

COMPARISON OF LUMINESCENCE IN LiGaO_2 ,
 Al_2O_3 -Ga AND Al_2O_3 -Li CRYSTALSL. Trinkler¹, A. Trukhin¹, Mitch M.C. Chou²¹Institute of Solid State Physics, University of Latvia,
8 Kengaraga Str., LV-1063 Riga, LATVIA²Center of Crystal Research, National Sun Yat-sen University,
Kaohsiung, TAIWAN
trinkler@latnet.lv

We have studied luminescence of LiGaO_2 , Al_2O_3 -Ga and Al_2O_3 -Li crystals in order to reveal the nature of luminescence centres and mechanisms in these crystals. In Al_2O_3 -Ga presence of Ga impurities determines occurrence of the 280 nm emission band, which demonstrates intra-centre character in photoluminescence and recombination character under X-ray irradiation. In Al_2O_3 -Li crystal lithium induced luminescence is presented with the 326 nm band, which has a recombination character. Basing on spectral similarity of the main luminescence bands in pure LiGaO_2 crystal with the dopant-induced emission bands in Al_2O_3 , and on peculiarities of the X-ray induced thermoluminescence, the adjustment of the previous luminescence interpretation is done. It is proposed that the donor-acceptor pairs with random separation distribution responsible for the 280 nm emission are represented with gallium Ga (plus an electron) and O (plus a hole) pairs, while the donor-acceptor pairs, producing the 330 nm emission band contain a lithium ion, presumably in the interstitial position Li_i^0 , and a neighbouring oxygen ion with a caught hole.

Keywords: *alumina, donor-acceptor pairs, exciton, lithium metagallate, luminescence*

1. INTRODUCTION

Recently we have studied luminescence properties of the wide band gap crystal lithium metagallate LiGaO_2 (LGO) (optical gap around 6 eV [1]) grown by authors of [2] and found out that the main emission bands are located at 280 and 330 nm, (4.43 and 3.76 eV), correspondingly, see Fig.1. [3]. The 280 nm band is excited only in the range of intrinsic absorption including the exciton-like sharp band at ~6 eV (206 nm), while the 340 nm band is also excited within optical transparency range peaking at 220 nm. The 280 nm band was assigned to recombination luminescence of randomly separated donor-acceptor pairs (DAPs); the 340 nm band also

demonstrated recombination character [3]. However, the components of the donor-acceptor pairs remained unknown. In the given paper, we present the results of the investigation of alumina Al_2O_3 (AO) doped with impurities Ga and Li, constituting the lattice of LGO, in order to find peculiarities in luminescence of these materials, which could shed light on luminescence mechanisms and DAP composition in LGO. On the other hand, investigation of Al_2O_3 with different dopants could enlarge the application range of this prospective material, mainly known for its outstanding dosimetric properties, when doped with carbon, causing the oxygen deficiency.

There are some studies of luminescence properties of Ga doped AO done before. Cathodoluminescence [4] studies showed presence of the emission band at about 4.5 eV, which was ascribed to Ga luminescence centre. The same emission band was found in the photoluminescence process, under UV light excitation above 6 eV [4]. The same emission band appeared in thermally stimulated luminescence (TL) after x-ray irradiation [4]. TL peaks were observed at ~ 200 K and ~ 580 K. According to our knowledge, there is no much information on luminescence properties of another object of investigation – AO doped with lithium.

In the given paper, we present luminescence parameters of LGO, AO-Ga and AO-Li obtained under pulsed and continuous photoexcitation as well as X-rays at different temperatures. Additionally X-rays induced TL processes were studied in these materials.

2. EXPERIMENTAL STUDY

The studied nominally pure LGO crystal sample was grown by Czochralski method [2]. The studied AO-Ga crystals were grown by the Verneil method from $\alpha\text{-Al}_2\text{O}_3$ powders containing 5 wt% of Ga and were the same as in [4]. Crystal AO-Li was obtained by adding 2 % Li_2O to powders.

Experimental equipment contains different light sources used for luminescence excitation: ArF laser (193 nm) and KrF laser (248 nm), model PSX-100, made by Neweks, Estonia, with pulse energy of about 5 mJ and duration of 5 ns and a deuterium lamp 30 W combined with 0.5 m Seya-Namioka vacuum monochromator. X-ray irradiation was performed by an x-ray tube with tungsten anode operating at 40 kV and 20 mA. A refrigerator with a special sample holder was used allowing cooling down to 10 K and heating up to 750 K.

3. RESULTS

3.1. Photoluminescence and TL of LGO

The newly obtained results on LGO refer to the X-ray induced processes, the main attention being paid to the 280 nm band. It was found that the 280 nm emission band was present in the X ray-induced luminescence (XL) (Fig. 2, curve 1) and in the XL afterglow when the irradiation was ceased (Fig. 2, curve 2). Besides, at temperatures below 80 K this band was also observed in X-ray induced TL emission (Fig. 2, curves 3 and 4), at higher temperatures this band disappeared from the TL emission spectrum (Fig. 2, curve 5). Such behaviour was also demonstrated by the

TL glow curve (Fig. 2, insert) obtained by selecting 280 nm emission. The presence of the 280 nm band in XL afterglow and TL emission spectrum gave an additional argument for the recombination nature of this luminescence band.

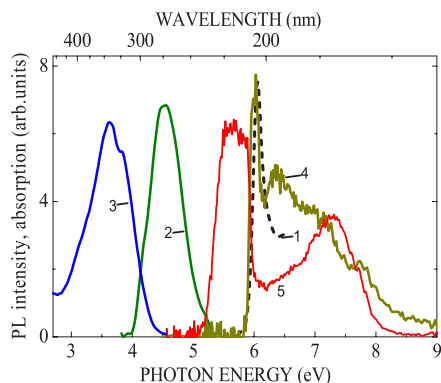


Fig. 1. LGO crystal optical absorption at RT (1) [1,3], PL at laser excitation 193 nm (2) and 248 nm (3); PLE of 280 nm emission (4) and 330 nm emission (5).

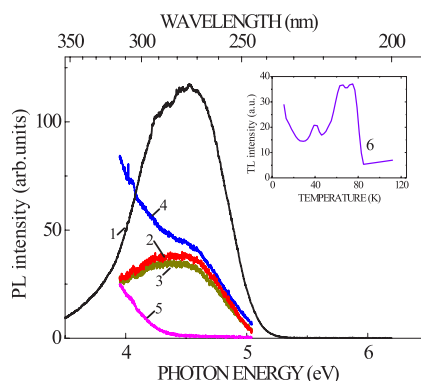


Fig. 2. LGO: XL spectrum at 10 K (1); XL afterglow at 10 K (2); TL emission at 35–45 K (3); 55–75 K (4); 85 K (5). Insert – TL curve (6) selecting luminescence with the 280 nm optical filter.

3.2. Photoluminescence of Al_2O_3 -Ga

The main spectral parameters of gallium doped alumina crystal are presented in Fig. 3. Apart from the sharp line in the red part of spectra tentatively assigned to Cr and/or Ti impurities and a blue luminescence bands, both typical for all samples of alumina crystal (not shown in the figures), there is a unique emission band characteristic only of AO-Ga at 280 nm (~ 4.5 eV) (Fig. 3, curve 1). The corresponding photoluminescence excitation (PLE) spectrum is presented as well (Fig. 3, curve 2) together with the optical absorption spectrum (Fig. 3, curve 3). Excitation band for luminescence at 280 nm starts at around 210 nm (6 eV) with a small band; the main excitation band is situated at 175 nm (7.2 eV).

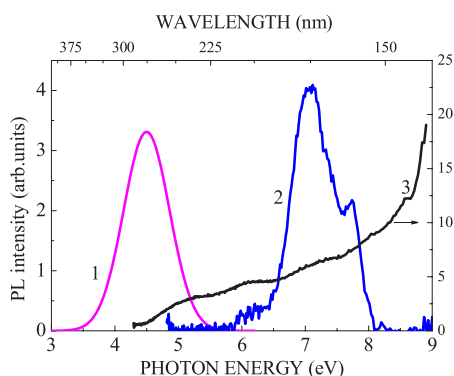


Fig. 3. Photoluminescence spectrum (1) of AO-Ga crystal excited with ArF laser (193 nm; 6,4 eV) and excitation spectrum of the 280 nm band (2) at 60 K. Optical absorption spectrum (3) presented as well.

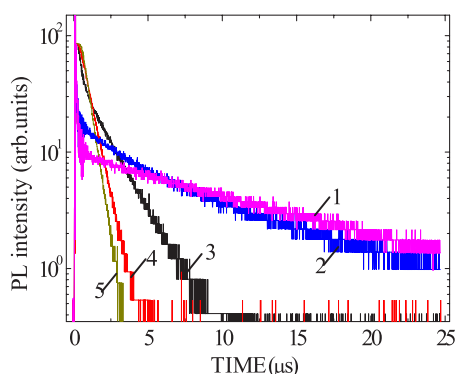


Fig. 4. PL at 280 nm (4.4 eV) decay kinetics of AO-Ga crystal excited with pulses of ArF laser at different temperatures: 60 K (1); 80 K (2); 210 K (3); 261 K (4); 270 K (5).

The 280 nm band in AO-Ga is the main object of interest, because by its spectral properties it resembles the 280 nm band in LGO. The decay kinetics curves under excitation with pulses of ArF laser (193 nm or 6.4 eV) have two components: the fast in the ns range and the slow in the μs range. Thermal evolution of the microsecond component is presented in Fig. 4. It is exponential in all thermal range. Decay time becomes faster with an increase of temperature. The 280 nm emission band of AO-Ga does not appear in afterglow when the ArF laser excitation is switched off. These features of the AO-Ga emission speak in favour of intra-center rather than recombination origin of the luminescence process. According to [4], the 280 nm band is assigned to Ga ion substituting for Al in AO-Ga.

Measuring the time-resolved spectra at 10 K (Fig. 5), we have also found a fast decay component, previously observed under cathode-excitation [4]. The fast component spectrum has a maximum at higher photon energies – 250 nm (4.9 eV) than that for the slow component. We ascribe presence of two emission subbands in the time-resolved spectra to the singlet-triplet splitting and therefore the slow component is ascribed to the triplet-singlet transitions, while the fast component – to the singlet-singlet transitions. In Fig. 6, the time resolved temperature dependence of intensity is compared with that of time constant, both obtained from the same kinetics curves. The thermal dependence of intensity is retarded with respect to the time constant dependence. That can be explained with an increase of transition probability along with an increase of the temperature. It is seen that thermal quenching for the fast luminescence at 250 nm takes place at 80 K. There is good correspondence between dependences of intensity and time constant.

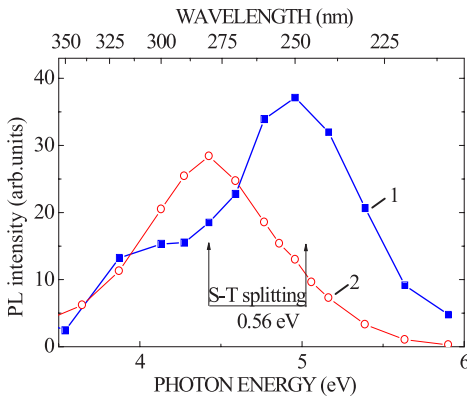


Fig. 5. Time resolved PL spectra of AO-Ga crystal for ns (1) and μs (2) components of decay excited with pulses of ArF laser at 10 K.

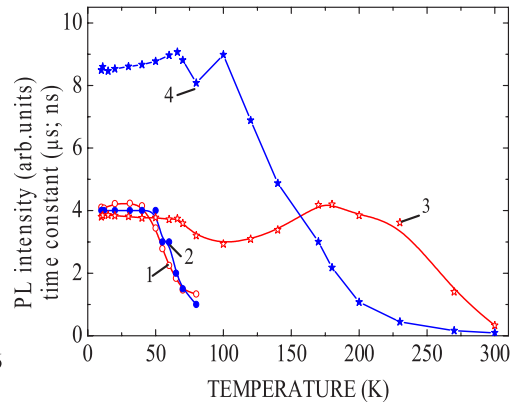


Fig. 6. Time resolved PL intensity and time constant temperature dependences AO-Ga excited with pulses ArF laser. Integral of fast (ns) decay (1); fast time constant (ns) (2); integral of slow (μs) decay (3); slow time constant (μs) (4).

3.3. Photoluminescence of $\text{Al}_2\text{O}_3\text{-Li}$

The AO-Li sample contains several PL bands. We will not discuss here those bands in the red and blue part of the luminescence spectrum, which are observed in all Al_2O_3 samples without intentional doping.

Spectral parameters of AO-Li luminescence related to Li are presented in Fig. 7. This sample has a band at 326 nm (~ 3.8 eV) excited with KrF laser (248 nm or 5 eV). Its PLE spectrum measured with use of the 340 nm interference filter (with FWHM 25 nm) shows a number of bands. Decay kinetics curves of the 340 nm luminescence are non-exponential and become faster with an increase of temperature (see Fig. 8).

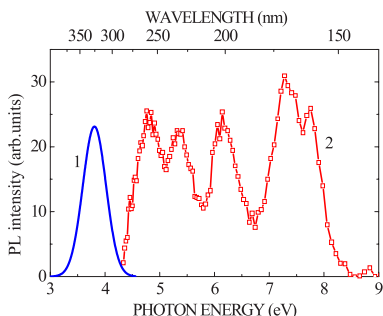


Fig. 7. PL excited at 248 nm (1) and PLE spectra of 330 nm emission of AO-Li (2) at 60 K.

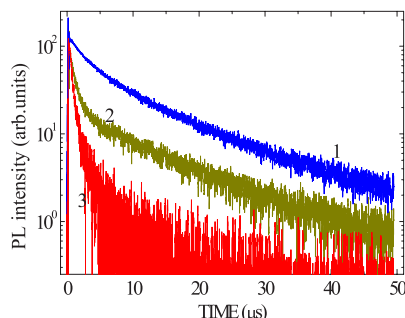


Fig. 8. Decay kinetics of the 320 nm emission band of AO-Li excited with ArF laser at 60 K (1); 80 K (2); 293 K (3).

3.4. Recombination Luminescence of Al_2O_3 -Ga and Al_2O_3 -Li

After ArF laser irradiation we have observed the TL process only in AO-Li crystal (not shown graphically). In AO-Ga TL has not been observed in similar conditions. The x-ray irradiation causes the TL process in both types of crystals. In Fig. 9 TL emission spectra are shown and compared with those of XL spectra. Under X-rays the doped AO samples in XL and TL emission demonstrate the same bands as in PL spectrum.

In AO-Ga the short wavelength band shifts to longer wavelengths from 280 nm to 300 nm with temperature rise. Another point is that AO-Li luminescence spectrum practically is not measurable in TL. Its XL intensity is also rather low, and what is interesting, higher at RT than at 80 K (see Fig. 9, curves 4 and 5). Figure 10 presents TL curves after x-ray irradiation at 80 K and XL growth and afterglow kinetics (inserts). The AO-Li glow curve contains one peak at 260 K. TL of AO-Ga sample contains the same peak, however, more intense, and also peaks at ~ 100 K and at 460 K.

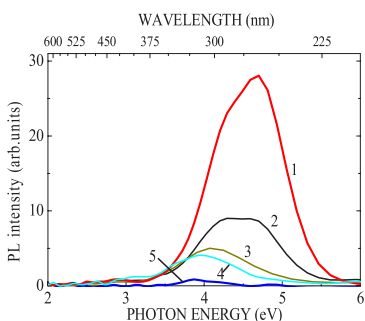


Fig. 9. AO-Ga: XL at 80 K (1); TL spectrum at 180 K (2); TL spectrum at 220 K (3); AO-Li: XL spectrum at 293 K (4); XL spectrum at 80 K (5).

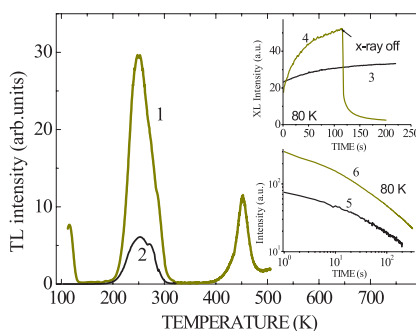


Fig. 10. TL curves of AO-Ga (1) and AO-Li (2) after X-ray irradiation at 80 K. Inserts – XL growth for AO-Li (3) and AO-Ga (4) and XL afterglow for AO-Li (5) and AO-Ga (6).

3. DISCUSSION

In this study, in order to determine the nature of the main PL emission bands of LGO located at 280 and 330 nm (4.43 eV and 3.75 eV), we have investigated luminescence of another wide band material – Al_2O_3 (AO) crystals doped with Li and Ga. In LGO Ga and Li ions belong to the host lattice cations, whereas in AO they are defects – impurity ions. First let us discuss the luminescence of the AO crystals doped with Ga and Li ions.

3.1. Al_2O_3 -Ga

We have shown that in AO-Ga presence of Ga impurity determines appearance of the 280 nm (4.43 eV) emission band, with excitation in the 170–210 nm (5.9–7.3 eV) range. Under UV laser irradiation its decay kinetics has two components – in ns and μs range, the latter being exponential. This emission band is not observed in PL afterglow and TL emission. These facts speak in favour of the intra-centre character of the Ga-related luminescence when excited in its own excitation band. The time resolved spectra of this sample allowed distinguishing of the 250 nm band with time constant ~ 4 ns and the 280 nm band with time constant about 15 μs and assignment of these bands to singlet-singlet and triplet-singlet transitions. The determined value of singlet-triplet splitting is about 0.56 eV, Fig.7. Here we note that in the pure Al_2O_3 luminescence of a self-trapped exciton with 0.25 eV singlet-triplet splitting was detected [5].

Under X-ray excitation the 280 nm emission of AO-Ga is observed in XL afterglow and TL emission, together with XL growth and decay characteristics it definitely confirms the recombination character of the luminescence. The TL curve contains a peak at 260 K, which is characteristic of AO crystal not dependent on dopants [6] and ascribed to an electron trap. The presence of the 260 K curve in the 280 nm TL emission means that there is a hole located on the Ga-related luminescence centre, which recombines radiatively with the released electron.

Summarising the experimental results, we can propose a model of the 280 nm luminescence centre in AO-Ga as a combination of gallium impurity ion and a neighbouring oxygen ion Ga-O. It produces the inter-centre luminescence under UV irradiation; whereas under X-rays it catches a hole, which recombines with an electron resulting in recombination luminescence.

3.2. Al_2O_3 -Li

Evidently, presence of Li impurity in AO crystal is responsible for occurrence of the 326 nm emission band, excited in the spectral region below 4.5 eV (150–270 nm). Contrary to the UV-induced PL of Ga-related centre the Li-related PL emission cannot be ascribed solely to the inter-centre process, because its decay curves are not exponential in the range of 50 μs . Both UV and X-ray irradiation produces TL and afterglow with presence of the 326 nm band in this material. These facts characterise the recombination character of the 326 nm emission in AO-Li. Similarly to the Ga case, presence of the 260 K peak in the TL of AO-Li, ascribed to depletion of

electron traps, implies that Li-related luminescence centre contains a hole. In some aspects (spectral position and decay kinetics), this luminescence reminds that from a complex centre in alkali-doped silica glass, containing ions of aluminium, alkali and oxygen [7]. Besides, luminescence of AO-Li is similar to silica glass doped with alkali ions [8]. We propose that in AO-Li, a complex hole defect containing Li and oxygen ions is responsible for the 326 nm emission of recombination character.

Al_2O_3 doped with Ga and Li ions produce TL response located in suitable for registration spectral and thermal region; however, its intensity, at least with the used dopant concentrations, is too low to be used for dosimetry needs.

3.3. LiGaO_2

The main luminescence bands of LGO at 280 (4.43 eV) and 330 nm (Fig. 1) have already been studied in [3]. The 280 nm band is excited in the spectral range, corresponding to the exciton states (a sharp feature at 6 eV) and band-to-band transitions. Based on the luminescence features such as superposition of exponents in the luminescence decay pulses (similar to luminescence properties in Ga_2O_3 crystal [9]), blue shift of the emission band and decrease of thermal quenching rate with an increase of the excitation light intensity, it has been proven that this emission results mainly from tunnel recombination of donor-acceptor pairs (DAP) with the random distribution of separation distance [3]. In the present study, we have got the additional confirmation of the recombination character of this emission – the 280 nm emission band has been observed in X-ray induced processes: XL afterglow and TL emission spectra at temperatures below 80 K. Presence of the DAP recombination with participation of the crystal host components means that the irradiation-produced charge carriers – electrons and holes – are self-trapped on the regular lattice sites. Comparing luminescence spectra of the studied crystals, one can find that the 280 nm emission band of LGO is similar to Ga-related emission band in AO-Ga: spectral position of emission and excitation coincides. From this fact, we can propose that the 280 nm band of LGO also results from a luminescence centres, containing Ga ion. The most probable candidates for DAP are Ga and O ions, with the self-trapped charge carriers – electrons and holes, correspondingly, producing Ga(e) and O(h) pairs with different separation distance. The closest pairs are identical to self-trapped excitons.

The 330 nm emission band in LGO was ascribed to recombination luminescence of geminate DAPs [3]. This band was observed in PL and UV-induced TL emission, dependence on excitation intensity was not found. It is comparable with the 326 nm Li-related emission band in AO-Li, the excitation range below 5 eV is also similar in these 2 crystals. Position of the excitation band in LGO below the conduction band implies that the luminescence centre is a defect of the crystalline lattice, while similarity with Li-related emission in AO speaks in favour of Li ion involvement. We propose that this could be interstitial lithium Li_i , perhaps with a lithium vacancy v_{Li} nearby. After irradiation an interstitial will catch an electron and convert into Li_i^0 , while a hole will be caught by an oxygen ion converting it to O^0 . Radiative recombination of such DAP containing Li_i produces the 330 nm emission band.

4. CONCLUSIONS

In the present paper, we have studied luminescence properties of Al_2O_3 -Ga and Al_2O_3 -Li and used the experimental results for adjustment of LiGaO_2 luminescence origin.

In Al_2O_3 -Ga, the presence of Ga impurity is responsible for the occurrence of the 280 nm luminescence band, excited in 170-310 nm range. We propose a model for the luminescence centre as combination of gallium ion substituting for aluminum ion and a neighbouring oxygen ion: Ga-O. Under UV excitation it produces the inter-centre PL, while under X-rays it catches a hole, which radiatively recombines with an electron.

In Al_2O_3 -Li lithium induced luminescence is presented with a 326 nm band, excited below 270 nm. We propose that in AO-Li, a complex defect containing Li and oxygen ions is responsible for the 326 nm emission of recombination character.

Spectral similarity is found between emission bands of LiGaO_2 and Al_2O_3 doped with Ga and Li ions, constituting lattice elements of LGO. Together with the newly found occurrence of the 280 nm in the X-ray induced luminescence afterglow and TL it allows for interpretation of this emission band in LGO as tunnel recombination of Ga (plus an electron) and O (plus a hole) pairs with random separation distance. Generation of these DAPs implies self-trapping of charge carriers; the closest pairs are identical to self-trapped excitons. The 330 nm band of LGO originates from geminate DAPs, involving lithium, presumably in the interstitial position Li_i^0 , and neighbouring oxygen with a hole.

TL measurements of Al_2O_3 -Ga and Al_2O_3 -Li show that these materials, at least with the used dopant concentration, are not suitable for dosimetry needs due to the low TL response to UV and ionizing radiation.

ACKNOWLEDGEMENTS

The present research has partly been sponsored by the Latvian Council of Science, Grant No. lzp-2018/1-0361

REFERENCES

1. Tumėnas, S., Mackonis, P., Nedzinskas, R., Trinkler, L., Berzina, B., Korsaks, V., ... Chou, M. M. C. (2017). Optical properties of lithium gallium oxide. *Applied Surface Science*, 421, 837–842.
2. Chen, C., Li, C.-A., Yu, S.-H., & Chou, M.M.C. (2014). Growth and characterization of β - LiGaO_2 single crystal. *J. Cryst. Growth*, 402, 325–329.
3. Trinkler, L., Trukhin, A., Berzina, B., Korsaks, V., Ščajev, P., Nedzinskas, R., ... Li, C.-A. (2017). Luminescence properties of LiGaO_2 crystal. *Optical Materials*, 69, 449–459.
4. Jansons, J., Kulis, A., Rachko, Z., Springis, M., Tale, I., & Valbis, J. (1983). Luminescence of Ga-Doped α - Al_2O_3 Crystals. *Phys. Stat. Sol.*, (b) 120. 511–518.
5. Namozov, B., Fominich, M., Myurk, V., & Zakharchenya, R. (1998). *Phys. Solid State* 40, 837–838.

6. Springis, M., Kulis, P., & Tale, I. (1995). Point defects related to 260 K thermostimulated luminescence in α - Al_2O_3 . *Radiation Effects and Defects in Solids*, 134, 481–483.
7. Trukhin, A.N., Jansons, J.L., & Truhins K. (2004). Luminescence of silica glass containing aluminum oxide. *Journal of Non-Crystalline Solids*, 347(1–3), 80–86.
8. Trukhin, A., & Rudenko, V. (1987). Spectral-kinetic investigations of luminescence centers – Non-bridging oxygen-one valence ion. *Soviet Glass Physics and Chemistry* 13, 236–241. (in Russian)
9. Binet, L., & Gourier, D. (1998). Origin of the blue luminescence of β - Ga_2O_3 . *J. Phys. Chem Solids*, 59, 1241–1249.

SALĪDZINOŠS LUMINISCENCES PĒTĪJUMS LiGaO₂, Al₂O₃-Ga UN Al₂O₃-Li KRISTĀLOS

L.Trinklere, A. Truhins, M. Čou

K o p s a v i l k u m s

LiGaO₂, Al₂O₃-Ga and Al₂O₃-Li kristālu luminescence tika pētīta, lai noskaidrotu luminescences mehānismus un centrus šajos materiālos. Kristālā Al₂O₃-Ga pateicoties Ga piemaisījuma klātbūtnēi parādās luminescences josla 280 nm, kurai piemīt iekšcentra raksturs fotoluminiscences gadījumā un rekombinācijas raksturs rentgenluminescencē. Kristālā Al₂O₃-Li luminescences josla 326 nm ir saistīta ar litija piemaisījumu, tai ir noteikts rekombinācijas raksturs. Tiek piedāvāta precizēta interpretācija litija gallija oksīda luminescencei, ņemot vērā LiGaO₂ galveno luminescences joslu līdzību ar piemaisījumu izraisītām luminescences joslām Al₂O₃ kristālos. Šajā materiālā 280 nm luminescences josla rodas pateicoties donoru-akceptoru pāru rekombinācijai, kur donori un akceptori ir Ga ar saķertu elektronu un O ar saķertu caurumu, bet 330 nm luminescences josla atbilst tādu donoru-akceptoru pāru rekombinācijai, kur piedalās litija jons Li₁⁰ un blakusesošais skābeklis ar saķertu caurumu.

20.11.2018.

Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART²