

Luminescence spectroscopy and electronic structure of Eu^{3+} -doped Bi-containing oxide compounds

S.Nedilko, V.Chornii, Yu.Hizhnyi, V.Scherbatskyi, M.Slobodyanik, K.Terebilenko, V.Boyko, V.Sheludko***

T.Shevchenko National University of Kyiv,
64/13 Volodymyrska Str., 01601 Kyiv, Ukraine

*National University of Life and Environmental Science of Ukraine,
15 Geroiv Oborony Str., 03041 Kyiv, Ukraine

**Glukhiv National Pedagogical University,
24 Kyjevo-Moskovs'ka Str., 41400 Glukhiv, Ukraine

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The photoluminescence (PL) studies of the set of undoped and doped with Eu^{3+} ions Bi-containing oxide compounds BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ as well as calculations of their electronic structures were performed. The intrinsic PL of undoped crystals was found under excitation in VUV and UV diapason of light (100–400 nm). The PL spectra possess several main components lying in the blue-green, green-orange and orange-red light diapasons (from 400 up to 850 nm). When Eu ions are incorporated into the crystals, the intrinsic PL diminishes and inner $f-f$ PL of Eu^{3+} ions becomes dominant. Comparison of the PL excitation spectra with the data of calculated partial density of electronic states allowed distinguishing the role of excitation transitions in bismuth-oxygen polyhedrons (BiO_8 or BiO_6), phosphate (PO_4^{3-}) and molybdate (MoO_4^{2-}) groups. Observed intrinsic PL mainly originates from the excitation transitions in Bi — oxygen polyhedrons followed by the related backward radiation transitions. Very strong excitation energy transfer from bismuth-oxygen polyhedrons to Eu^{3+} ions was observed for all investigated Eu-doped compounds.

Проведены исследования фотолюминесценции (ФЛ) ряда нелегированных и легированных европием оксидных соединений BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ и $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ наряду с расчетами их электронной структуры. Обнаружена собственная ФЛ нелегированных кристаллов при возбуждении их светом в ВУФ и УФ спектральных областях (100–400 нм). Спектры ФЛ нелегированных образцов состоят из нескольких основных компонент в сине-зеленом, зелено-оранжевом и оранжево-красном спектральных диапазонах (от 400 до 850 нм). При легировании кристаллов ионами европия собственная ФЛ затухает и в спектрах доминируют линии ФЛ, связанные с внутрицентровыми $f-f$ переходами в ионах Eu^{3+} . Сравнение спектров возбуждения ФЛ с результатами расчетов парциальной плотности электронных состояний позволило проанализировать участие в процессах ФЛ электронных возбуждений в висмут-кислородных полиэдрах (BiO_8 или BiO_6), фосфатных (PO_4^{3-}) и молибдатных (MoO_4^{2-}) группах. Наблюдаемая собственная ФЛ формируется электронными возбуждениями и последующими излучательными переходами в висмут-кислородных полиэдрах. Во всех рассмотренных соединениях, легированных европием, наблюдается эффективная передача энергии фотовозбуждения от висмут-кислородных полиэдров к ионам Eu^{3+} .

1. Introduction

Phosphate and molybdate compounds with rigid three-dimensional framework have attracted much attention because of their high chemical and thermal stability combined with the possibility of effective doping with luminescent rare-earth (RE) ions [1–3]. The Bi^{3+} and RE^{3+} ions possess close ionic radii and therefore the Bi-containing compounds could be easily doped with luminescent ions like Eu^{3+} , Yb^{3+} , etc. It was demonstrated recently that $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4):\text{Eu}^{3+}$ is a perspective phosphor for white light-emitting diodes [4]. Yb^{3+} and Nd^{3+} -doped $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ is considered as a promising material for laser in the near-IR region [5, 6].

The properties of Eu^{3+} -related photoluminescence in several types of phosphate-based Bi-containing hosts (in particular, $\text{BiCa}_4(\text{PO}_4)_3\text{O}$ [7], $\text{Y}_{0.85}\text{Bi}_{0.1}\text{Eu}_{0.05}\text{V}_{1-y}\text{P}_y\text{O}_4$ [8] and $\text{Na}_3\text{Y}(\text{PO}_4)_2$ [9]) have been investigated up to now. At the same time, the photoluminescence (PL) properties of undoped Bi-containing phosphates and molybdates has attracted less attention. Intrinsic PL properties of only few types of Bi-containing oxide compounds have been studied so far and the centers of their intrinsic PL were associated with Bi^{3+} ions in the oxygen surrounding [10, 11]. A thorough physical explanation for properties of the RE-containing luminophores cannot be given without understanding of the role of the crystal hosts in the luminescence processes. The present paper aims at overcome this lack using available methods of spectroscopic studies combined with the electronic structure calculations. The luminescence properties of pure and Eu-doped BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ crystals are analyzed against the structural peculiarities of the crystal hosts and the electronic structure results.

The electronic structures of all investigated crystals are calculated for the first time.

2. Experimental and calculation procedures

Bi-containing phosphate and molybdate compounds BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ have been prepared from $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{Bi}_2\text{O}_3-\text{MoO}_3$ molten system [1, 12]. Calculated amounts of K_2MoO_4 , MoO_3 , Bi_2O_3 , and KPO_3 for each synthesis were melted at 1000°C and kept at this temperature for 1 h. Afterwards, it was cooled down

with a rate of 30°C to 520°C (BiPO_4), 580°C ($\text{K}_3\text{Bi}_5(\text{PO}_4)_6$), 650°C ($\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$) and 690°C ($\text{K}_5\text{Bi}(\text{MoO}_4)_4$). For a synthesis of Eu^{3+} — doped compounds 1 % mol. of Eu_2O_3 was added as an additional component. The annealing time in this case was widened up to 3 h to reach the homogeneity. Crystalline products were leached out from the solidified melt with boiling deionized water and their purity and structures were proved by X-Ray powder diffraction (Shimadzu XRD-6000 diffractometer, curved pyrolytic graphite counter monochromator, CuK_α radiation $\lambda = 1.54184 \text{ \AA}$, $2\theta = 5-90^\circ$ operating in Bragg-Brentano ($\theta/2\theta$) geometry). The colorless transparent crystals with typical linear dimensions in range 0.1–1 mm were obtained. The detailed information concerning synthesis procedure and specific structural features of investigated compounds could be found elsewhere [1, 12].

The VUV-excited photoluminescence and PL excitation spectra were studied on a SUPERLUMI station at HASYLAB (DESY), Hamburg, Germany in 90–330 nm region of excitation photon wavelengths λ_{ex} (or 3.7–14 eV region of excitation energies) and $T = 8 \text{ K}$ [13]. The PL excitation spectra in 300–600 nm (2–4 eV) spectral region were obtained with powerful Xenon lamp DKSL-1000 as an excitation source. The samples were placed into a flow-type helium cryostat. All spectra were corrected by the system response.

The electronic structures of perfect BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ crystals were calculated using the WIEN2k program package [14] in which the full-potential linear-augmented-plane-wave (FLAPW) method is implemented within the framework of the density-functional theory (DFT). The Perdew and Wang generalized gradient approximation was employed [15] for the exchange-correlation potential. The relativistic effects were treated in the scalar relativistic approximation. The partial densities of electronic states (PDOS), optical properties and components of dielectric tensor were calculated using well-known relations implemented in the WIEN2k program code [14].

3. Results and discussion

The XRD patterns of all studied samples are presented in Fig. 1. The XRD data of BiPO_4 , $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ and $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ correspond to the reference ones from PDF2 X-Ray powder database (file numbers PDF2

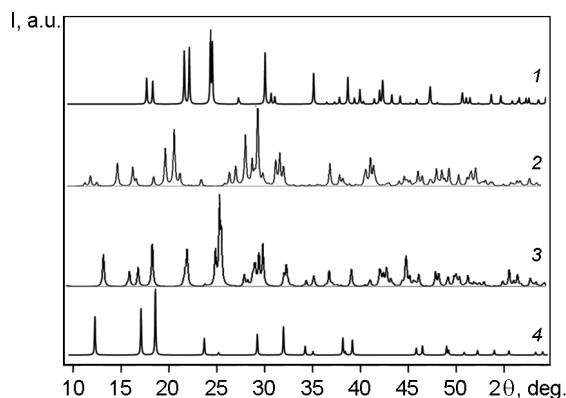


Fig. 1. XRD patterns of undoped BiPO_4 (1), $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ (2), $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ (3), and $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ (4) crystals.

No.77-2208, PDF2 No.29-0986 and PDF2 No.71-0503 respectively) and do not demonstrate any additional reflexes. The pattern of $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ is taken from [12]. As Fig. 1 shows, the XRD results confirm purity of all synthesized samples.

The PL emission spectra of all investigated compounds are shown in Fig. 2. The emission spectrum of BiPO_4 measured at $\lambda_{exc} = 260$ nm reveals broad asymmetric band (Fig. 2a). The main peak of the band is located at 475 nm and an additional long-wavelength emission component is clearly distinguishable in 550–650 nm spectral region. The PL emission band with similar spectral characteristics was observed for Bi^{3+} -related emission in $\text{LaPO}_4:\text{Bi}$ [16]. Taking into account similarity of surrounding of Bi^{3+} ions in LaPO_4 and BiPO_4 , there is a full reason to assume an analogous origin of PL emission bands in these two compounds. The origin of the long-wavelength component of BiPO_4 emission requires further studies.

The intrinsic PL emission spectrum of $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ crystal (Fig. 2b) substantially differs from the case of BiPO_4 . Two overlapped components with approximately equal intensity are clearly distinguishable at ~500 and ~580 nm and the third component undoubtedly arises when longer excitation wavelength is applied (Fig. 2b, curves 3 and 4). The bismuth ions in BiPO_4 and $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ hosts have eight oxygens in the nearest surrounding and in the both cases form irregular 8-vertex polyhedra BiO_8 . However, three nonequivalent positions of Bi ions exist in $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ lattice and each of them is characterized by specific geomet-

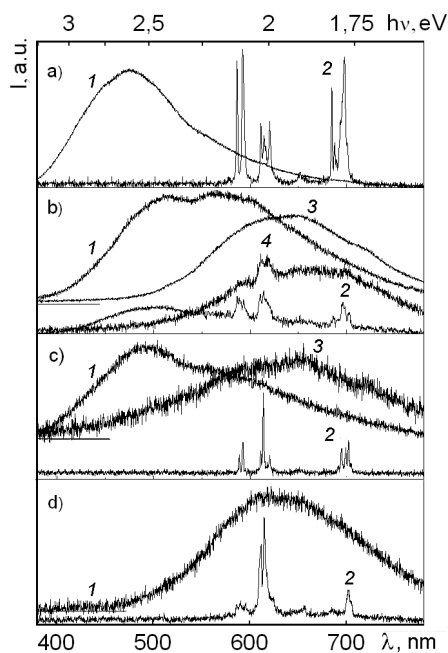


Fig. 2. PL emission spectra of undoped (1, 3) and Eu^{3+} -doped (2, 4) BiPO_4 (a), $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ (b), $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ (c) and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ (d) crystals obtained under synchrotron excitation with $\lambda_{exc} = 260$ nm (1, 2) and 330 nm (3, 4); $T = 8$ K.

ric structure of BiO_8 polyhedron [1, 17]. At the same time, it is well known that spectral properties of Bi^{3+} -related emissions (peak position and half-width) in various oxide hosts strongly depend on configuration of the nearest oxygen surrounding [18]. Taking into account these facts, two spectral components of $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ emission can be tentatively ascribed to emission of the Bi^{3+} -related centers which originate from three nonequivalent lattice positions of the bismuth ions.

It is known that emission of Bi^{3+} ions at low temperatures originates from $^3P_0 \rightarrow ^1S_0$ transitions. At higher temperatures the emission occurs mainly from the higher level 3P_1 and transition $^3P_1 \rightarrow ^1S_0$ becomes allowed due to spin-orbit coupling of 3P_1 and 1P_1 states. Generalizing the data on the luminescence properties of Bi^{3+} ions in oxygen coordination we can note that spectral position of the PL bands depend on number of the oxygen ions in the nearest surrounding, the symmetry of this surrounding and the presence of defects, first of all the oxygen vacancies in it. Dependence between these structural characteristics and Stokes shift of luminescence was found too [19]. Analysis of this dependence leads to the

conclusion that described above emission components should be attributed to the transitions in Bi^{3+} ions in polyhedral oxygen coordination — $[\text{BiO}_8]^{13-}$ -groups. Really, the further studies are required to verify this assumption.

The PL emission spectrum of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ at short λ_{ex} (Fig. 2c) resembles the case of BiPO_4 , however with higher relative intensity of the long-wavelength component. This suggests the Bi^{3+} -related origin for (at least) the main emission component of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ peaking near 490 nm. However, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ contains molybdate groups MoO_4^{2-} which are known as centers of intrinsic PL in the various types of molybdate crystals and can cause the PL emission bands peaking in 500–600 nm spectral region (see e.g. [20–22]). So, both Bi^{3+} - and MoO_4^{2-} -related centers should be considered and the further studies are required to clarify this assumption.

The PL emission spectrum of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ contain a broad band peaking near 620 nm (Fig. 2d). The peak position and the half-width of this spectrum are similar to corresponding spectral peculiarities of intrinsic PL emission of $\text{NaBi}(\text{MoO}_2)_2$ crystals which was ascribed to the molybdate groups [10]. At the same time, $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ reveals no emission components near 500 nm which were found for three other Bi-containing crystals studied here and assumed to have the Bi^{3+} -related origin (see above). So it is the most probably, that MoO_4^{2-} groups play a dominant role in the processes of intrinsic PL emission in $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ crystals. However, further studies are obviously required to verify this assumption.

The PL emission spectra of all Eu-doped samples reveal narrow lines of Eu^{3+} -related emission grouped around lines peaked at 592, 615, 650 and 700 nm (Fig. 2). The lines originate from intra-configurational $4f^6$ transitions of Eu^{3+} ions (detailed assignment of the groups to specific $f-f$ transitions will be presented below in this paper). Doping of the crystals with Eu ions leads to substantial decrease of an intensity of the intrinsic PL emission and therefore the intrinsic emission can be not observed at some λ_{ex} (Fig. 2).

The PL excitation spectra of all Eu-doped samples contain well-known narrow excitation lines (grouped near 322, 365, 380, 400 and 470 nm) which should be evidently ascribed to intra-configurational ($f-f$) absorp-

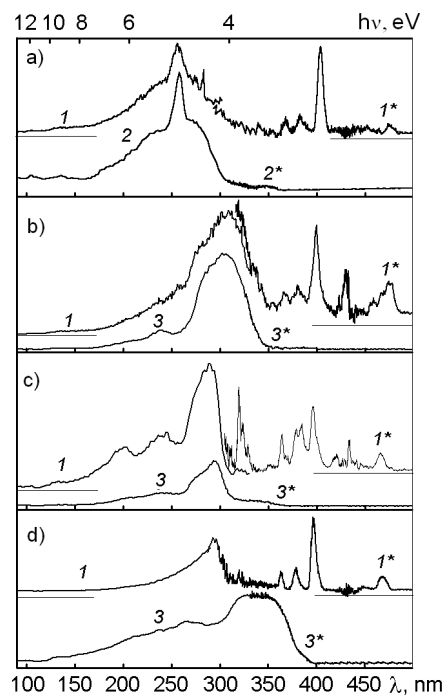


Fig. 3. PL excitation spectra of Eu^{3+} — doped (1) and undoped (2, 3) BiPO_4 (a), $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ (b), $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ (c) and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ (d) crystals obtained under synchrotron and Xe-lamp excitations (the last one indicated by numbers with asterisk symbols *) with $\lambda_{reg} = 614$ nm (1), 500 nm (2) and 600 nm (3); $T = 8$ K.

tion transitions in Eu^{3+} ions: (Fig. 3 curves with asterisk). The mentioned lines are ascribed in the following way: the short-wavelength lines in 315–330 nm region with peak near 322 nm belong to the set of transitions from the ground 7F_0 to the excited state ${}^5H_{3,6}$; the lines peaking near 365 nm correspond to ${}^7F_0 \rightarrow {}^5D_4$ transition; the lines near $\lambda_{ex} = 380$ nm originate from the set of ${}^7F_0 \rightarrow {}^5G_3$ transitions and the most intensive line at $\lambda_{ex} \sim 400$ nm is attributed to ${}^7F_0 \rightarrow {}^5L_6$ transition. The group of lines with peak at 470 nm originates from ${}^7F_0 \rightarrow {}^5D_2$ transition [4].

As Fig. 3 shows, peculiarities of the PL excitation spectra in the short wavelength regions (100–350 nm) for undoped and Eu-doped phosphate samples are similar. In particular, the PL excitation spectra of BiPO_4 and $\text{BiPO}_4:\text{Eu}$ crystals are similar below ~ 300 nm (Fig. 3a). The spectra of undoped and Eu-doped samples are similar below ~ 350 and ~ 310 for $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ and $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, respectively (Fig. 3b and c). This feature implies that an efficient

energy transfer from the crystal hosts to Eu^{3+} -emission centers takes place and the similar bands in PL excitation spectra of undoped and Eu-doped samples most probably should be attributed to the band-to-band host excitations.

In the case of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, such similarity between the PL excitation spectra of undoped and Eu-samples is observed at lower wavelengths, only below ~ 250 nm (Fig. 3d). However at longer wavelengths, the PL excitation spectra of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4\cdot\text{Eu}$ differ substantially: the main excitation bands of pure and doped samples are observed near ~ 340 and ~ 290 nm samples, respectively.

In order to clarify peculiarities of the intrinsic PL excitation, we have calculated the electronic structure of all studied crystals. In order to illustrate results of these calculations, in this paper we present the results for $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$. This crystal can be considered as the most representative case since it comprises all structural elements which can be found in the studied set of compounds: Bi^{3+} and K^+ cations, as well as PO_4^{3-} and MoO_4^{2-} molecular groups. Calculated PDOS dependences of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ crystals are presented in Fig. 4. The origin of energy scale is chosen at the Fermi level. As the Fig. 4 shows, Bi 6s, Mo 4d and O 2p electronic states form the valence band (VB) of the crystal (-7.3 to 0 eV). Contribution of P 3s, P 3p and Bi 6p states into the VB is appreciable only below -4 eV. The top of the VB is formed mainly by O 2p states, however with valuable contribution of Bi 6s states. The states of Bi 6s also form a separated sub-band below the bottom of the VB (-10.6 to 9.2 eV region). The region of relatively high density of the states (3.6 – 8.0 eV) in the conduction band (CB) of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ is followed by a region with lower PDOS levels (above 8.0 eV). Mo 4d and Bi 6p states clearly dominate in the lower (3.5 – 8.0 eV) region of the CB. The CB above 8.0 eV is formed mainly by Bi 6p, P 3p and O 2p states that have almost equal contribution here. The bottom of the CB is formed mainly by Mo 4d states, however with some contribution of Bi 6s and O 2p states.

So, the calculations indicate that both Bi^{3+} ions and MoO_4^{2-} molybdate groups can participate in the processes of intrinsic PL excitation since their states are present at the band edges (at the top of the VB and the bottom of the CB). $\text{Bi}^{3+} 6s \rightarrow \text{Bi}^{3+} 6p$ transi-

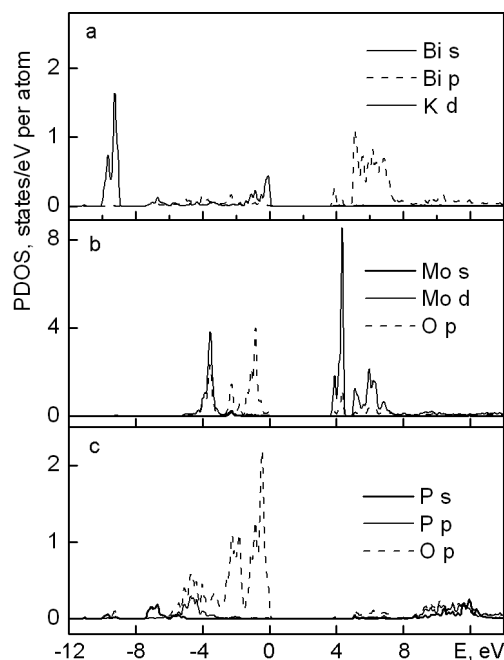


Fig. 4. Calculated partial densities of states (PDOS) of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ crystal. The densities of oxygen states are presented separately for atoms that belong to molybdate MoO_4 (b) and phosphate PO_4 (c) groups of the crystal.

tions undoubtedly have to contribute to the absorption of the crystal just above the fundamental absorption edge (see upper part of Fig. 4).

The PDOS results can also be interpreted as that charge-transfer transitions in bismuth-oxygen polyhedra can also contribute to the PL excitation since the states of all oxygen ions (from both phosphate and molybdate groups) contribute to the top of the VB.

The charge-transfer (CT) transitions of $\text{O} \rightarrow \text{Eu}^{3+}$ type (which are usually observed in PL excitation spectra of Eu-doped oxide compounds) most probably are hidden against the background of the mentioned above excitations formed by transitions of the crystal hosts. The $\text{O} \rightarrow \text{Eu}^{3+}$ CT transitions can be manifested only in the case of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, where the bismuth-oxygen polyhedra have BiO_6 structure rather than BiO_8 in three other crystals. As it was stated above, the excitation spectrum of Eu^{3+} -related PL differs from the excitation spectrum of the intrinsic luminescence of a host only in the case of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ (Fig. 3d). The excitation band of Eu^{3+} PL in $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ with peak position near 300 nm

can be tentatively ascribed to $O \rightarrow Eu^{3+}$ CT transitions. The spectral position of this band corresponds to positions the CT excitation bands of the Eu^{3+} PL usually observed in the analogous phosphate and molybdate hosts.

At the same time, the role of PO_4^{3-} phosphate groups in the PL excitation processes should be less important if compared with the role of Bi^{3+} ions and MoO_4^{2-} groups. As the PDOS picture shows, $O \rightarrow P$ transitions should have energies which are well above the bandgap and phosphate groups PO_4^{3-} can determine the PL excitation only at excitation energies well above the fundamental absorption edge (probably, in 100–250 nm region of excitation wavelengths).

The PL emission spectra of Eu^{3+} -doped samples under the Xe-lamp excitation with $\lambda_{ex} = 400$ nm are shown in Fig. 5. This excitation wavelength corresponds to intra-center Eu^{3+} ion ${}^7F_0 \rightarrow {}^5L_6$ $f-f$ transitions. As well as band-to-band synchrotron excitation (see Fig. 2), all investigated compounds doped with europium manifest the luminescence emission in the orange-red spectral region (570–720 nm). Such spectra are typical for radiation transitions in threefold-charged Eu ions. The PL spectra consist of four well-distinguished groups of lines in 585–605, 605–640, 640–670 and 670–750 nm regions. The observed groups of lines should be associated with the radiation transitions from excited 5D_0 level to 7F_J ($J = 1, 2, 3, 4$) manifold levels of the ground state of Eu^{3+} ion [23–25]. In addition, a group of the lines with low intensity caused by ${}^5D_0 \rightarrow {}^7F_0$ transitions can be distinguished near 575 nm only for Eu^{3+} -doped $K_5Bi(MoO_4)_4$ crystals. A group of the lines of ${}^5D_0 \rightarrow {}^7F_2$ transition becomes the most intensive in the spectra of $K_2Bi(PO_4)(MoO_4)$ and $K_5Bi(MoO_4)_4$ crystal (Fig. 5). In the cases of Eu^{3+} -doped $BiPO_4$ and $K_3Bi_5(PO_4)_6$ the most intensive group of lines corresponds to ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions, respectively.

It is well-known that ${}^5D_0 \rightarrow {}^7F_{0,1}$ transitions for Eu^{3+} are governed by selection rules for intermediate magnet-dipole coupling $\Delta J = 0, +1$. ${}^5D_0 \rightarrow {}^7F_{2,4,6}$ are allowed electric-dipole transitions [23, 26]. It is also well known that the largest numbers of lines in the groups of ${}^5D_0 \rightarrow {}^7F_J$ transitions have to be equal to 1, 3, 5, 7 and 9 for $J = 0, 1, 2, 3$ and 4, respectively, if the symmetry is low and degeneracy of the states is completely removed. As our data show, the

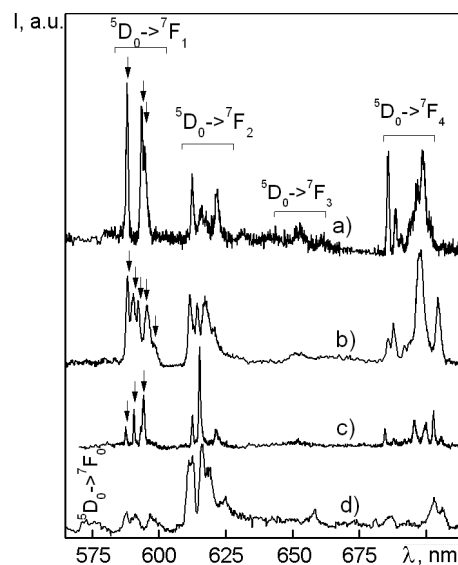


Fig. 5. PL emission spectra of Eu^{3+} — doped $BiPO_4$ (a), $K_3Bi_5(PO_4)_6$ (b), $K_2Bi(PO_4)(MoO_4)$ (c) and $K_5Bi(MoO_4)_4$ (d) crystals obtained under Xe-lamp excitation with $\lambda_{exc} = 400$ nm; $T = 4.2$ K.

number of lines in the group of ${}^5D_0 \rightarrow {}^7F_1$ transition (such analysis is correct since the lines are well separated here) corresponds to theoretical limit for all studied crystals excluding $K_3Bi_5(PO_4)_6$. So, the symmetry of the nearest surrounding of Eu^{3+} ions in $BiPO_4$, $K_2Bi(PO_4)(MoO_4)$ and $K_5Bi(MoO_4)_4$ hosts obviously corresponds to the site symmetry of Bi^{3+} ions in these crystals: C_s , C_2 and D_{3d} , respectively.

At the same time, the number of experimentally observed lines exceeds indicated maximal theoretical limits for $K_3Bi_5(PO_4)_6:Eu^{3+}$ crystal. In particular, at least 5 lines can be distinguished in the group of ${}^5D_0 \rightarrow {}^7F_1$ transitions for $K_3Bi_5(PO_4)_6:Eu^{3+}$ (the lines are indicated by vertical arrows in Fig. 4 and theoretical limit for their number is 3). So, there it is a full reason to assume that more than one type of the luminescence centers related to Eu^{3+} ions exist in this compound. Since Bi^{3+} ions occupy three different types of positions in $K_3Bi_5(PO_4)_6$ lattice (site symmetries are C_1 , C_1 and C_2), the different types of surrounding of Eu^{3+} ions are quite expectable for this host. It is obvious that additional studies are required in order to obtain more detailed inferences on the nearest surrounding of Eu^{3+} ions in the compounds studied.

4. Conclusions

The photoluminescence properties of the set of undoped and Eu^{3+} -doped Bi-containing oxide compounds BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ were studied. Theoretical calculations of the electronic structures of the set of undoped crystals were carried out. All mentioned above undoped compounds reveal intrinsic PL under excitation in the VUV and UV regions of light (100–400 nm) and the PL spectra comprise components in the blue-green (peaking at 475 or 490 nm), green-orange (peaking at ~500 and ~580 nm) and orange-red (peaking near 620 or 670 nm) regions of light. The components spectral contribution depends on the type of the compound which results in shift of the peak positions in the PL emission spectra from 475 nm (for BiPO_4) up to 670 nm (for $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$). Comparison of the PL excitation spectra with the data of calculated partial density of electronic states allowed distinguishing the role of excitation transitions in bismuth-oxygen polyhedrons (BiO_8 or BiO_6), phosphate (PO_4^{3-}) and molybdate (MoO_4^{2-}) groups. Observed intrinsic PL mainly originates from the excitation transitions in Bi-oxygen polyhedrons followed by the related backward radiation transitions. Excitation energy transfer from the host to Eu^{3+} ions was observed for all investigated Eu-doped compounds. The Eu-doped samples at VUV, UV and visible excitation reveal narrow lines of Eu^{3+} -related emission grouped around the main lines peaking at 575, 592, 615, 650 and 700 nm which originate from intra-configurational $4f_6$ transitions in Eu^{3+} ions (radiative transitions from the excited $5D_0$ level to $7F_J$ ($J = 0, 1, 2, 3, 4$) manifolds of the ground state). It is shown that peculiarities of the PL excitation spectra in the short-wavelength regions (100–350 nm) for undoped and Eu-doped phosphate samples are similar. This feature confirms existence of the efficient energy transfer from the crystal hosts to Eu^{3+} -emission centers.

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Люмінесцентна спектроскопія та електронна структура Ві-вмісних оксидних сполук легованих іонами Eu^{3+}

***С.Неділько, В.Чорній, Ю.Хижний, В.Щербацький,
М.Слободяник, К.Теребіленко, В.Бойко, В.Шелудько***

Проведено дослідження фотолюмінесценції (ФЛ) низки нелегованих та легованих європієм бісмут-вмісних оксидних сполук BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ та $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ разом із розрахунками їх електронної структури. Виявлено власну ФЛ нелегованих кристалів при збудженні світлом у ВУФ та УФ спектральних діапазонах (100–400 нм). Спектри ФЛ нелегованих зразків складаються із декількох основних компонентів у синьо-зеленому, зелено-оранжевому та оранжево-червоному спектральних діапазонах (від 400 до 850 нм). При легуванні кристалів іонами європію власна ФЛ загасає і в спектрах домінують лінії ФЛ, пов'язані із внутрішніми $f-f$ переходами в іонах Eu^{3+} . Порівняння спектрів збудження ФЛ із результатами розрахунків парціальних густин електронних станів дозволило проаналізувати участь у процесах ФЛ електронних збуджень у бісмут-кисневих поліедрах (BiO_8 або BiO_6), фосфатних (PO_4^{3-}) та молібдатних (MoO_4^{2-}) групах. Спостережена власна ФЛ, в основному, формується електронними збудженнями та подальшими випромінювальними переходами у бісмут-кисневих поліедрах. В усіх розглянутих сполуках, легованих європієм, спостерігається ефективна передача енергії збудження від бісмут-кисневих поліедрів до іонів Eu^{3+} .