour centres in them. The conclusion that oxygen defects as well as Fe impurities play a significant role in the colour centres formation in these crystals.

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## 1. Introduction

The SrLaAlO<sub>4</sub> (SLA) and SrLaGaO<sub>4</sub> (SLG) single crystals having a tetragonal structure of K<sub>2</sub>NiF<sub>4</sub>-type are considered as promising substrate materials for high-temperature superconductor (HTSC) film epitaxy and as a laser host material as well. For both applications high quality crystals are required but many investigators [1-5] note a series of difficulties in growing crystals by the Czochralski method. The process of growing is very sensitive to the purity and the technique of raw material preparation, the charge stoichiometry, the growth thermal configuration, the growth and pulling rate, the pulling direction orientation and crystal-melt interface shape, the composition of the atmosphere, etc. Deviations from the optimal growing conditions cause colouring of the crystal to light-yellow, yellow, green or brown colour and may even cause clouding and cracking of the crystal or appearance of foreign phase inclusions [5]. Colouring is more intense when the axial temperature gradient during the crystal pulling is greater. In Ref. [5] it was also noted that crystal colouring was not uniform throughout the bulk of crystal: the core was usually a bit lighter than the outer parts of the crystal.

The present work is devoted to an investigation by optical spectroscopy methods of colour centres in SLA and SLG single crystals grown under different conditions and subjected to the influence of gamma-irradiation.

## 2. Experimental details

The SLA single crystals were grown in (100) direction by the Czochralski method in nitrogen atmosphere (with 1% oxygen). They were cooled and then stored at room temperature. Flat plates cut out of single crystals perpendicular to the growth axis, were the subjects of the investigation. The thickness of the samples was in the range of 0.27–0.6 mm. One of the SLA samples had no markedly visible colouring [5]. All other SLA samples were yellow coloured of different tints starting from light-yellow to saturated yellow and each of them had inhomogeneity of colouring described in Ref. [5]. The SLG samples under investigation had light-yellow or green colour. The green SLG samples had well-boarded areas of red-brown colour that were disposed on the plates' edges in [001] directions.

Absorption spectra of samples were investigated as well as the additional absorption (AA) spectra induced by the influence of irradiation treatment of the samples. Optical absorption of a sample was calculated from the optical transmission spectra without taking into account the reflection. The induced AA was found by the following formula:

$$\Delta k = 1/d \ln(T_1/T_0),$$

where  $d$  is the thickness of the sample,  $T_0$  and  $T_1$  are the optical transmissions before and after the treatment. The optical transmission spectra were registered at room temperature in the range of 50000–11000  $\text{cm}^{-1}$  (0.2–0.9  $\mu\text{m}$ ) with the help of a spectrophotometer Specord-M40 attached to PC. The irradiation of the samples with gamma-quanta was executed by  $^{60}\text{Co}$  source with an average energy of gamma-quanta of 1.25 MeV to the absorbed dose  $10^3$ – $10^6$  Gy. The exposition dose intensity was about 170 R/s and the temperature of the sample during irradiation did not exceed 50°C.

## 3. Results

The typical absorption spectra of the investigated SLA samples are shown in Fig. 1a. In all the samples, the colourless one including, the absorption band is observed in the range of 32000–36000  $\text{cm}^{-1}$ . In the coloured samples the band is much more intense and besides it, another band is observed around 26000  $\text{cm}^{-1}$  (which, it seems, is probably connected with yellow colouring of the crystals) and as well as darkening near the fundamental absorption edge (FAE). In the coloured samples the darkening in the range of 32000–36000  $\text{cm}^{-1}$  has a more complex structure. Beside the quantitative difference of absorption, by comparing curves 2 and 3 in Fig. 1a, a considerable difference in the spectrum shape is displayed, which is caused, it seems, by the difference in the absorption spectra's structure. This difference was found and investigated earlier in our work [6]. According to those results the coloured SLA samples may be divided into two groups by the absorption bands observed in the spectra. The majority of them had an absorption band maximum at 33500  $\text{cm}^{-1}$  and an absorption near 38000  $\text{cm}^{-1}$  against the background of the widened FAE. The second group of samples has absorption consisting of bands with maxima 36000 and 32000  $\text{cm}^{-1}$ .

The SLG crystal absorption spectra are presented in Fig. 1b. The spectrum of light-yellow sample (see the curve 1 in Fig. 1b) has a likeness with the absorption

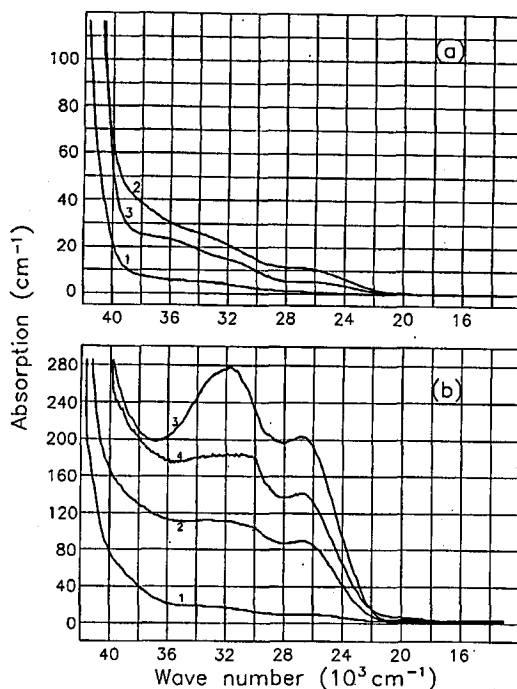


Fig. 1. Absorption spectra of the SLA (a) and SLG (b) crystals: curves in (a) correspond to absorption of the colourless sample (1) and the sample of the first group (2) and the second one (3); curves in (b) correspond to the yellow sample (1), light-green (2), intense-green (3) and red-brown (4) areas of the green sample.

spectrum of the majority of the SLA samples (see the curve 2 in Fig. 1a), i.e. it contains the absorption bands with maxima near  $33500$  and  $26000 \text{ cm}^{-1}$  and the shoulder near  $38000 \text{ cm}^{-1}$  against the background of the widened FAE. The spectra of green samples differ one from another by intensity of absorption only. They differ from the spectra of yellow samples by much more increased absorption in the bands near  $33500$  and  $26500 \text{ cm}^{-1}$ . The curves 2–4 show the absorption spectra measured locally in light-green (curve 2), intense-green (curve 3) and red-brown (curve 4) regions of the same green sample. One can see from the comparison of these curves that the red-brown colouring is accompanied by a superposition of the own bands of green sample with another features. Using the differential spectrum technique [6] we have found that the main feature of the last spectrum is a presence of absorption near  $20000\text{--}22000 \text{ cm}^{-1}$ .

The spectra of the AA induced in the investigated samples by the gamma-irradiation are shown in Fig. 2. The irradiation causes clearing near the FAE in the SLA crystals and in the adjacent bands and also leads to darkening in the region of  $20000\text{--}30000 \text{ cm}^{-1}$ . In the clearing region the bands being characteristic of each group manifest themselves in the samples of the first group ( $33500$  and  $38000 \text{ cm}^{-1}$

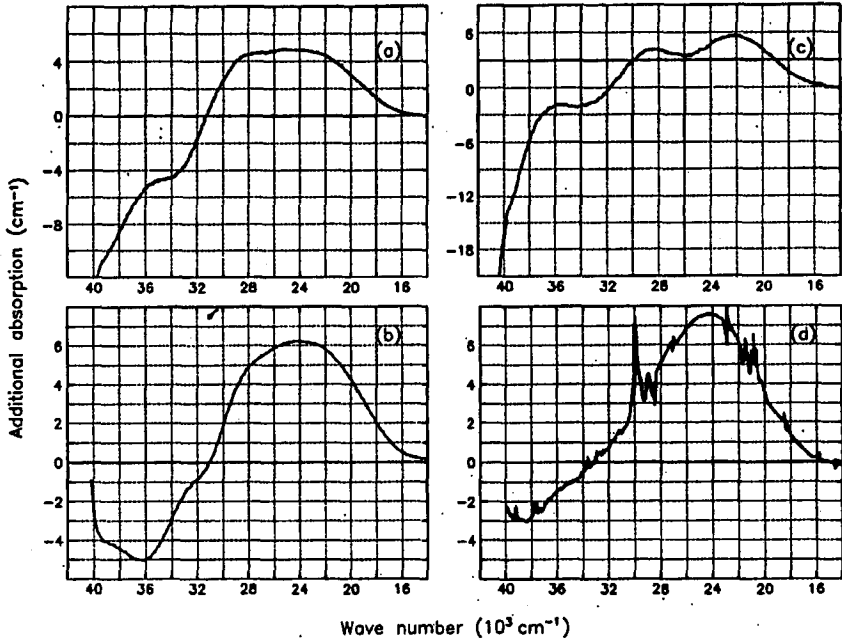


Fig. 2. The additional absorption spectra induced by gamma-irradiation in the SLA crystals of the first group (a) and the second one (b), in the SLG crystal (c) and in the  $\text{CaNdAlO}_4$  crystal (d).

in Fig. 2a) and the second one ( $32000$  and  $36000 \text{ cm}^{-1}$  in Fig. 2b). In the region of induced absorption of the samples of the first group two bands with maxima at  $22000$ – $23000 \text{ cm}^{-1}$  and  $28000 \text{ cm}^{-1}$  can be distinguished (Fig. 2a). The induced AA of the samples of the second group is placed in the same region but it has no clear structure. Its maximum is located near  $24000 \text{ cm}^{-1}$ , but on the short-wave slope of the band the weakly marked shoulder is observed (Fig. 2b) associated perhaps with the band at  $28000 \text{ cm}^{-1}$ .

The AA spectrum induced in yellow SLG crystal by the gamma-irradiation of the  $10^3 \text{ Gy}$  dose is pictured in Fig. 2c. They contain a clearing part in the short-wave region and two bands with maxima near  $28000$  and  $24000 \text{ cm}^{-1}$ . In the short-wave clearing region the spectral absorption bands with maxima at  $33500$  and  $38000 \text{ cm}^{-1}$  are clearly seen. The long-wave part of the spectrum remains almost invariable with a dose increase up to  $10^6 \text{ Gy}$ . The behaviour of absorption near FAE is not so clear due to its much higher value and as a consequence a much lower accuracy of measurements. The large absorption of green samples in UV region of spectrum has not allowed to obtain an AA spectrum with a clear structure.

For comparison the AA spectrum of  $\text{CaNdAlO}_4$  single crystal irradiated by gamma-quanta with a dose of  $10^5 \text{ Gy}$  is shown in Fig. 2d. Although the corresponding curve has a series of distortions caused by the presence of a lot of narrow intense  $f-f$  transition lines of the Nd ion, one can see in the figure that changes

of spectra of  $\text{CaNdAlO}_4$ , SLA and SLG crystals induced by irradiation have the same character and, it seems, the same origin.

#### 4. Discussion and conclusions

Colouring in SLA and SLG single crystals is accompanied by the appearance of a signal in the ESR spectrum (D-line) [5, 7]. Its intensity increases with the colouring saturation in the following range of colours: colourless, light-yellow, yellow, green, dark-green [5]. But the simultaneously observed signal, caused by iron impurities, remains approximately the same. An addition of  $1.5 \times 10^{-2}$  wt.% Fe-impurity into a melt decreases the D-line intensity. In Ref. [7] it was mentioned that the D-line is also observed in the ESR spectrum of  $\text{CaNdAlO}_4$  crystal, although this crystal did not reveal any detectable ESR signal of the Fe-impurity. From these results a conclusion was reached that colouring of the SLA and SLG crystals is connected with the rise of oxygen defects during the crystal growth process [5]. This seems to be quite probable because of the insignificant difference between Sr and La ion radii (0.113 and 0.115 nm, respectively) which, due to a small variation of the temperature gradient, may easily cause a local disorder in the distribution of two- and three-valent ions in the crystal structure [8] and in consequence leads to the appearance of oxygen defects.

The comparison of absorption spectra of the SLA and SLG crystals as well as the AA spectra shows that many of their absorption bands coincide and therefore the colour centres in these crystals may have the same nature. On the other hand the gamma-irradiation in the absorbed dose range up to  $10^7$  Gy causes usually the defect recharge processes in oxide crystals [9]. The saturation of induced changes is an evidence of that. Then the comparison of the AA spectra induced by the gamma-irradiation in the SLA, SLG and  $\text{CaNdAlO}_4$  single crystals (which are very similar too) allows us to suggest that those defects are the oxygen related ones. In this sense the presented results coincide with the previously obtained ones.

But it should be noted that the segregation-like red-brown regions observed in green SLG crystals may be connected with the iron impurity. The corresponding absorption manifests itself mainly by a tail in the region of  $22000\text{--}18000\text{ cm}^{-1}$ . The absorption near  $20000\text{ cm}^{-1}$  was also observed in the SLA crystals of the second group and was clearly distinguished as a spectral band in thermal changes of their spectra [6]. If it is so then the difference between the SLA crystals of the first and second group, that was found in spectral positions of the characteristic defects' bands and absorption behaviour under thermal treatment in Ref. [6], might be explained as a mutual influence of defects related to Fe-impurity and oxygen sites. The reducing of intensity of D-line with iron doping [5] indicates this fact too.

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