X-RAY SPECTROSCOPIC PROPERTIES AND ELECTRONIC STRUCTURE OF $Ca_3Ga_2Ge_4O_{14}$

I. D. Shcherba[1] [ID], L. V. Kostyk[1] [ID], L. V. Bekenov[2] [ID], M. Rudko[1] [ID], D. Uskoković[3] [ID],
H. Noga[4] [ID], R. M. Bilyk[1] [ID], B. M. Yatcyk[5], V. A. Denys[1]

[1]*Ivan Franko National University of Lviv, 6/8, Kyrylo & Mefodiy St., Lviv, UA–79005 Ukraine*
[2]*G. V. Kurdyumov Institute for Metal Physics of the N.A.S. of Ukraine,*
36, Academician Vernadsky Boul., Kyiv, UA–03142, Ukraine
[3]*Institute of Technical Sciences of SASA, 35/IV, Knez Mihailova, PO Box 37711000 Belgrade, Serbia*
[4]*Institute of Technology, University of Pedagogy, 2, Podchorazych, 30–084 Krakow, Poland*
[5]*Lviv National University of Veterinary Medicine and Biotechnologies, 50, Pekarska St., Lviv, UA–79000, Ukraine*

We have obtained X-ray emission spectra of Ga and Ge in $Ca_3Ga_2Ge_4O_{14}$, X-ray emission $OK\alpha$-spectra in $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_4O_{14} + Ce3\%$, and $Ca_3Ga_2Ge_3O_{12} + Eu4\%$ and X-ray photoelectron spectra in $Ca_3Ga_2Ge_4O_{14}$. Our X-ray spectral studies of the $Ca_3Ga_2Ge_4O_{14}$ gallogermanate have shown that the top of the valence band near the Fermi level is formed mainly by p states of gallium and germanium as well as p states of oxygen, whose intensity is sufficiently low. The middle of the valence band is formed by gallium $3d$ states with oxygen $2s$ states lying below them. These states are hybridized with $4p$ states of gallium and germanium because of which there are $K\beta''$-satellites in the $K\beta_2$-subbands of gallium and germanium. The bottom of the valence band is formed by $3d$ states of germanium, whose contribution to chemical bonding is insignificant. The X-ray emission bands of Ga and Ge in $Ca_3Ga_2Ge_4O_{14}$ and the photoelectron spectrum of the valence electrons of $Ca_3Ga_2Ge_4O_{14}$ are in good agreement. The $OK\alpha$-band changes its fine structure only slightly upon doping $Ca_3Ga_2Ge_4O_{14}$ with Ce or Eu. The investigations of intrinsic luminescence under X-rays excitation of $Ca_3Ga_2Ge_4O_{14}$ gallogermanate are presented.

Key words: X-ray emission spectra, Ca-gallogermanate, electronic structure, luminescence.

I. INTRODUCTION

In recent years, a family of crystals isomorphic to calcium galogermanate $Ca_3Ga_2Ge_4O_{14}$ with space group D_3^2–$P321$ has attracted great interest [1, 2]. A significant feature of this family of crystals is the disordering of their structure, which, in particular, is characteristic of the $Ca_3Ga_2Ge_4O_{14}$ compound. The disorder of $Ca_3Ga_2Ge_4O_{14}$ crystals is associated with the statistical occupation of $3f$ tetrahedra and $1a$ octahedra by the Ga^{3+} and Ge^{4+} cations. The structure of $Ca_3Ga_2Ge_4O_{14}$ was reported in the 1980s [2] and specified in 2013 [3]. Gallogermanate $Ca_3Ga_2Ge_4O_{14}$ reveals a unique combination of physical properties such as luminescent, laser, resilient, piezoelectric, and acoustoelectronic ones [2–6]. These crystals are optically positive $(n_e > n_o)$, optically active and posses a significant optical birefringence and liner dichroism. The disorderd $Ca_3Ga_2Ge_4O_{14}$ compound is known as an effective material of quantum electronics, which combines the functions of generation and transformation of laser irradiation frequency [4–7, 11–13].

Statistical disordering of the cation sublattice results in a partial disordering of the crystals' microstructure, causing, in its turn, some fluctuation of the crystal field on activator ions. Therefore, the luminescence spectrum of rare earth ions in the $Ca_3Ga_2Ge_4O_{14}$ compound is characterized by broadened lines, which are superpositions of radiative transitions in impurity centers of different structures having closely related characteristics of Stark energy levels splitting. Many papers are devoted to

the studies of their physical properties and the effect of various impurities on them. For example, the authors of Ref. [8] measured and analyzed the absorption spectra, the spectra of circular dichroism and magnetic circular dichroism of pure and Cr-doped $Ca_3Ga_2Ge_4O_{14}$. The crystal-field parameters and the transition frequencies of Cr^{3+} ions are calculated. The location of Cr^{3+} and Cr^{4+} ions in oxygen octahedra and tetrahedra is confirmed.

The upconversion spectroscopy of $Ca_3Ga_2Ge_4O_{14}$ 5% Er^{3+} crystals at 10 K was studied in Ref. [9]. Fluorescence was observed from the $^4S_{3/2}$ and $^4S_{3/2}$ multiplets for both resonant and non-resonant excitation of the $^4F_{9/2}$ multiplet with a single DCM dye laser. Degradations in the expected power dependence of these upconversion fluorescences can be explained in terms of the cycling of Er^{3+} ion excitation via cross relaxation energy transfer. In Ref. [10], circular dichroism, absorption and luminescence spectra of single crystalline manganese doped calcium gallogermanate $Ca_3Ga_2Ge_4O_{14}$: Mn were investigated in 300–850 nm wavelength region in a wide temperature range 8–300 K. It has been established that manganese ions doping the crystal matrix of $Ca_3Ga_2Ge_4O_{14}$ incorporate into lattice in $1a$ octahedral site-positions substituting Ga^{3+} ions.

Nevertheless, the electronic structure of the base $Ca_3Ga_2Ge_4O_{14}$ compound has remained unexplored so far. One of the most fundamental techniques uniquely describing the density of electronic states over the whole valence band is certainly the high-energy spectroscopy.

The aim of this paper is to study experimentally the electronic structure of the $Ca_3Ga_2Ge_4O_{14}$ gallogermanate by high-energy spectroscopy and to

establish the influence of cerium and europium impurities on the structure of the $OK\alpha$ band and also the investigations of X-ray luminescence spectra of undoped $Ca_3Ga_2Ge_4O_{14}$ crystals.

II. CRYSTAL STRUCTURE OF Ca-GALLOGERMANATE

$Ca_3Ga_2Ge_4O_{14}$ is a member of the family of compounds with a Ca-gallogermanate-type structure. More than 200 langasite-type compounds belonging to this family have been synthesized [1, 2]. The space group of these systems is $P321$ (the point symmetry 32) with one molecule per unit cell. The $Ca_3Ga_2Ge_4O_{14}$ structure was described in detail in [2, 3, 12]. These crystals belong to disordered materials and have a layered structure that is formed by tetrahedral layers perpendicular to the c axis, between which there are layers of octahedra

$(1a$ sites, symmetry $D_3)$ and distorted Thomson cubes populated by large Ca^{2+} ions ($3e$ sites, symmetry C_2). There are two types of tetrahedra around the cations at the $2d$ and $3f$ sites (symmetries C_3 and C_2, respectively). The Ga^{3+} and Ge^{4+} cations statistically occupy $1a$ and $3f$ sites. The statistics of the filling of $1a$ and $3f$ sites with Ga^{3+} and Ge^{4+} cations depends on the technological conditions of the crystal growth and varies from sample to sample.

In the $Ca_3Ga_2Ge_4O_{14}$ crystal structure, two types of oxygen $6g$-sites are distinguished: O(2) and O(3) with coordination numbers 4 and 3, respectively. Each oxygen O(2) is surrounded by one Ge^{4+} ion at the $2d$ site, two Ca^{2+} at $3e$ sites, and one Ga^{3+} or Ge^{4+} at $3f$ site. Each oxygen O(3) is surrounded by one Ca^{2+}($3e$), one Ga^{3+} or Ge^{4+} at $3f$ site, and one Ga^{3+} or Ge^{4+} at $1a$ site. The $3e$ sites in the $Ca_3Ga_2Ge_4O_{14}$ lattice can be occupied by impurity rare earth ions, such as Ce^{3+}, Lu^{3+}, Tb^{3+}, or La^{3+}.
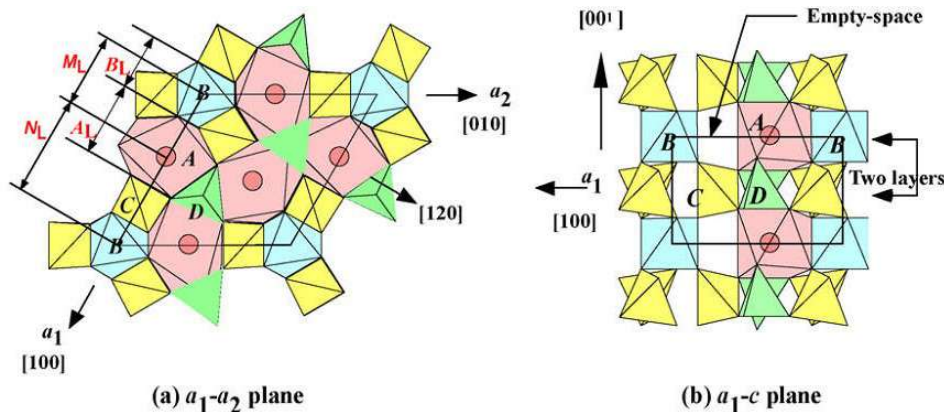

Fig. 1. Ca-gallogermanate-type structure (a) — perpendicular to the z axis and (b) — perpendicular to the x axis [13]

III. EXPERIMENT

The investigated crystals were grown using the Czochralski technique in the atmosphere of argon with adding oxygen using platinum crucible. Appropriate amounts of dried $CaCO_3$, Ga_2O_3, GeO_2, and oxides Ce_2O_3 or Eu_2O_3 (for doping) with purity not less than 99.99% on a cation basis were used as starting materials. The Ce doping level was up 0.3 at. % and the Eu doping level was up 0.4 at. %. The samples were plates 0.1–0.5 mm thick, cut in a (0001) plane.

The X-ray fluorescence $OK\alpha$ spectra of the $Ca_3Ga_2Ge_4O_{14}$ crystals were obtained using a SARF-1 vacuum (10^{-6} Torr) spectrometer with a single RbAP crystal ($2d = 26.136$Å, R = 500 mm) as a dispersing element, and Au as the anode material. The sample holder was water cooled, so the sample surface temperature did not exceed 60° C. High accuracy of the measurements of the $OK\alpha$ centroid positions was achieved by repetition and accumulation of the fast spectra survey. Such conditions provided the statistical dispersion of measured values of the order of 0.01 eV. The energy resolution was about 0.5 eV. The X-ray

emission spectra (XES) of Ga (Ge) in $Ca_3Ga_2Ge_4O_{14}$ were obtained using a tube-spectrometer with an RKD-01-1 X-ray coordinate detector of original design[14]. The XES were brought to the binding energy scale relative to the Fermi level using core level peak positions measured with a Kratos Series 800XPS analytical spectrometer, which utilizes an Al $K\alpha$ X-ray source with a photon energy of 1486.6 eV. All the reported X-ray photoelectron spectra (XPS) are referenced to the C $1s$ (285.0 eV). The samples could charge up during XPS acquisition followed by the binding energy scale corrections. The C $1s$ peaks were single, defined, and similar in shape for both samples, indicating the absence of non-uniform sample charging. The energy scale of the spectrometer was calibrated using well defined binding energies (E_b) of electrons in Au $4f_{7/2}$ ($E_b = 84.0$ eV); the full width at half-maximum (FWHM) was 1.2 eV.

The steady-state X-ray luminescence (XRL) spectra of crystals were measured using the MDR-12 monochromator. Scanning and recording of the X-ray luminescence spectra were carried out with a computerized system. Emission was measured in the single photon mode using FEU-51 photomultiplier. X-ray excitation was provided by a URS-55A X-ray

generator and Mo-target BSV-2 X-ray tube (U=45 kV, I=10 mA). The XRL spectra were investigated in the non-polarized light, in the temperature range 80-300 K.

IV. DISCUSSION

The comparison of the XES of Ga and Ge with the photoelectron spectrum of the valence band of the $Ca_3Ga_2Ge_4O_{14}$ crystal was performed in the unified energy scale using the energies of the $2p_{3/2}$ core levels of Ga and Ge, respectively, and the energies of their X-ray $K\alpha_1$ photons (Fig. 2). The X-ray emission $K\beta_{2,5}$-band of Ga has a fine structure, which is normally absent from intermetallic compounds.
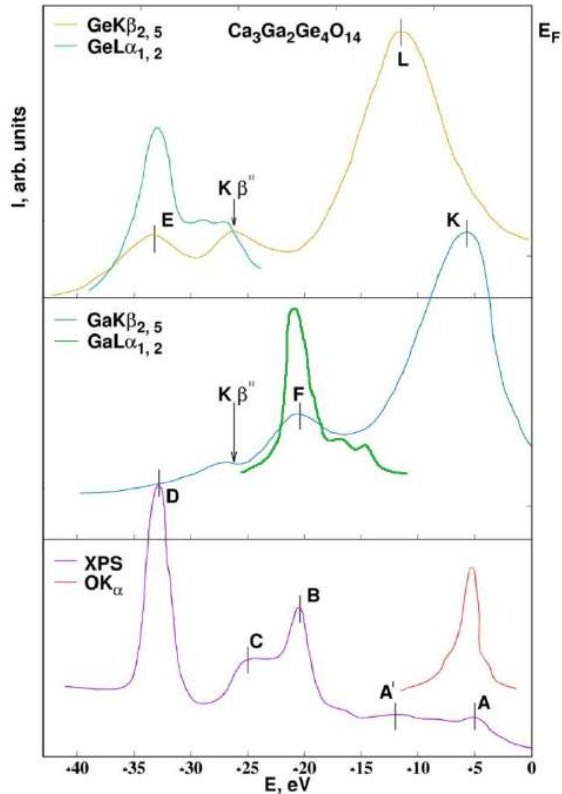

Fig. 2. The X-ray emission spectra of O, Ga and Ge, as well as the X-ray photoelectron spectrum of valence electrons in $Ca_3Ga_2Ge_4O_{14}$

We found in [15] that the $K\beta_2$-subband of Ga is a superposition of emissions from two Ga atoms, which in $R_3Ga_5O_{12}$ compounds occupy two non-equivalent crystallographic sites, namely, octahedral, and tetrahedral. In the above compound, Ga occupies preferably the octahedral, crystallographic site. Therefore, there is no additional maximum in its $K\beta_2$-band in the main maximum region.

The $K\beta_{2,5}$-band of germanium in $Ca_3Ga_2Ge_4O_{14}$ has no fine structure as in a pure semiconductor, which is associated with a considerable width of the K-level scanning ($\sim$2 eV). Unlike the $K\beta_{2,5}$-bands of $3d$ transition metals, in germanium it comprises two distinct $K\beta_2$- and $K\beta_5$-subbands. The energy distance between them

is 22.6 eV. The $K\beta_5$-subband of germanium (peaks E (XES) and D (XPS)) reflects the distribution of d states, and one can make conclusions about the participation of $3d$ electrons in chemical bonding from the changes in its parameters. In the $Ca_3Ga_2Ge_4O_{14}$ compound, the $K\beta_2$-subband shifts toward low-energies, resulting in the increase in the overlapping of Ge p and Ge d wave functions. The comparison of the $K\beta_{2,5}$-bands of germanium with the photoelectron spectrum of the valence electrons shows that the peak L of the distribution of Ge p states coincides in energy with the peak A' of the X-ray photoelectron spectrum, while the main peak K of the Ga $K\beta_2$-band coincides with the XPS peak A. The XPS peak A also reflects the contribution of oxygen $2p$ states. As can be seen from Fig. 3, the XPS peak B coincides with the peak F of the Ga $K\beta_5$-subband. In our opinion, the most probable reason for the appearance of the XPS peak C is that the oxygen $2s$ states are in the valence band.
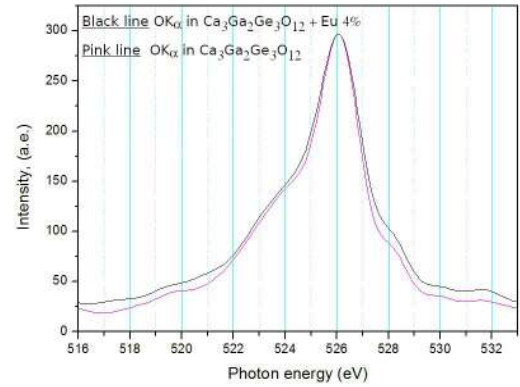

Fig. 3. X-ray emission $OK\alpha_{1,2}$-spectra of $Ca_3Ga_2Ge_3O_{12}+$ 4 at. % Eu^{3+} and $Ca_3Ga_2Ge_3O_{12}$ garnets
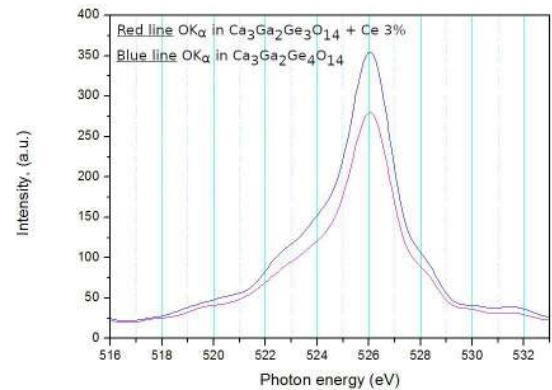
Fig. 4. X-ray emission $OK\alpha_{1,2}$-spectra of $Ca_3Ga_2Ge_4O_{14}+3$ at. % Ce^{3+} and $Ca_3Ga_2Ge_4O_{14}$ gallogermanate

To establish the effect of doping with a rare earth (RE) element on the structure of the valence band of compounds, we investigated $OK\alpha_{1,2}$-bands of un-doped $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_4O_{14} + 3$ at.% Ce^{3+},

$Ca_3Ga_2Ge_2O_{12}$ + 4 at. % Eu^{4+}, and Figs. 3 and 4 show the $OK\alpha_{1,2}$ X-ray emission spectra of the investigated samples. According to the dipole selection rules for XES and due to the localized character of the initial core state, they reflect the valence band distribution of occupied O $2p$ electronic states. Oxygen does not have an X-ray band that could be used as an internal standard to determine the density of valence O $2p$ orbitals. However, shifts of $OK\alpha_{1,2}$-bands can be used as a characteristic sensitive to the changes of this density. As can be seen, the energy position of the main $OK\alpha_{1,2}$-band peak does not change in all the spectra.

The low-energy part of the $OK\alpha$-band mainly reflects the states of the Ge (Ga)–O bonds, whereas the high-energy part represents the Ca (RE)–O bonds. The range of medium energies is formed by the states that mainly correspond to the oxygen sub-lattice. As can be seen from Figs. 3 and 4, the $OK\alpha$-band changes its fine structure only slightly with the changes in the chemical composition of the studied gallogermanate and garnet crystals.

The spectrum of the steady-state X-ray luminescence (XRL) of undoped $Ca_3Ga_2Ge_4O_{14}$ single-crystals at 80 K is a wide asymmetric band in the spectral region of 2–4.2 eV with a maximum near 3.2 eV (Fig. 5). On the higher energy slope of this band, a shoulder at 3.7–3.4 eV is observed. Asymmetry of the luminescence band of the XRL spectrum of un-doped $Ca_3Ga_2Ge_4O_{14}$ demonstrates that it is a superposition of several elementary bands. The analysis of the spectrum composition shows that experimental XRL curves can be fitted with three elementary bands with maxima at 3.51 eV, 3.1 eV, and 2.55 eV, which strongly overlap with each other and the correlation of intensities between which depends on the temperature of investigations. The fitting of XRL band on elementary components was carried out using the Alenceva–Foka method.

The shape of the complex luminescence band and the position of its maximum strongly depend on the temperature. The maximum of the XRL spectrum shifts to 2.9 eV at 300 K. Furthermore, the same XRL bands are observed in $Ca_3Ga_2Ge_4O_{14}$ crystals doped with Ce^{3+}. However, the activator luminescence bands are not observed in $Ca_3Ga_2Ge_4O_{14} : Ce^{3+}$ crystals. The temperature dependence of the UV and blue luminescence intensity is presented in Fig. 6. As can be seen from Fig. 6, the UV and blue luminescence is almost quenching in the temperature range of 120–240 K. The decrease in this intrinsic luminescence intensity near 200–250 K may be related to non-radiative relaxation of electronic excitations and their re-capturing by defect centers.

The temperature dependence of the 2.55 eV luminescence band differs from the temperature dependence of the UV and blue bands. This band has a low luminescence yield at 80 K and its relative intensity increases when heated to 300 K. At higher temperatures, a decrease in the intensity and complete quenching of the 2.55 eV luminescence band is observed. The luminescence band with maxima near 2.55 eV is weakly excited by photons with energies that match the band-to-

band transitions. This band, in contrast to the bands in the UV region, is characterized by an excitation maximum in the transparency region of the crystal, peaking at 4.92 eV. It should be noted that similar intrinsic luminescence bands and their temperature behavior were observed in the chemical composition of $Ca_3Ga_2Ge_3O_{12}$ of garnet crystals [18, 20]. Perhaps this is due to the similarity of the structure valence bands of these compounds.

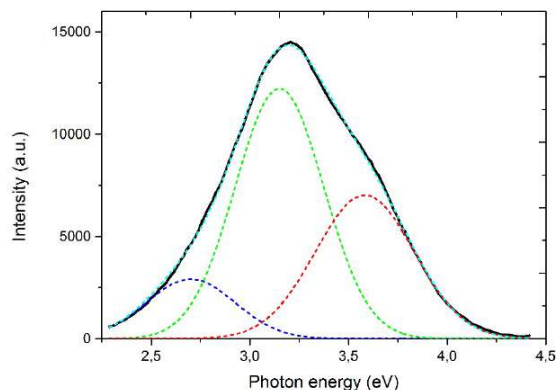Fig. 5. XRL luminescence spectra of un-doped $Ca_3Ga_2Ge_4O_{14}$ crystals. The dashed lines show the elementary components of the luminescence band (red line — UV band with maximum at 3.51 eV; green line — blue band with maxima at 3.1 eV; blue line — luminescence band with maxima near 2.55 eV)
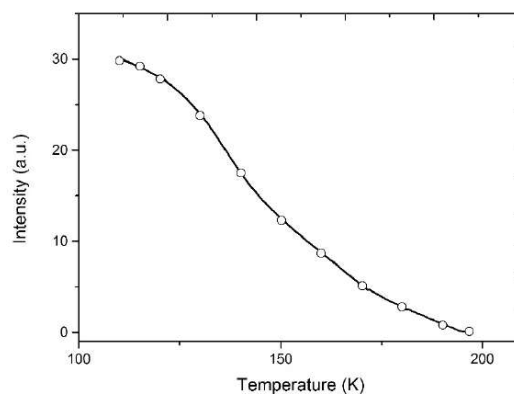

Fig. 6. Temperature dependence of the XRL luminescence of un-doped $Ca_3Ga_2Ge_4O_{14}$ crystals

It is known that the existence of intrinsic luminescence bands is typical of other complex oxide crystals, in which oxygen ions occupy low symmetry sites. There are several points of view in literature regarding their nature, e. g. [16–20]. Often, low-temperature luminescence bands are interpreted as radiation decay of self-trapped excitons, which are formed by the relaxation of large radius excitons and trapped exciton emission or in recombination of electrons with holes, localized on their own or impuri-

ty defects of the crystal lattice. Some bands of intrinsic luminescence in oxides correspond to the emission of anti-site defects or recombination luminescence of active structure defects such as vacancies and others.

In our opinion, the most reasonable interpretation of the low temperature UV band with a maximum at 3.51 eV in $Ca_3Ga_2Ge_4O_{14}$ crystals is the radiation emission of self-trapped excitons. It can be suggested that the self-trapped exciton is formed as a result of the primary self-trapping of a hole with subsequent capture of an electron by it. This is indirectly confirmed by the fact that in the $Ca_3Ga_2Ge_4O_{14}$ crystals irradiated by ultraviolet or X-rays, O-hole centers were revealed by EPR [21]. More longwave and intensive low temperature intrinsic emission bands with maxima at 3.1 eV can be associated with radiation exciton annihilation, located on impurity or intrinsic defects. The luminescence occurs as a result of the radiation annihilation of these excitons.The XRL luminescence with maxima at 2.55 eV, which is effectively excited inthe transparency range, may be associated with the recombination luminescence of donor-acceptor pairs, which include F centers. Given the fact that the oxide compounds can have a noticeable concentration of anion vacancies, the investigated crystal can be considered to have F-type luminescence centers.

V. SUMMARY

Our X-ray spectroscopic studies of $Ca_3Ga_2Ge_4O_{14}$ show that the top of its valence band near the Fermi level is formed mainly by Ga and Ge p states as well as O p states, whose intensity is sufficiently low. The middle of the valence band is formed by Ga $3d$ states, with O $2s$ states lying below them. These states are hybridized with $4p$ states of Ga and Ge, because of which there are $K\beta''$-satellites in the Ga and Ge $K\beta_2$-subbands. The bottom of the $Ca_3Ga_2Ge_4O_{14}$ valence band is formed by Ge $3d$ states, whose contribution to chemical bonding is insignificant.

The X-ray emission bands of Ga and Ge in $Ca_3Ga_2Ge_4O_{14}$ and the photoelectron spectrum of the valence electrons of $Ca_3Ga_2Ge_4O_{14}$ are in good agreement.

The $OK\alpha$-band changes its fine structure only slightly upon doping $Ca_3Ga_2Ge_4O_{14}$ with Ce or Eu.

The low temperature UV-blue bands with maxima at 3.51 eV and 3.1 eV revealed in the $Ca_3Ga_2Ge_4O_{14}$ compound are similar in nature to those found in close in chemical composition of $Ca_3Ga_2Ge_3O_{12}$ garnet crystal and other oxide crystals. The possible nature of the luminescence bands in $Ca_3Ga_2Ge_4O_{14}$ have been discussed.

[1] E. L Belokoneva, N. V Belov, Dokl. Akad. Nauk SSSR **260**, 1363 (1981).

[2] A. A. Kaminskii, Sov. Phys. Usp. **27**, 548 (1984); https://doi.org/10.3367/UFNr.0143.1984071.0495.

[3] A. Dudka, B. V. Mill', Crystallogr. Rep. **58**, 593 (2013); https://doi.org/10.1134/s1063774513040081.

[4] A. Nosenko, R. Leshchuk, V. Kravchishin, J. Phys., IV **04**, C4-455 (1994); https://doi.org/10.1051/jp4:19944109.

[5] M. F. Dubovik, Inorg. Mater. **28**, 1999 (1992).

[6] Ya. Shopa, N. Ftomyn, Opt. Appl. **43**, 217 (2013); https://doi.org/10.5277/oa130202.

[7] X. Zhang *et al.*, Opt. Mater. Express **5**, 977 (2015); https://doi.org/10.1364/OME.5.000977.

[8] Z. B. Perekalina, T. F. Veremeichik, K. A. Kaldybaev, A. D. Tynaev, Crystallogr. Rep. **45**, 304 (2000); https://doi.org/10.1134/1.171185.

[9] J.-P. R. Wells, T. P. J. Han, G. Mcconnell, Radiat. Eff. Defects Solids **149**, 329 (1999); https://doi.org/10.1080/10420159908230176.

[10] V. Burkov, L. Alyabyeva, B. Mill, V. Kotov, Opt. Mater. **79**, 317 (2018); https://doi.org/10.1016/j.optmat.2018.03.057.

[11] A. A. Kaminskii *et al.*, Phys. Status Solidi **86**, 345 (1984); https://doi.org/10.1002/pssa.2210860139.

[12] E. L. Belokoneva, M. A. Simonov, A.V. Butashin, B. V. Mill, N. V. Belov, Sov. Phys. Dokl. **25**, 954 (1980).

[13] N. Araki et al., J. Eur. Ceram. Soc. **27**, 4099 (2007); https://doi.org/10.1016/j.jeurceramsoc.2007.02.177.

[14] I. D. Shcherba, *High-Energy Spectroscopy of Compounds* (Ivan Franko National Universuty of Lviv, 2018).

[15] I. D. Shcherba *et al.*, J. Alloys Compd. **179**, 137 (1992); https://doi.org/10.1016/0925-8388(92)90212-R.

[16] V. Murk, A. Kuznetsov, B. Namozov, K. Izmailov, Nucl. Instrum. Meth. **91**, 327 (1994); https://doi.org/10.1016/0168-583X(94)96240-5.

[17] Yu. Zorenko *et al.*, Rad. Measur. **38**, 677 (2004); https://doi.org/10.1016/j.radmeas.2004.02.009.

[18] A. E. Nosenko, L. V. Kostyk, Radiat. Prot. Dosim. **65**, 127 (1996); https://doi.org/10.1093/oxfordjournals.rpd.a031603.

[19] B. Padlyak, Ukr. J. Phys. Opt. **8**, 235 (2007); https://doi.org/10.3116/16091833/8/4/235/2007.

[20] L. Kostyk *et al.*, Acta Phys. Pol. **133**, 943 (2018); https://doi.org/10.12693/APhysPolA.133.943.

[21] A. E. Nosenko, R. Ye. Leshchuk, B. V. Padlyak, A. A. Sel'skii, Phys. Solid State **39**, 938 (1997); https://doi.org/10.1134/1.1130148.

I. D. SHCHERBA, L. V. KOSTYK, L. V. BEKENOV *et al.*

РЕНТҐЕНІВСЬКІ СПЕКТРОСКОПІЧНІ ВЛАСТИВОСТІ ТА ЕЛЕКТРОННА СТРУКТУРА $Ca_3Ga_2Ge_4O_{14}$

І. Д. Щерба[1], Л. В. Костик[1], Л. В. Бекенов[2], М. Рудко[1], Д. Ускоковіч[3], Г. Нога[4], Р. М. Білик[1],
Б. М. Яцик[1], В. А. Денис[1]

[1] *Львівський національний університет імені Івана Франка, Україна*
[2] *Інститут металофізики ім. Г. В. Курдюмова НАН України України, Київ, Україна*
[3] *Інститут технічних наук САСА, Белград, Сербія*
[4] *Інститут технології, Педагогічний університет, Краків, Польща*
[5] *Львівський національний університет ветеринарної медицини та біотехнологій, Україна*

Кристали зі структурою Ca-ґалоґерманату є перспективними матеріалами для квантової електроніки, датчиків високої температури тощо. Просторовою групою цих систем є $P321$ з однією молекулою на елементарну комірку. Ці кристали належать до невпорядкованих матеріалів і мають шарувату структуру, що утворена тетраедричними шарами, перпендикулярними до осі c, між якими є шари октаедрів та спотворених кубів Томсона, заселених великими йонами Ca^{2+}. Є два типи тетраедрів навколо катіонів у місцях $2d$ і $3f$. Катіони Ga^{3+} і Ge^{4+} статистично займають $1a$- і $3f$-стани, статистика їх заповнення залежить від технологічних умов вирощування кристалів.

Спектри рентґенівського випромінювання Ga і Ge в $Ca_3Ga_2Ge_4O_{14}$ отримано на тубус-спектрометрі з рентґенівським координатним детектором РКД-01-1 оригінальної конструкції. $OK\alpha$-спектри рентґенівського випромінювання в $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_4O_{14} + 3$ at. % Ce^{3+}, $Ca_3Ga_2Ge_3O_{12} + 4$ at. % Eu^{3+} отримано на САРФ-спектрометрі. На рентґенівському фотоелектронному спектрометрі фірми "Кратос" виміряно спектри остових рівнів та валентної зони в $Ca_3Ga_2Ge_4O_{14}$. Наші рентґенівські спектральні дослідження ґранату $Ca_3Ga_2Ge_4O_{14}$ показали, що вершина валентної зони поблизу рівня Фермі утворена переважно p-станами ґалію та ґерманію, а також p-станами кисню, інтенсивність яких є достатньо низькою. Середина валентної зони утворена $3d$-станами галію, нижче котрих розташовані $2s$-стани кисню. Ці стани гібридизуються з $4p$ станами галію та германію, через що в $K\beta_2$-підсмугах ґалію та германію виникають $K\beta''$-сателіти. Дно валентної зони утворено $3d$-станами германію, внесок яких у хімічний зв'язок незначний. Смуги рентґенівського випромінювання Ga і Ge в $Ca_3Ga_2Ge_4O_{14}$ і фотоелектронний спектр валентних електронів $Ca_3Ga_2Ge_4O_{14}$ демонструють хорошу відповідність. $OK\alpha$-смуга лише незначно змінює свою тонку структуру під час леґування $Ca_3Ga_2Ge_4O_{14}$ Ce або Eu.

Подано дослідження власної люмінесценції під час збудження рентґенівськими променями кристалів $Ca_3Ga_2Ge_4O_{14}$ галлогерманату. УФ-фіолетові смуги з максимумами за 3.51 eV і 3.1 eV, виявлені в сполуці $Ca_3Ga_2Ge_4O_{14}$, і за своєю природою подібні до тих, що виявляються в близькому за складом ґранаті $Ca_3Ga_2Ge_3O_{12}$ та інших оксидних кристалах. Обговорено можливу природу смуг люмінесценції в $Ca_3Ga_2Ge_4O_{14}$.

Ключові слова: спектри рентґенівського випромінювання, Ca-ґалоґерманат, електронна структура, люмінесценція