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Growth conditions influence on thermally stimulated luminescence of sapphire single crystals

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Abstract. The results of investigation of thermally stimulated and photoluminescence as well as absorption spectra of a-sapphire grown by a technique of horizontally directed crystallization in a protective gas medium of varying composition and pressure are presented. This technique has an advantage of minimization of W and Mo erosion, thus providing a considerably reduced prime cost. At the same time, there are some problems connected with emergence of considerable number of anion vacancies, whose in-axis concentration gradient is directed oppositely to that of dopants (mainly Ti). The correlations are found between the conditions of α-sapphire growing and the data of absorption and luminescent spectroscopy. An interaction between the anion vacancies and Ti dopants, which induces a transition from electric-charge state Ti^{4+} to Ti^{3+}, is discussed.

Keywords: sapphire, thermally stimulated luminescence, titanium dopant, anion vacancy, absorption, photoluminescence.

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1. Introduction

Last time the single crystalline sapphire (α-Al_2O_3) finds new fields of application. We will mention only those ones related to electronics. First of all sapphire is the basic substrate material for electronic devices, particularly light emitting diodes (LEDs). Today's priority is development of white LEDs, which in the outlook have to replace the less energy-effective incandescent lamps [1]. As a result of several design programs, the various working models of such devices have been elaborated and tested, and at the same time the influence of impurity and defect states in sapphire substrate on the spectrum and chromatic coordinate of the resulting radiation was revealed [2]. Attempts are going on to make active laser media on F-centers, which are genetically related with anion vacancies in sapphire [3]. The authors of [4] proposed to use the sapphire with F-centers in a new generation of dosimetric devices. The works are going to improve the beam strength of sapphire single crystal elements for high-power UV optics [5]. All the above examples show that the impurity/defect subsystem in the single crystalline sapphire plays a significant role in Al_2O_3-based electronic devices and its properties depend in its turn on the growth technology.

The Institute of single crystals of NASU for several years develops the basics of a "cheap" growth technology allowing to obtain the single crystalline sapphire of commercial quality in protective gaseous atmosphere [6,8]. One of the advantages of this technology is the minimal erosion of tungsten and molybdenum during the growth process. It is one of the reasons of its low prime cost. However the variation of growth conditions must be accompanied by the change in single crystalline impurity/defect subsystem. The thermally stimulated luminescence (TSL) is a well-known effective method for study of defect states of various nature. Taking into account the above considerations the aim of the present study is a search for correlations between the technological conditions of sapphire crystal growth and its TSL signal as well as analysis of the origin of TSL peaks. The sapphire samples grown both in gaseous ambient of various compositions (Ar + CO, CO, CO + O_2, Ar + air) under different pressure (10^{-1}÷100 torr) and by common vacuum technology (10^{-5} torr) have been studied.

2. Experimental technique

The sapphire single crystals were grown in a 10^{-4} torr vacuum or protective gas media of different composition

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and pressure with using the graphitized-carbon or W-Mo thermal units [6-8] by means of horizontally directed crystallization. For crystal growing a charge with low content of main impurities was used (see Table 1). During the crystal growing, the impurities in the charge were either evaporated, or pushed off by the inter-phase interface. As a result, the composition of impurities changes gradually from the beginning of the crystal to its ending. Then the disk-like samples of diameter 10 mm and thickness 1 mm were cut from the single crystals with subsequent grinding and polishing.

Table 1. Content of impurities in the charge.

Element	Ca	Cr	Fe	Ga	Mg	Na	Si	Ti
Concentration, ppm	< 5	< 2	< 4	< 3	< 2	< 10	< 15	< 10

The transmission spectra were measured at $T = 295$ K by the spectrophotometer of "Specord-UV-VIS" type in the spectral region 200÷800 nm. An absorption coefficient K(l) had been determined after correction by the reflection and unity-thickness normalization were carried out. To measure the TSL curves, the samples were exposed to X-ray irradiation in the air atmosphere at $T = 295$ K during a time period of 70 min (Cu anode, 40 kV, 10 mA), then heated with a constant rate of 1 K/s up to $T = 600$ K. TSL signal was received by a photomultiplier FEU-106 operating in the photons-count mode and processed by an automated setup. To distinguish components of the TSL signal, the normalized absorption filters with known transparency band were placed between the sample and the photomultiplier.

3. Results and discussion

When describing the obtained results we will proceed from the following well-known regularities of defects' formation in the course of growing the a-sapphire single crystals by means of horizontally directed crystallization in a protective gas ambient of varied reduction potential [8]. A characteristic feature of such a growth is the presence of O^{2-} anion vacancies (F-centers), which are located in the initial part of the ingot. The concentration of such centers is directly proportional to the reduction potential of gas medium. As to the terminal part of the ingot, the impurities of the extrinsic origin emerge here under the action of crystallization front. The Ti dopant makes the most significant contribution to the optical properties of a-Al_2O_3, while the anion vacancies play a main role in determining the charge state of the Ti dopant (Ti^{4+} or Ti^{3+}). Therefore, the gradient of the vacancies' concentration and that of the Ti dopant, which are directed oppositely, form a complicated non-uniform distribution of defect/dopant complexes determining optical and functional characteristics of the sapphire. This is the basis on which we will consider the obtained experimental results.

a) The absorption spectra of sapphire crystals grown in the medium with various reduction potential are shown in Fig. 1. In the spectra of crystals grown in the graphitized-carbon thermal unit in the CO ambient with low reduction potential, the wide absorption band in the wavelength range 200÷230 nm, which is associated with the presence of Ti impurity in its Ti^{4+} charge state [9,10], was prevailing (Fig. 1, curves 1 and 2). Similar band was also observed in spectra of crystals grown under neutral conditions, for instance, in the W-Mo thermal unit and vacuum of $P = 10^{-4}$ torr (curve 4), or crystals grown by Verneyl's method. In the crystals grown under condition of high reduction potential, the compensation of excessive positive electric charge takes place in accordance with the following reaction: $(V_o^{++} + 2e) + Ti^{4+} \rightarrow (V_o^{++} + e) + Ti^{3+}$, with V_o^{++} being an oxygen vacancy, and e – an electron. In the absorption spectra of such crystals a band with $\lambda_{max} \approx 205$ nm, that is connected with the presence of considerable concentration (up to 10^{17} cm^{-3}) of F-centers [10, 11], was dominating (Fig. 1, curve 3). The intensity of this band increased with the gas pressure rise (Fig. 2). It should be noted that under UV irradiation the Ti^{4+} impurity is reduced by the reaction: $O^{-2} + Ti^{4+} + h\nu \leftrightarrow O^{-} + Ti^{3+}$. So, the O^{-} ions appear as a result of the Ti^{4+} ions reduction, and form centers of coloring, which lead to formation of the wide absorption band with λ_{max} about 400 nm. The Ti^{3+} ions absorb in the region 500÷550 nm, while the peaks of emission of F^{+}-centers, F-centers and Ti^{3+} ions are located at 335 nm, 413 nm and 720 nm, respectively [9, 10].

b) At the temperature interval 295÷600 K, the peaks at $T_{m1} = 425$ K, $T_{m2} = 440$ K, $T_{m3} = 480$ K and $T_{m4} = 560$ K

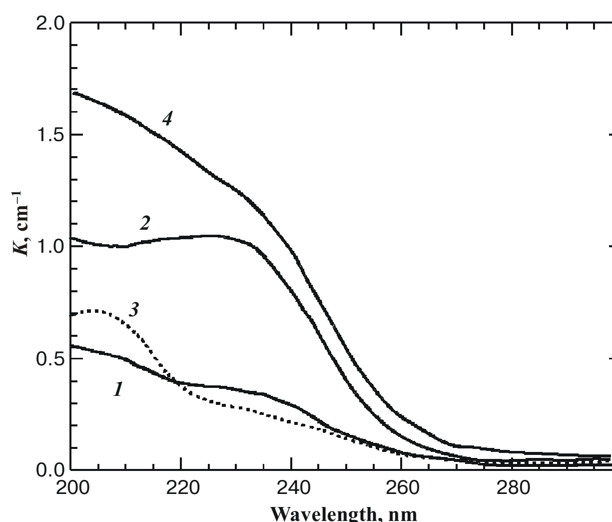

Fig. 1. Absorption spectra of crystals grown in media with low (*1*, *2*, *4*) and high (*3*) reduction potentials. CO medium: $P = 0.05$ torr, beginning (*1*) and ending parts (*2*) of the crystal; Ar+CO medium: $P = 10$ torr, terminal section of the crystal (*3*); Ar+CO medium: $P = 10^{-4}$ torr, W-Mo thermal unit (*4*).

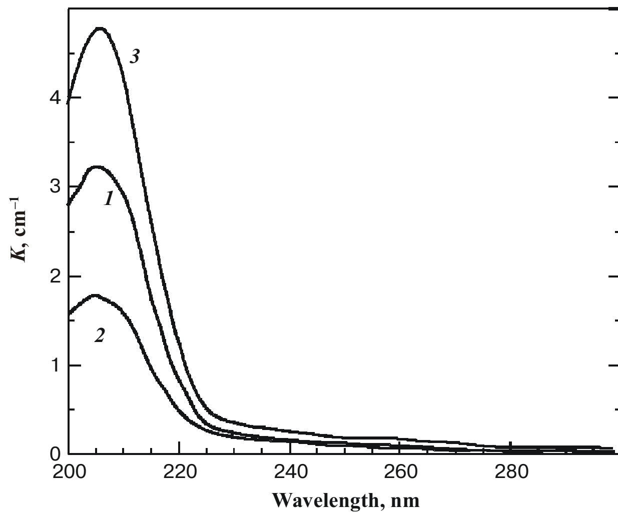

Fig. 2. Absorption spectra of crystals grown in the Ar+CO medium with high reduction potential: P = 10 torr, beginning part of the crystal (*1*); P = 30 torr, terminal (*2*) and initial (*3*) sections of the crystal (*3*).

were found on the TSL curves of sapphire crystals. The number of peaks and their amplitudes depend on the growth conditions and the position of crystal's section which a sample was cut out from. Two emission bands, one being within the interval 335÷480 nm and another one lying in the wavelength region with λ > 560 nm, contribute to the T_{m1} peak. In an explicit form this peak is manifested only for crystals grown in media with high reduction potential (Fig. 3, curves 1, 2 and 3). Intensity of this peak increases with the rise of (Ar+CO) ambient pressure (Fig. 3), as for the F-centers' absorption band. The concentrations of the F-centers in samples 1, 2 and 3, as estimated from the absorption spectra, are $6.0 \cdot 10^{16}$ cm^{-3}, $3.4 \cdot 10^{16}$ cm^{-3} and $9.2 \cdot 10^{16}$ cm^{-3}, respectively. Therefore, one can suppose the T_{m1} peak of the TSL to be connected with F-centers. For crystals grown in the media of low reduction potential, this peak does not manifest explicitly, being masked by the more intense TSL peak with maximum at T_{m2} = 440 K.

The T_{m2} peak is predominantly formed by the emission in the region of $\lambda \geq 560$ nm and, for crystals grown in the CO medium with low reduction potential, this TSL peak was by an order of magnitude more intensive than the other ones (Fig. 4, curve 2). Provided that the reduction potential of the medium rises, the peak intensity is coming down in a manner analogous to that of the Ti dopant's absorption band, which corresponds to its charge state Ti^{4+}. In particular, for a crystal grown in CO medium under the pressure P = 0.05 torr, the intensity of the T_{m2} peak for a sample cut out from a beginning part of the crystal is as twice as compared to that for the ending-part sample (Fig. 4, curves 1 and 2), that is parallel to the concentration change of Ti^{4+} ions (Fig. 1, curves 1 and 2). This TSL peak was also observed for the crystal grown in the W-Mo thermal unit in vacuum, i.e. under conditions close to neutral (Fig. 4, curve 3). That is why one can suppose this peak to be associated with presence of the Ti^{4+} ions.

At the temperature region of peak T_{m3} = 480 K the emission with li560 nm was mainly observed. Alike the TSL peak at T_{m1} = 425 K, this one is also observed only in crystals grown in media of high reduction potential, and its intensity increases along with the reducing power of a medium (Fig. 3, curves 1, 2, and 3), when Ti dopant is mainly in its electric-charge state Ti^{3+} [9]. Hence, this TSL peak is likely originated by presence of the Ti^{3+} ions. Analogously to the T_{m1} peak, this one does not also manifest itself explicitly for crystals grown in low-reducing-potential media, that is apparently conditioned by

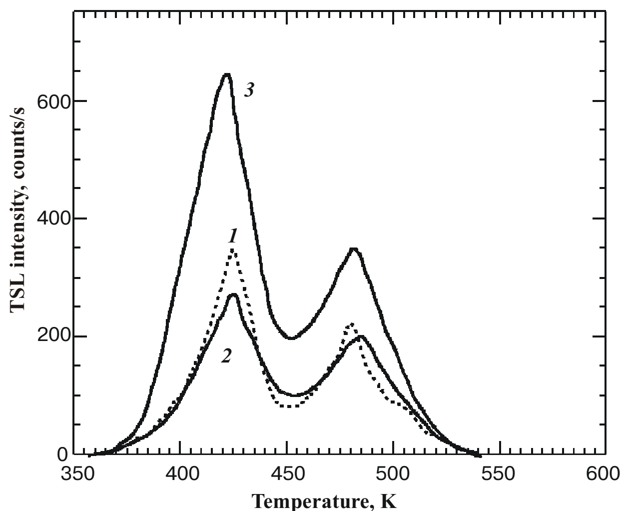

Fig. 3. TSL curves of crystals grown in the Ar+CO medium with high reduction potential: P = 10 torr, initial part of the crystal (*1*); terminal part of the crystal, P = 30 torr (*2*), P = 400 torr (*3*).

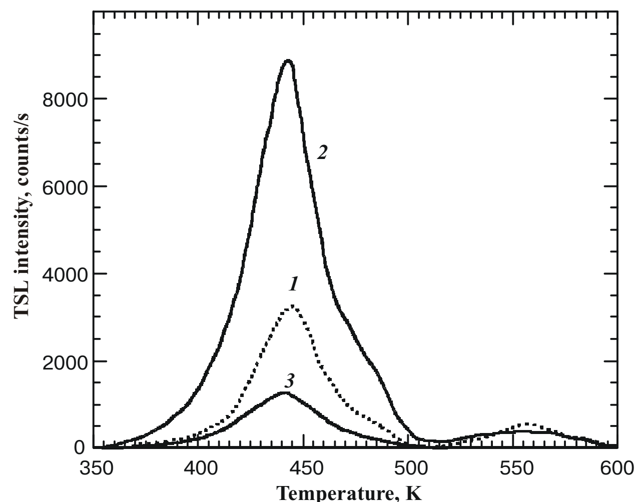

Fig. 4. TSL curves of crystals grown in the CO medium with high reduction potential: P = 0.05 torr, beginning (*1*) and ending (*2*) sections of the crystal; vacuum, W-Mo thermal unit (*3*).

the presence of much more intense adjacent TSL peak observed at T_{m2} = 440 K.

The TSL peak at T_{m4} = 560 K is formed by the emission region of 335ë720 nm. It is observed, along with the T_{m1}-related peak, for crystals grown in a low-reduction-potential medium, whose absorption spectra are characterized by the Ti^{4+} ions' band in the range of 200÷230 nm. The behavior of the T_{m4}-related peak is anticorrelative with that of the T_{m2}-related peak, namely, the maximal intensity of the T_{m4}-related peak was achieved for the sample with the minimal intensity of the T_{m2}-related one (Fig. 4, curves 1 and 2). The T_{m4}-related peak was not revealed in TSL curves of crystals grown in both the neutral (Fig. 4, curve 3) and high-reduction-potential (Fig. 3) media, i.e. it is connected with simultaneous presence of both the doping and the intrinsic defects of the lattice. Thus, this peak is probably originated from traps of less trivial nature, more likely with the complexes of the type: cathion impurity-anion vacancy.

Therefore, the crystals grown in reducing media of CO or CO+Ar types can be grouped in two following classes with respect to the TSL signal behavior: for crystals grown in high-reduction-potential media, only the T_{m1}- and T_{m3}-related TSL peaks were observed, while for those ones grown in low-reduction-potential media, the T_{m2}- and T_{m4}-related peaks dominate in TSL curves (Figs 3 and 4). This classification is also proved by the results obtained for a crystal grown in the medium with relatively high reduction potential, namely, Ar+CO upon P = 10 torr (see Fig. 5).

The following information is important for data analysis. A composition of the medium has not been monitored during the growing, yet from the results of previous investigations [7] it is known, that under such conditions the concentration of the reducing component (CO) does not decrease, but even increases close to termination of the crystallization. It is also known, that in the terminal

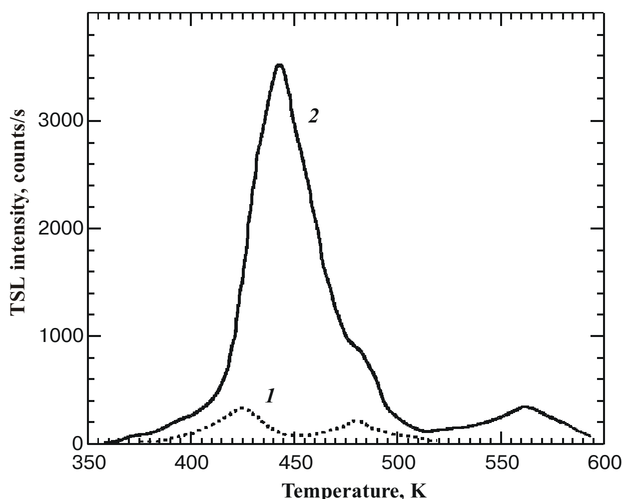

Fig. 5. TSL curves of samples cut from the beginning (*1*) and ending parts (*2*) of the crystal grown in the Ar+CO medium, P = 10 torr.

section of a crystal the content of Ti dopant is by 2 or 3 times higher than that in the initial one. It was found that in the absorption spectrum of a sample cut out from the initial part of the crystal, the band associated with F-centers (λ_{max} = 205 nm), was prevailing (Fig. 2, curve 1). For the sample from crystal's central part the intensity of this band was lower, and, accordingly, for the terminal section the characteristic wide band associated with presence of Ti^{4+} ions, was observed in the region 200ë230 nm (Fig. 1, curve 3). Simultaneously, the T_{m1}- and T_{m3}-related TSL peaks were observed for the initial section of the crystal, whereas for the terminal part they were hidden by much more intensive T_{m2}-related peak (Fig. 5). Besides, the T_{m4}-related TSL peak emerged for the last case, while it was absent for a sample from the initial section of the crystal.

The phenomena observed may be explained as follows. In the sapphire crystals under consideration, the concentrations of the anion vacancies and Ti dopants are of the same order of magnitude (10^{17} cm^{-3}) [7]. Seemingly, in the initial part of the crystal owing to the presence of anion vacancies and low Ti concentration, the conditions are provided for effective Ti reduction by the reaction: $(V_o^{++} + 2e) + Ti^{4+} \rightarrow (V_o^{++} + e) + Ti^{3+}$. As the Ti concentration increases while one moves towards the terminal section of the crystal, the reduction capability become poorer and the considerable part of Ti dopant remains in the Ti^{4+} state. It should be noted that lowering of the absorption peak of neutral F-centers is caused with a partial conversion of neutral F-centers into F^+-centers as a result of the above reaction. It is quite possible that this is the thermally activated charge transfer between closely situated defects (impurity-vacancy pairs) that gives rise to appearance of the T_{m4}-related TSL peak, which was observed only for the crystals with intermediate degree of the Ti dopant reduction, and was not observed for crystals grown in a neutral medium as well as in crystals with high degree of Ti reduction.

c) Photoluminescence (PL) spectra of five types of sapphire single crystals, each grown with its own specific procedure, have been studied:

type 1 – the crystal is grown in CO medium under pressure of 0.1÷0.3 torr (reducing atmosphere), not containing microparticles;

type 2 – the crystal is grown in CO medium under pressure of 0.1÷0.3 torr (reducing atmosphere), containing about 10^5 cm^{-3} microparticles;

type 3 – the crystal is grown in Ar + 10 % H_2 medium under pressure of 800 torr (reducing atmosphere), containing about $3 \cdot 10^6$ cm^{-3} microparticles;

type 4 – the crystal is grown in vacuum of about 10^{-4} torr in the W-Mo thermal unit (neutral medium), not containing microparticles;

type 5 – the crystal is grown from a pure raw material in CO medium of 0.1÷0.3 torr pressure (reducing atmosphere), not containing microparticles.

Photoluminescence has been excited at room temperature in polished disk-shaped sapphire samples (with diameter 20 mm and thickness 5 mm) by the 337-nm radia-

tion of pulsed 8-ns N_2-laser with 5 kW peak power. To record the spectra in 440÷750 nm spectral range a diffraction spectrometer equipped with CCD array has been used.

Only the samples 2 and 3 have a measurable luminescence under the excitation conditions mentioned above, while the luminescence intensity of the rest samples was negligibly small. The luminescence spectra of the samples 2 and 3 are given in Fig. 6. They look like wide structureless bands in the 450÷700 nm range with peak at 550 nm. It should be emphasized that the samples 2 and 3 contain microparticles. From the absorption spectra of all five types of the samples it follows, that exactly the samples 2 and 3 have a noticeable absorption at 337 nm, which apparently is due to the microparticles presence. The known luminescence bands of F-centers (413 nm) and Ti^{4+} centers (425 nm) are situated outside the measurement range. Luminescence bands of Cr^{3+} center (690 nm) and Ti^{3+}centers (720÷770 nm) are much narrower and we have not really detected them. Moreover, all the indicated centers can be excited efficiently only by more short-wavelength radiation at the range 200÷250 nm. Thus it is advisable to interpret the detected emission band as the luminescence of microprecipitates with the estimated size of 1ё2 mcm. The observed twofold difference in luminescence intensity for these two samples can not be easily explained. Really, the sample 2 has twice as high the luminescence signal as the sample 3 has, though the latter features higher microparticle concentration. Apparently we observe the concentration quenching of luminescence caused by the high microparticle concentration.

4. Conclusion

Thus, it was established that the TSL curves of sapphire crystals may be sorted into two types depending on the reducing capability of a gas ambient upon growth. For crystals grown in the CO or Ar+CO medium with high reduction potential ($P \geq 10$ torr), the peaks at 425 K and 480 K prevailed in TSL signal. We suppose the origin of these peaks to be connected with presence of the F-centers and Ti dopant in its Ti^{3+} charge state. If the crystals were grown in a medium with low reduction potential ($P \leq 10$ torr) or close-to-neutral medium, then the TSL peaks at 440 K and 560 K were dominating. The former peak is most probably associated with the Ti dopant in the Ti^{4+} charge state, while the latter one is connected with anion defect-Ti impurity interaction.

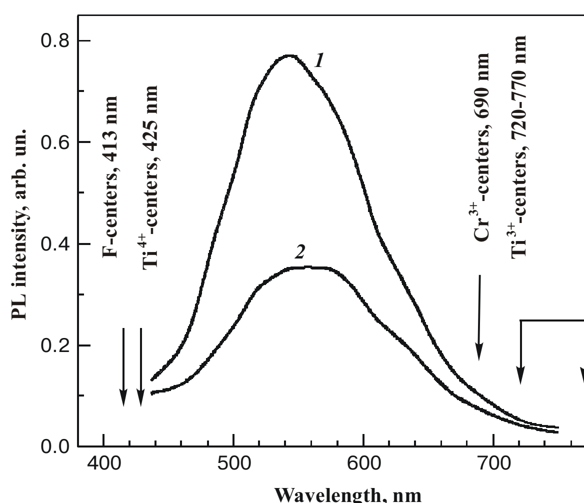

Fig. 6. Photoluminescence (PL) spectra of type 2 sample grown in the CO medium, P = 0.1–0.3 torr (*1*) and type 3 sample grown in the Ar+10% H_2 medium, P = 800 torr (*2*).

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