Blue fluorescence of Ti^{3+} ions in Ti^{3+}-doped, γ-irradiated SrAl$_{0.5}$Ta$_{0.5}$O$_3$:LaAlO$_3$ crystals

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Abstract Titanium-doped SrAl$_{0.5}$Ta$_{0.5}$O$_3$: LaAlO$_3$ (SAT:LA) perovskite solid solution single crystals were grown by the Czochralski method for two Ti concentrations: 1 wt.% (LSAT1) and 2 wt.% (LSAT2). It was stated that incorporation of Ti into SAT:LA crystal takes place in a non-uniform way. Ti^{3+} ions enter the crystal mainly in its conical part and mainly inside a thin (2–3 mm) layer within the crystal boundary. At room temperature, crystals from the conical part of the boule reveal strong absorption centered at about 529 nm for the case of LSAT1 single crystal while at about 451 nm and 651 nm for the case of LSAT2. Low temperature measurements have shown two absorption peaks centered at about 489 and 562 nm. Moreover, the 850 nm peak is clearly observed. The intensity of the above described absorption coefficient strongly depends on the dopant concentration and reaches even 80 cm^{-1}. The above bands seem to be connected with non emitting Ti^{3+} centers. After γ-irradiation, additional absorption is observed peaked at about 423 nm which gives two emission bands placed near 400 and 800 nm (375 nm excitation wavelength). They seem to be Ti^{3+} emissions coming from Ti^{3+} ions, occupying two different lattice octahedral positions one of which being octahedral (Al, Ta) site. Blue fluorescence is self-evident.

Key words absorption • Czochralski method • emission • growth • Ti^{3+} centers

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Introduction

Ti^{3+}-doped crystals have attracted considerable interest in view of their potentials as tunable solid-state laser materials. Cubic perovskite hosts of the solid solutions allow us to introduce many dopants of rare-earths in positions A as well as transition metal ions in the B positions of the single crystals. Doped crystals may be very interesting for optical applications especially if there are no structural phase transitions and low-angle twins present in the crystals.

Perovskite crystals have been widely studied due to their ferroelectric, piezoelectric or non-linear optical properties. The most important drawback of the above mentioned perovskites are phase transitions which lead to twinning and sample surface roughening. Almost all simple perovskite compounds have one or more structural phase transitions. LaGaO$_3$ (LG) and SmAlO$_3$ undergo the first-order phase transitions from rhombohedral to orthorhombic structures at around 423 and 1058 K, respectively. Second-order phase transition has been observed in LaGaO$_3$ at 1453 K, NdGaO$_3$ (NG) at 1223 K, and LaAlO$_3$ (LA) at around 773 K [9].

In 1990, Brandle *et al.* [4] published data on the synthesis of double perovskites with calcium and strontium ions in position A and mixture of aluminum and tanthalum or gallium and niobuim ions in position B. They found few interesting cubic perovskites without twins and phase transitions. The most interesting in this group were SrAl$_{0.5}$Ta$_{0.5}$O$_3$ (SAT) and SrAl$_{0.5}$Nb$_{0.5}$O$_3$ (SAN). In 1991, Mateika *et al.* [8] reported data on the synthesis and crystal growth method of several interesting perovskites with cubic and tetragonal structure by the Czochralski. The most

interesting in this group are two cubic perovskites solid--solution crystals obtained by the Czochralski method: first one 70 mol.% of SAT with 30 mol.% of LaAlO$_3$ (LA) and the second 61 mol.% of SAT with 39 mol.% of NdAlO$_3$ (NA).

Results published in 1994 by Guo *et al.* [6] and later Bhalla *et al.* [3] proved that cubic perovskites that do not undergo any phase transitions should be searched between crystals based on strontium perovskites such as Sr(Al$_{1/2}$Ta$_{1/2}$)O$_3$ (SAT) and Sr(Al$_{1/2}$Nb$_{1/2}$)O$_3$ (SAN) and their solid solutions with LA and NdGaO$_3$ (NG). However, the Czochralski growth of the solid solutions has been verified only for one composition (70% SAT and 30% LA) [8, 10] and was not examined in which concentration range they crystallize in the cubic lattice.

Now, the best known system of cubic perovskite solid solutions is the SAT:LA (LSAT) system. The melting point of these materials is close to 2123 K indicating a high thermal and sufficient chemical stability. One of the discussed components of the solid SAT solution adopts cubic perovskite structure without phase transitions, however, it undergoes a strong reduction with partial decomposition during growth from the melt and, therefore, cannot be obtained by the Czochralski method. The second component, LA melts congruently and may be grown by the Czochralski method. Since they crystallize in the deformed perovskite structure, these crystals have twins and also exhibit phase transitions. It has been proved [1] that these solid-solutions exist in a wide concentration range (from 0 to 50 mol.% of LA), adopt the cubic perovskite structure, do not undergo phase transitions, melt congruently and may be grown by the Czochralski method.

In the present paper, we describe crystallization and doping tests of LSAT single crystals, where part of Al and Ta ions is expected to be replaced by Ti ions.

Setup

Titanium-doped LSAT perovskite solid solution single crystals containing about 30 mol.% of LA were grown by the Czochralski method with two Ti concentrations: 1 mol.% (LSAT1) and 2 mol.% (LSAT2). The crystals were grown using <111> and <100> oriented seeds at a pulling rate of 2 mm/h and the rotation rate 20 rpm from a 40 mm diameter iridium crucible.

A series of measurements were performed for powdered crystals using a D5000 Siemens diffractometer with the aim at determining lattice constants and the real structure of the crystal.

1 mm thick flat-parallel plates were cut perpendicularly to the <100> growth direction from the obtained single crystals and were next both-side polished. Two types of samples were prepared: LSAT11-15 cut from a LSAT1 single crystal and LSAT21-22, cut from a LSAT2 crystal. They were optically investigated before (LSAT11-22) and after the treatments (LSAT15): annealing in H$_2$ and next in air, and γ-irradiation from a ^{60}Co source. The crystal was annealed in hydrogen at 1473 K and in air at 1673 K for 1 h at the Institute of Electronic Materials Technology, Warsaw, Poland, and divided into two pieces, irradiated by γ-rays from the ^{60}Co source with doses from 10^5 Gy to 10^6 Gy at the Institute of Nuclear Chemistry and Technology in Warsaw, Poland. Room temperature transmission measurements were performed at the Institute of Optoelectronics, MUT, Poland, using Lambda-900 and FTIR-3025 spectrophotometers. The additional absorption coefficient of a given sample was calculated from the formula:

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

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

Low temperature measurements were performed at the Kyoto Sangyo University, Japan. For low temperature absorption measurements, we used a Cary-5E spectrophotometer in the 190-3100 nm range. Crystals were placed inside a cryostat with a He-gas refrigerator which makes it possible cooling down to 12 K.

Photoluminescece measurements were carried out using a SS-900 Edinburgh Inc. spectrophotometer and were performed at the Institute of Optoelectronics, MUT, Poland.

Results

Growth of Ti-doped LSAT single crystals

Single crystals grown from the melt containing 22 mol.% of LA and higher concentrations were light yellow if the processes were carried out in pure nitrogen with an oxygen level in the output gas below 500 ppm. Crystals grown from the starting composition of 20 mol.% of LA and less were dark, almost non transparent. They had a tendency to an unstable growth (e.g. spiral growth) that increased with decreasing LA concentration. The growth of crystals containing more than 40% of LA requires an extreme slow growth rate. It was stated that the incorporation of Ti into LSAT crystal takes place in a non-uniform way. Single crystals of 18 mm in diameter were light yellow but Ti entered the crystal mainly in its conical part, forming regions violet in color and mainly inside a thin (2–3 mm) layer within the crystal boundary (Fig. 1).

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Fig. 1. SAT-LA:Ti (LSAT15) – (2) and SAT-LA:Ti (LSAT12) – (1) samples.

X-ray measurements

Precise X-ray diffractographs obtained for powdered crystals have shown a coexistence of two types of reflexes. The narrow, strong reflexes may be described as corresponding to the cubic perovskite cell with Pm3m space group and the lattice constant equal to 3.87 Å, while the wide reflexes, with lower intensity, may be described as coming from F-43m space group, with the lattice constant equal to about 7.74 Å. This means that in the real structure of the crystal accidental deposition of oxygen actahedra by Al and Ta ions exist (Pm3m space group and single elementary cell). These octahedra are perfect, not distorted. In the crystal there also exist regions showing a far order structure (superstructure) with respect to Al and Ta deposition. This means that the neighbouring octahedra are deposited in an alternate way by Al and Ta ions. In such a case, regions showing long-range ordering could have an elementary cell created from eight perovskite elementary cells of F-43m space group and doubled lattice parameter ($a = 2a_c$). In the concentration range from 22 to 42% of LA, in which we performed proper investigations for crystals grown by the Czochralski method, the contribution of the regions connected with the above mentioned structure decreases nearly linearly with increasing LA concentration [2].

We have actually found that LSAT single crystals grown by the Czochralski method crystallize in the double cubic perovskite structure with the lattice constant in the range from 2×3.876 Å to 2×3.85 Å at the La concentration of 22% and 42%, respectively. They have neither structural phase transition nor twins.

Absorption measurements. Room temperature

Figure 2 shows the room temperature absorption coefficient of LSAT:Ti (LSAT13) single crystal in the range 200–7000 nm. Its fundamental absorption edge is about 300 nm, lattice absorption is observed at about 6200 nm. As one can see, a strong (28 cm^{-1}) asymmetric absorption band is observed, centered at about 500 nm. This band may be due to absorption of Ti^{3+} ions. We must also pay attention
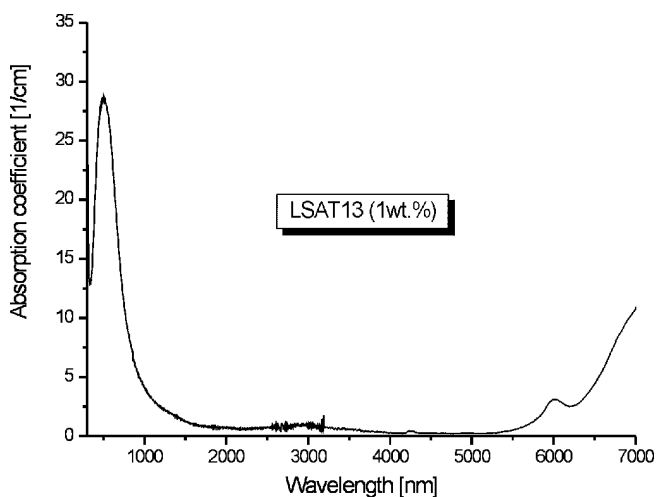

Fig. 2. Room temperature absorption coefficient of LSAT:Ti (LSAT13) single crystal in the range 300–7000 nm.
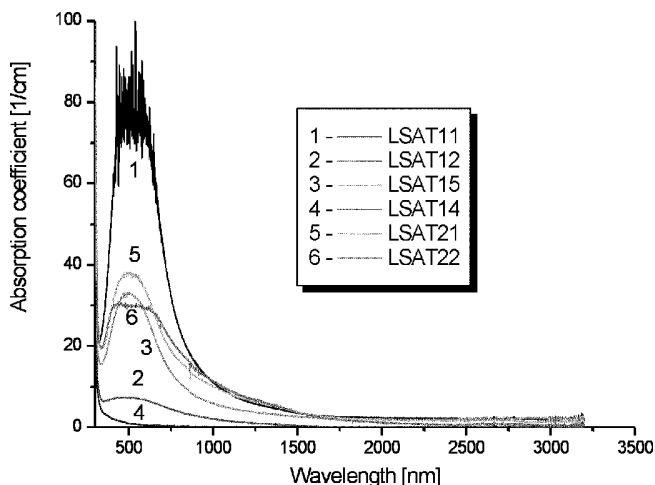

Fig. 3. Room temperature absorption coefficient of the all measured samples in the range 300–3200 nm.

to the 2700–2800 nm range where weak but clearly sharp lines are observed. They may be due to a weak absorption of Ti^{2+} ions. Moreover, Ti^{4+} ions may be also present in our crystal. They do not contribute to the absorption in the whole investigated range.

Figure 3 shows the absorption coefficient for all the investigated samples. Comparing LSAT13 and LSAT22 samples one can clearly see a double structured absorption spectrum for the LSAT22 sample with higher Ti concentration. The 500 nm absorption band observed in this sample may reach a maximum as high as 80 cm^{-1} which depends on the doping level and on the position of the sample cut with respect to the seed position.

We performed fluorescence measurements for all the crystals and found that they did not reveal any fluorescence.

Low-temperature measurements

With the aim of checking the real structure of the 500 nm band, we performed low temperature measurements. Figs. 4a and 4b show low-temperature and high-temperature optical densities of LSAT21 and LSAT11 samples in the range 300–1500 nm, respectively. One can see an appearance of at least three absorption bands at 489, 562 and 850 nm. The first two bands correspond to 500 nm band observed in the room temperature absorption spectrum. The third band appears at a low temperature only. It seems that 489 and 562 nm bands are due to $^2T_2$-^2E d-d transition of Ti^{3+} while 850 nm band is due to Ti^{3+}-Ti^{4+} pairs. Because the emission due to the above bands is not observed, and, the 489 and 562 peaks do not show any shift towards lower energies at low temperature, we suppose that these are transitions of Ti^{3+} and Ti^{4+} ions placed at interstitials or Ti^{3+} ions in octahedron with vacancy of ligand O^{2-} ion [9].

Annealing of LSAT:Ti crystals in the air and in hydrogen atmosphere

In order to check which ions are responsible for the 500 nm absorption we performed annealing experiments in hydrogen and in air. Figure 5a shows results of comparative measurements of the absorption coefficient of LSAT12 (cut
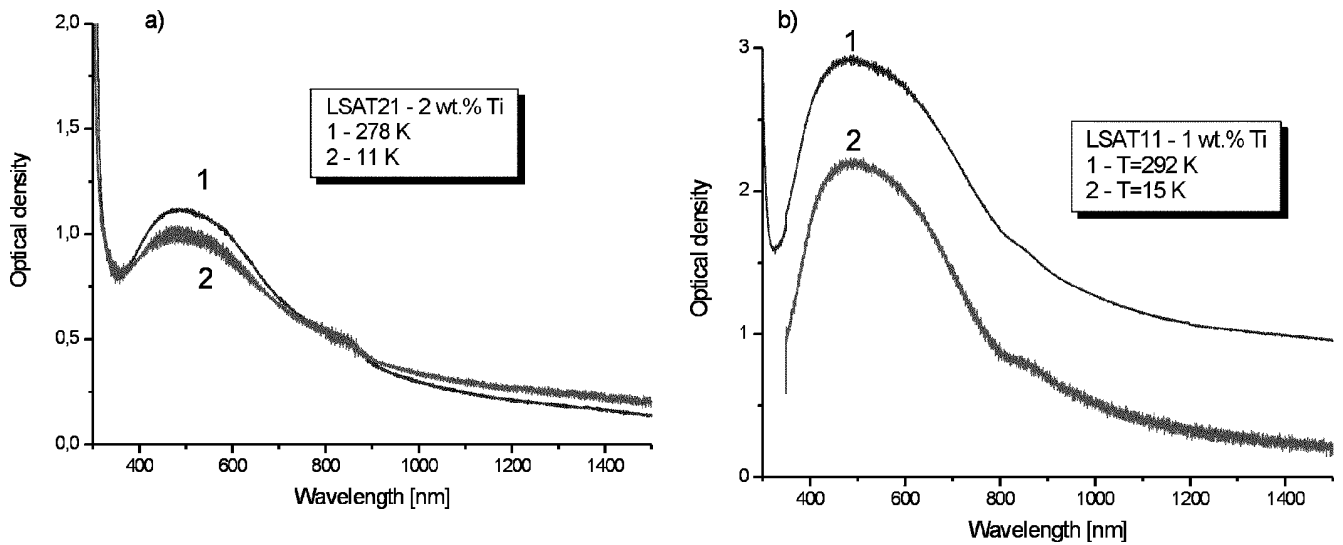
Fig. 4. a) – Low-temperature (11 K) and high-temperature (278 K) optical density of LSAT21 sample; b) – low-temperature (15 K) and high-temperature (292 K) optical density of LSAT11 sample.

near the seed position) and LSAT15 (cut far from the seed) samples. As one can see, the 500 nm band does not appear for the SAT15 (boule) sample cut far from the seed.

Figure 5b shows results of additional absorption measurements after annealing of LSAT15 sample in hydrogen and next in air. Annealing of the LSAT15 sample in hydrogen at 1473 K for 1 h leads to arising of a double structured deep negative additional absorption (bleaching) with two extremes centered at about 375 nm and 430 nm. This fact confirms the hypothesis on Ti^{3+} origin of the 500 nm band. Annealing in air at 1673 K for 1 h leads to arising of one wide, unstructured band centered at about 410–430 nm. Such a type of band was previously determined as Ti^{3+} transition of ion placed at a perfect octahedron [7]. Emission characteristics of the band revealed wide structured emission presented in Fig. 6. It may be due to Ti^{3+} emission.

Figure 5c presents results of measurements of additional absorption after annealing treatments in hydrogen (1) and in air (2). As one can see, Ti^{2+} absorption peaks placed near 2700 nm arises after annealing in hydrogen.

Subsequent annealing of the sample in air leads to the disappearing of the spectrum.

Gamma irradiations

We expect that not all ions entered in LSAT1 crystal at interstitials or at octahedra with missing O^{2-} ion not giving luminescence. It is possible to check the hypothesis performing irradiation of the investigated crystal with gamma rays. We expect a change in the Ti valency and to obtain Ti^{3+} emitting centers. Two doses of gamma ^{60}Co irradiations were applied: 10^5 Gy and 10^6 Gy.

As is seen from Fig. 7, independently of the applied dose, two additional absorption bands can be clearly distinguished: 423 and 2762 nm. The first band seems to be related to Ti^{3+} transitions [9], while the latter may be the Ti^{2+} absorption band [5]. We also observed Ti^{2+} bands in the crystals annealed in hydrogen (see Fig. 5c). 10^6 Gy irradiation does not result in increase in the absorption coefficient and does not introduce color centers.
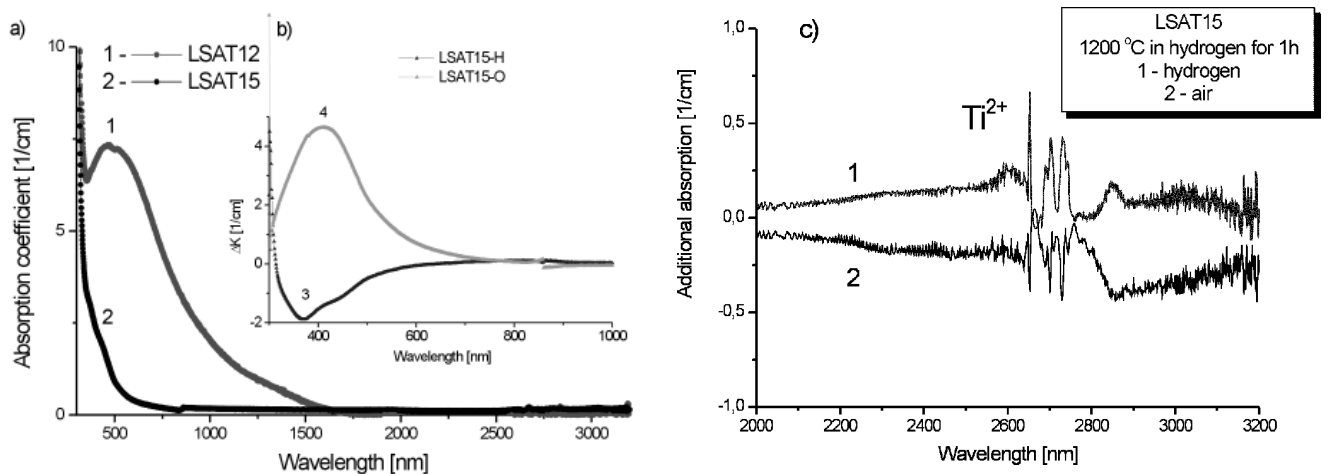

Fig. 5. a) – Room-temperature absorption coefficient of LSAT12 (1) and LSAT15 (2) samples in the range 300–3200 nm; b) – additional absorption of LSAT15 sample after annealing in hydrogen at 1473 K (3) and in air at 1673 K (4); c) – the same picture as (b) in the range 2000–3200 nm.
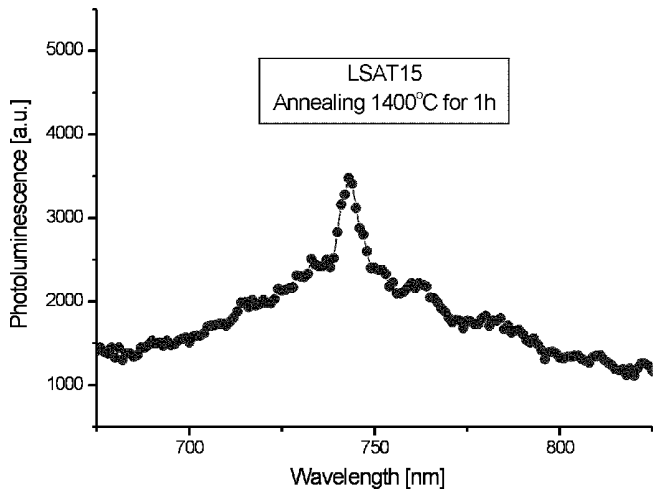
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Fig. 6. PL of LSAT15 sample annealed in air at 1673 K for 1 h.
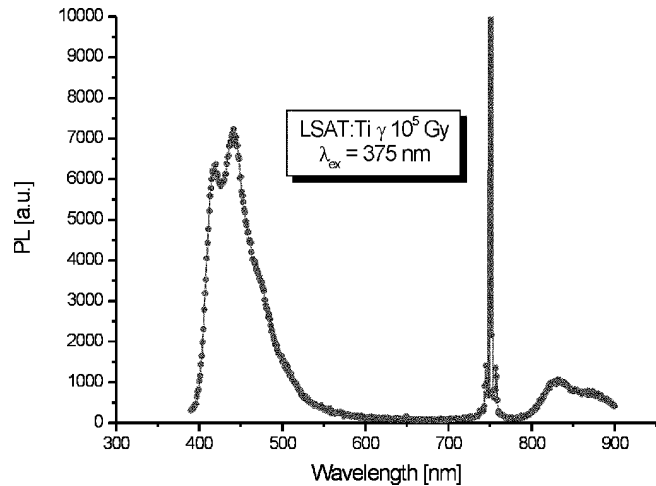

Fig. 8. Photoluminescence of LSAT15 sample after γ-10^5 Gy irradiation. Excitation wavelength 375 nm.

Figure 8 shows photoluminescence of LSAT:Ti single crystal excited with 375 nm. The wavelength of excitation is taken out as the maximum wavelength of excitation for 830 nm emission. Two double structured emission spectra are observed: 420–440 nm and 833–883 nm. The double structure of the bands suggests that they are both coming from Ti^{3+} ions with ^{2}T$_2$ clearly split ground state.

Figure 9 presents an excitation spectrum of LSAT15 sample for λ_{em} = 441 nm after g 10^5 Gy irradiation. The same type of spectrum was obtained for 420 and 830 nm emissions. This means that these two emission bands, 420–440 and 830–860 nm may be connected with Ti^{3+} emission for Ti^{3+} ions placed at two different lattice sites: high-field and low-field. The latter band seems to be responsible for ^{2}E-^{2}T$_2$ emission from Ti^{3+} ions located at the distorted octahedra (Al, Ta) positions. The 420–440 nm emission seems to be related to Ti^{3+} ions located in other type of octahedral site (perfect octahedron) or other site.

Thus there are at least three lattice sites where Ti^{4+} ions locate themselves being next transferred to Ti^{3+} due to the electron delocalization effect: Ti^{4+} + e$^-$ → Ti^{3+}. These are Al, Ta high and low field sites and interstitials.

Discussion and conclusions

The Ti^{3+} ion has the 3d^1 electron configuration outside the closed shells and a resulting ^{2}D ground state for the free ion. In octahedral coordinated sites, ^{2}D splits into ^{2}E and ^{2}T$_2$ states, separated in energy by the octahedral crystal field energy. The Ti^{3+} ion substitutes for Al^{3+} in crystals such as Al$_2$O$_3$ and Y$_3$Al$_5$O$_{12}$ where the symmetry is distorted by trigonal displacements of the environment. Such distortions in concept with the spin-orbit coupling completely remove the fivefold orbital degeneracy of the 3d^1 configuration [11]. The consequences of these splitting and the strong electron-phonon coupling are the two overlapping absorption bands in the visible region. This type of absorption band is also observed in the case of SrAl$_{0.5}$Ta$_{0.5}$O$_3$:LaAlO$_3$ solid-solution crystal as the 500 nm room temperature absorption.

Photoluminescence transitions occur from the lower excited state to the three components of the electronic ground state. If the ground-state splitting is less than the width of the band due to the transition, the luminescence results in a single broad band.
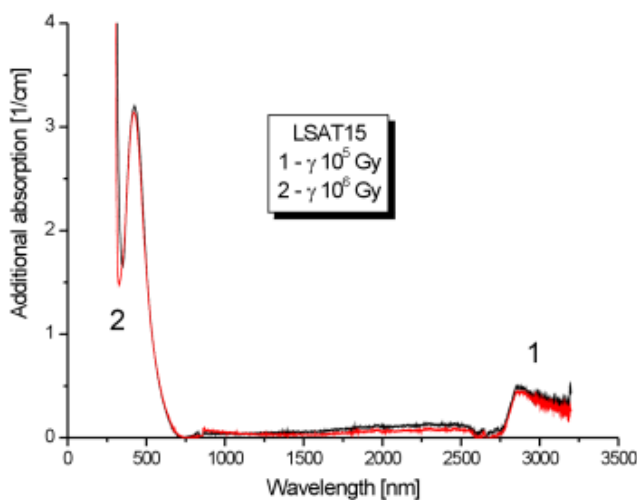

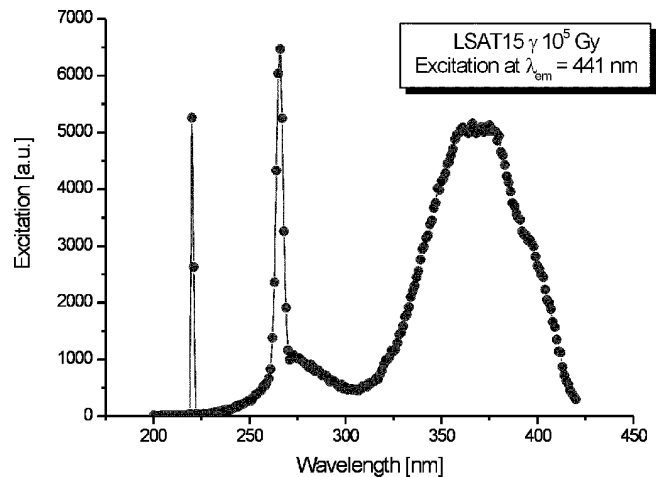**Fig. 7.** Additional absorption band of LSAT15 crystal after gamma irradiation with a dose of 10^5 Gy (1) and 10^6 Gy (2).

Fig. 9. Excitation spectrum of LSAT15 γ-irradiated sample for λ_{em} = 441 nm.

The 500 nm asymmetric band (489 and 562 nm bands as was stated due to low temperature measurements) does not give any emission spectra probably due to O^{2-} deficiency (O^{2-} missing ion in oxygen octahedron) [7]. It is also possible that the absorption is connected with Ti^{3+} ions placed at interstitials.

Compounds in the lower oxidation states – I, II, III are readily oxidized to titanium (IV) by air, water or other reagents. In consequence, Ti^{3+}-doped crystals must be grown in middle-reducing or neutral atmospheres to prevent oxidation to the Ti^{4+} state. The presence of Ti^{3+} ions in the thin layer outside the crystal is connected with the growth atmosphere which is poor of oxygen outside the growing crystal. Thus, the violet coloration of the outside thin layer is due to reduction phenomenon.

X-ray measurements have shown that the neighbouring octahedra in the LSAT crystal are substituted in an alternate way by Al and Ta ions. Moreover, in the crystal there also exist regions showing long-range order with respect to Al and Ta substitution. This is conducive to arising different types of Ti sites. Their farther differentiating is due to $Ti^{4+} \rightarrow Ti^{3+}$ transformation under gamma irradiation or annealing treatment.

From X-ray measurements it also results that oxygen octahedra in the investigated crystal are not distorted, so that introduction of Ti^{3+} into Al, Ta sites seems to be difficult and most of Ti ions should enter as Ti^{4+} at Al, Ta sites and in the interstitial positions. The results of the X-ray crystal structure analysis suggested that radiative Ti^{3+} centers occupy perfect octahedra, whereas the nonradiative Ti^{3+} centers may be accompanied by the vacancy of the O^{2-} ligand ion in the Ti^{3+} octahedron [7].

If oxygen octahedron around Al^{3+} site is not distorted, one can obtain only one Ti^{3+} absorption band [7]. Such a situation is observed in the case of LSAT15 sample exposed to γ-irradiation at 375 nm absorption. Moreover, the ground state seems to be split more than the width of the band due to the transition, so in consequence a double structure of the luminescence spectrum is seen. More detailed confirmation of the above conclusions can be obtained using the electron spin resonance technique. It demands farther investigations.

We suppose that in the LSAT:Ti as grown crystal, Ti^{3+} and Ti^{4+} ions are present at interstitials and at octahedra with missing O^{2-} ligand ion (violet regions at conical and boule part of the crystal). This conclusion was confirmed by low-temperature measurements and annealing treatments. Moreover, some amount of Ti^{4+} ions at octahedral Al, Ta sites is observed that change to Ti^{3+} under gamma irradiation and annealing treatment. Annealing in hydrogen and γ-irradiation may also produce a small amount of Ti^{2+} ions [10]. This was confirmed by annealing and irradiation experiments and photoluminescence measurements.

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