INVESTIGATION OF AS GROWN AND INDUCED STRUCTURAL DEFECTS IN SrLaXO$_4$ (X = Al, Ga) CRYSTALS

W. Ryba-Romanowski, S. Gołąb, P. Dereń, G. Dominiak-Dzik, W.A. Pisarski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences
P.O. Box 937, 50-950 Wrocław, Poland

AND A. Gloubokov

Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland

SrLaGaO$_4$ and SrLaAlO$_4$ substrates grown by the Czochralski method have no twins or subgrains however they show strong tendency to form point defects. The nature of these defects is not well understood yet. They may be associated with deviations from stoichiometry and/or oxygen atoms located in the interstitial positions. Virtually all title crystals grown by the Czochralski method display various colours from light green to deeply red owing to light absorption by point defects. Absorption centres appear to be very stable in time and resistant to usual thermal treatment. UV excitation increases the density of defects and gives rise to strong photoluminescence, otherwise too weak to be observed.

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1. Introduction

The fundamental UV optical absorption edge of SrLaAlO$_4$ crystal was located experimentally in the region 220–240 nm [1], and very similar results were found for the SrLaGaO$_4$ crystal. The highest measured absorption coefficient was only 200 cm^{-1}, therefore the wavelengths given above may be treated as a lower limit for the actual absorption edge. In any case, the conduction band in these compounds is not lower than about 5.2 eV. In the energy gap, localized states of impurities such as rare-earth ions or transition metal ions may appear.

However, the SrLaAlO$_4$ and SrLaGaO$_4$ crystals grown by the Czochralski method display intense colours. Most frequently they are yellow or light green, but dark green or brown crystals were also obtained [2, 3]. Growth of colourless

crystals by the Czochralski method has been found very difficult. It necessitates the chemicals of the highest purity together with a reduction of temperature gradient near liquid–solid interface [4]. Stability of crystals is related to their colour, intensively coloured ones disintegrate into small pieces during small changes of temperature. Yellow crystals are not influenced by thermal treatment. Obviously, the colour of crystals is associated with structural defects which are created in the phase of the growth. The nature of these defects is not clear, however. They may be due to unintentional impurities and deviation from stoichiometry.

In this work we present the results of optical absorption and emission measurements on $SrLaAlO_4$ and $SrLaGaO_4$ single crystals which have the most typical features i.e. good quality and stability but looking yellow.

2. Experimental

Crystals were grown from iridium crucible of 50 mm in diameter and 50 mm height, and the contents of melt 450 g and 480 g, respectively for $SrLaAlO_4$ and $SrLaGaO_4$. Crystal growth was conducted in pure nitrogen and in a mixture of nitrogen containing about 1 vol% of oxygen. Pulling rates in the range of 1–3 mm/h and rotation rates about 15–20 rpm proved satisfactory. To find the best conditions of growth of $SrLaAlO_4$ and $SrLaGaO_4$ crystals, various orientations of seeds were used. The crystals were grown in [110], [100] and [001] directions. The crystals were completely twin-free and had neither iridium inclusions nor gas bubbles. In the cylindrical part they show parallel (001) faces on the two opposite sides. These surfaces are flat.

Properties of crystals depend on conditions of growth. By using a passive afterheater (gradient 10°C/mm), 4N purity reagents and pure nitrogen atmosphere, the crystals were mainly yellow coloured. Sometimes, green colour appeared at the beginning part and, if excess of oxygen was present in the system (up to 2 vol% O_2), sometimes colourless in their central part. Some growth experiments were performed in the laboratory of the Institute of Crystal Growth (IKZ) in Berlin with an active afterheater (gradient lower than 5°C/mm) and the $SrLaAlO_4$ crystals were mainly colourless and sometimes light-yellow [4]. It must be noted that the colour of $SrLaGaO_4$ crystals changed from yellow to yellow-reddish with increasing number of grown crystals from the same melt and at the same crystal growth conditions (thermal configuration, gas, pulling and rate growth). Colourless core in the $SrLaGaO_4$ crystals grown in the [100] and [001] directions was observed sometimes and crystals were of poor quality. The changes of colour, such as "colourless", "yellow", "yellow-reddish" (or "green"), were also observed in the solidified melts.

An excimer laser ALPα100 (Lambda Physik) working at $\lambda = 308$ nm was used as a source of irradiation and excitation of photoluminescence. The laser emitted pulses having an energy of 150 mJ and duration of 20 ns FWHM. The laser beam cross-section was sufficiently large to give an uniform irradiation with an energy density of about 0.54 J/m^2 per pulse. Absorption spectra of as grown and irradiated samples were measured with a Varian Model 2300 Spectrophotometer. Luminescence spectra and luminescence decay curves were recorded using a Jobin

Yvon Model TIIR 1000 monochromator equipped with an R 928 photomultiplier (IIamamatsu).

3. Results and discussion

In Fig. 1 we present optical absorption spectra recorded at room temperature with as grown and UV-irradiated crystal of $SrLaAlO_4$. The absorption spectrum of as grown $SrLaGaO_4$ is qualitatively similar to that recorded with $SrLaAlO_4$ crystal and contains the features which are common to crystals displaying different colours. The spectrum consists of a broad band centered at about 380 nm and of considerably weaker tail reaching far into the red region of the spectrum. Between about 330 nm and a fundamental absorption edge, the absorption rises smoothly with decreasing wavelength. In this region an additional band was recorded for several samples [5]. Relative intensities of these features differ significantly from sample to sample, even when samples originate from the same boule. The colour of the crystal is related to the intensity of the 380 nm band and to the weak tail in the visible. In colourless samples these two features are absent, but the absorption in the 240–330 nm spectral region is still important. Optical absorption in the UV and in visible was observed in numerous oxide crystals, however an identification of these spectra is not a trivial task. Absorption band peaking at 260 nm in $Y_3Al_5O_{12}$ crystals was attributed to iron impurity [6]. Bands centered at longer wavelengths, among others a band at about 380 nm in both the aluminium and gallium garnets are believed to be associated with structural defects, but their nature is not identified [7]. ESR measurements revealed that all our
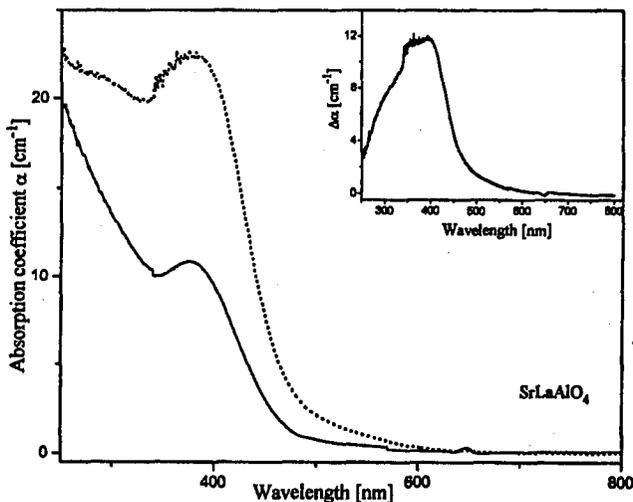

Fig. 1. Absorption spectra of $SrLaAlO_4$ recorded at room temperature. Solid line — as grown sample, dotted line — UV-irradiated sample. Difference spectrum is shown in the inset.
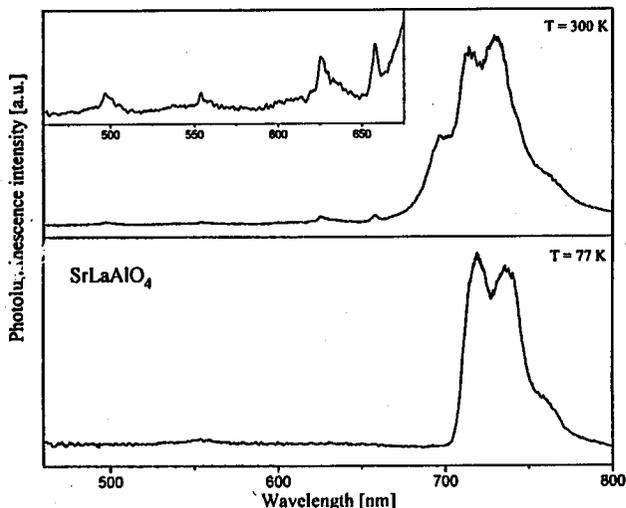
Fig. 2.   Photoluminescence spectra of SrLaAlO$_4$ recorded at 300 K and 77 K.

crystals contain Fe ions with concentrations inferior to 10^{-3} wt%, thus the iron may contribute to the absorption. It can be seen in Fig. 1 that the UV irradiation of a crystal by a 308 nm line of an excimer laser increases the absorption band at 380 nm. The band saturates during several seconds of irradiation indicating that it is associated with centres produced by colouring existing defects. Several types of centres may be involved: one electron trapped at an anion vacancy (F$^+$ centre), two electrons trapped at an anion vacancy (F centre), a hole trapped at a cation vacancy and a variety of more complex structures. The centres created in our samples by UV irradiation are relatively stable, they disappear within several days at room temperature. Whereas the energy of UV light absorbed by as grown centres is dissipated by lattice vibrations, the induced centres show strong photo-luminescence. Spectra of photoluminescence following the excitation of SrLaAlO$_4$ and SrLaGaO$_4$ crystals by a 308 nm line of an excimer laser are shown in Fig. 2 and Fig. 3 respectively. The emission bands in the two crystals are quite similar, implying that the luminescent centres have the same nature. Slight narrowing of emission bands can be seen in low temperature spectra, but the band positions do not change. The inset in Fig. 2 shows a magnified portion of an apparently flat line between 400 and 700 nm, weak and relatively sharp lines visible in the inset were attributed to traces of trivalent praseodymium, since they are consistent with luminescence spectra of Pr^{3+} in SrLaAlO$_4$ [8]. Excitation process leading to the population of the luminescent $^3P_0$ level of Pr^{3+} involves an excitation energy transfer from colour centres to praseodymium or direct $4f-5d$ transition of Pr^{3+} ions.

Decay of photoluminescence recorded at room temperature with a SrLaAlO$_4$ sample is indicated by a dotted line in Fig. 4. The decay involves a fast component with a nearly single-exponential time dependence and a considerably slower com-
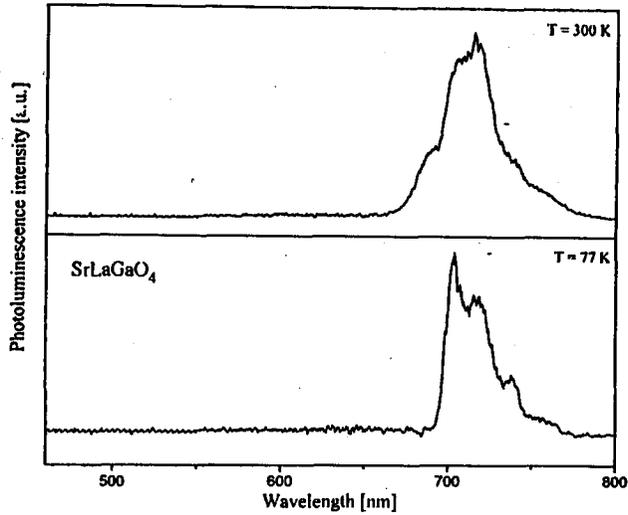
Fig. 3. Photoluminescence spectra of SrLaGaO₄ recorded at 300 K and 77 K.
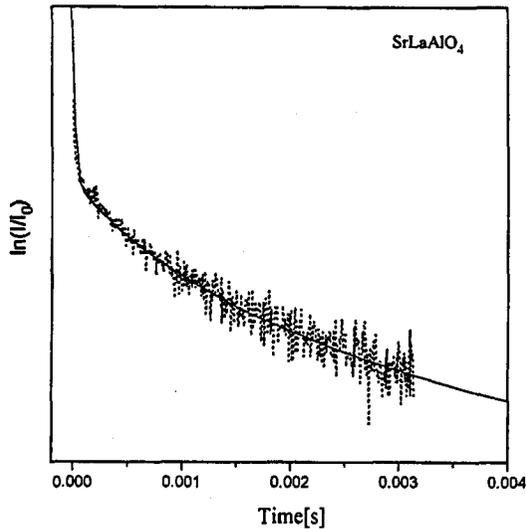

Fig. 4. Photoluminescence decay in SrLaAlO₄. Dotted line represents the experimental data, solid line — see text for explanation.

ponent, which is nonexponential. Such a decay kinetics may be accounted for by assuming that the emission involves a first-order process followed by a second-order process. With this assumption the photoluminescence decay curve $I(t)/I_0$ may be approximated by an expression

$$\frac{I(t)}{I_0} = \exp\left(-\frac{t}{\tau}\right) + \frac{1}{(A + Bt)^2}.$$

(1)

Solid line in Fig. 4 represents the best fit of Eq. (1) to experimental data, with $\tau = 16 \times 10^{-6}$ s, $A = 1.8$, $B = 1.8 \times 10^3$. It can be seen that the agreement between the experimental and hypothetical time dependence is quite good. These data are not sufficient to determine the nature of luminescent centres, nevertheless they provide a deal of insight into systems under study. Thus, the 1.9 eV Stokes shift between absorption and emission in $SrLaAlO_4$ and $SrLaGaO_4$ crystals is quite large. It may correspond to the excitation and decay of F centres. Occurrence of F centres in the two crystals has been inferred from ESR study [9]. However, the kinetics of luminescence decay excludes this hypothesis. The electronic structure of F centre may be treated as a helium atom. In this system the long lived emission, associated with a spin forbidden triplet–singlet transition should occur, whereas very fast decay was recorded with our samples. Therefore, we supposed that the optical absorption and emission in $SrLaAlO_4$ and $SrLaGaO_4$ crystals is associated with F^+ centres coupled to impurity traps. Capture and subsequent release of an electron from a trap may be the origin of the slow, nonexponential component of the photoluminescence decay.

Acknowledgments

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