

Origin of intrinsic luminescence in oxide crystals containing Bi cations and XO_4 ($\text{X} = \text{P}, \text{Mo}, \text{W}$) molecular anionic groups

Yu.A.Hizhnyi

T. Shevchenko National University of Kyiv,
64 Volodymyrska St., 01601 Kyiv, Ukraine

Received October 2, 2015

Intrinsic photoluminescence (PL) of BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{KBi}(\text{MoO}_4)_2$, $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ and $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ crystals is studied in 2.8–14 eV range of excitation photon energies. The electronic band structures of the crystals are calculated by the Full-Potential Linear Augmented Plane Wave Method. Origin of intrinsic luminescence in studied compounds is analyzed on the ground of obtained experimental and computational results. It is found that PL emission components of BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{KBi}(\text{MoO}_4)_2$ in the violet-green spectral region are related to radiative transitions in Bi^{3+} ions. The red PL components of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{KBi}(\text{MoO}_4)_2$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ have MoO_4^{2-} -related origin. The red PL component of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ luminescence is presumably related to the molybdenum impurities. The intrinsic PL emission band of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ is probably not related to Bi^{3+} ions.

Keywords: luminescence, bismuth, oxide crystal, electronic structure.

Проведены исследования собственной люминесценции кристаллов BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{KBi}(\text{MoO}_4)_2$, $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ и $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ в области энергий возбуждающего света 2,8–14 эВ. Электронная структура исследуемых кристаллов рассчитана полнопотенциальным линейаризованным методом присоединенных плоских волн (FP-LAPW). На основе результатов экспериментальных исследований и теоретических расчетов проанализирована природа собственной люминесценции исследуемых кристаллов. Установлено, что компоненты люминесценции BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ и $\text{KBi}(\text{MoO}_4)_2$, характеризующиеся максимумами в фиолетово-зеленой области спектра, связаны с излучательными переходами в ионах Bi^{3+} . Полосы люминесценции $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{KBi}(\text{MoO}_4)_2$ и $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, максимумы которых расположены в красной области спектра, сформированы переходами в MoO_4^{2-} группах. Красная полоса люминесценции $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$, предположительно, связана с существованием в этих кристаллах примесей молибдена. Люминесцентное свечение $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ скорее всего не связано с переходами в ионах Bi^{3+} .

Природа власної люмінесценції оксидних кристалів, що містять катіони Бі та молекулярні аніонні групи XO_4 ($\text{X} = \text{P}, \text{Mo}, \text{W}$). Ю.А.Хижний.

Проведено дослідження власної люмінесценції кристалів BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{KBi}(\text{MoO}_4)_2$, $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ та $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ в області енергій збуджуючого світла 2,8–14 еВ. Проведено розрахунки електронної структури кристалів повнопотенціальним лінеаризованим методом приєднаних плоских хвиль (FP-LAPW). За результатами експериментальних та розрахункових досліджень проаналізовано природу власної люмінесценції досліджених сполук. Встановлено, що компоненти люмінесценції BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ та $\text{KBi}(\text{MoO}_4)_2$, які мають максимуми у фіолетово-зеленій спектральній ділянці, слід пов'язувати із випромінювальними переходами в іонах Bi^{3+} . Смуги люмінесценції $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{KBi}(\text{MoO}_4)_2$ та

$K_5Bi(MoO_4)_4$, максимуми яких розташовані у червоній ділянці спектра, сформовані переходами в MoO_4^{2-} групах. Червона смуга люмінесценції $K_2Bi(PO_4)(WO_4)$ імовірно пов'язана з існуванням у цих кристалах домішок молібдену. Люмінесцентне свічення $K_{6.5}Bi_{2.5}W_4P_6O_{34}$ скоріш за все не пов'язане з переходами в іонах Bi^{3+} .

1. Introduction

Bismuth-containing compounds can be easily doped with rare-earth (RE) ions since Bi^{3+} ionic radius is close to ionic radii of the lanthanides. For this reason, oxide crystals with bismuth cations are intensively studied at present as perspective hosts for luminescent RE^{3+} ions [1–6]. However in most cases of these studies, intrinsic luminescence of the undoped hosts was not analyzed. At present, origin of intrinsic luminescence and mechanisms of the excitation energy transfer in Bi-containing phosphate, molybdate and tungstate crystals are topical questions. In this paper, the origin of intrinsic PL processes in set of Bi-containing oxide hosts is analyzed in complex experimental and computational studies.

Intrinsic PL properties and electronic structures of Bi-containing oxide crystals were analyzed in our recent papers. $BiPO_4$, $K_3Bi_5(PO_4)_6$, $K_2Bi(PO_4)(MoO_4)$, $K_2Bi(PO_4)(WO_4)$ and $K_5Bi(MoO_4)_4$ crystals were studied in [7, 8], $KBi(MoO_4)_2$ in [9] and $K_{6.5}Bi_{2.5}W_4P_6O_{34}$ in [10]. In this work, we present comparative analysis of the PL properties and the electronic structures of all mentioned above compounds, thus generalizing our inferences on the origin of intrinsic luminescence in Bi-containing oxide hosts.

2. Experimental and calculation details

Polycrystalline powders of $BiPO_4$, $K_3Bi_5(PO_4)_6$, $K_2Bi(PO_4)(MoO_4)$ and $K_5Bi(MoO_4)_4$ were prepared from K_2O – P_2O_5 – Bi_2O_3 – MoO_3 molten system (see details in [11, 12]). Polycrystalline samples of $KBi(MoO_4)_2$ were obtained by crystallization from the melts of $KBi(MoO_4)_2$ – $K_6Mo_7O_{24}$ system (see [9]). The polycrystalline samples of $K_2Bi(WO_4)(PO_4)$ and $K_{6.5}Bi_{2.5}W_4P_6O_{34}$ were synthesized by flux method (see [13, 14]).

The PL properties under VUV synchrotron excitations were studied on SUPERLUMI station at HASYLAB (DESY), Hamburg, Germany [15]. The PL spectra were obtained for 3.7–14 eV region of excitation photon energies in 8–300 K temperature range. The PL studies under excitations in the UV and visible regions were carried out by computerized set-up for spectroscopic measurements (DFS-12 diffraction spec-

trometer, 0.2 mm/Å linear dispersion) with use of 1000W Xenon-arc lamp as excitation source. All PL emission and excitation spectra were corrected on instrumental response.

The electronic structures of the crystals were calculated using WIEN2k program package [16], in which the full-potential linear-augmented-plane-wave (FP-LAPW) method is implemented within the framework of the density-functional theory (DFT). The Perdew and Wang generalized gradient approximation was employed [17] for the exchange-correlation potential. The relativistic effects were treated in the scalar relativistic approximation. The modified tetrahedron method was used for the Brillouin zone (BZ) integration [18]. Atomic coordinates and lattice parameters of the crystals were taken from literature (see details in [7, 9, 10]).

The muffin-tin radii R_{MT} were chosen from condition of "almost touching" MT spheres. In all cases, energy of separation between core and valence states was chosen as 6.0 Ry. The potential and charge density in the MT spheres were expanded in spherical harmonics with $l_{max} = 10$. The plane wave cutoff parameter $R_{MT}K_{max}$ was equal to 6.0. The magnitude of the largest vector G_{max} in the charge density Fourier expansion was 14.0. The convergence criterion was chosen as 0.0001 Ry convergence of the total energy. The partial densities of electronic states (PDOSes) were calculated using well-known relations implemented in WIEN2k program code [16].

3. Results and discussion

The PL emission spectra of studied crystals are presented in Fig. 1. As the Figure shows, the spectra of $BiPO_4$ reveal broad asymmetric band peaking in the blue spectral region with a shoulder in the violet region. An additional long-wavelength emission component of $BiPO_4$ is also clearly distinguishable in 550–650 nm region. The intrinsic PL emission spectrum of $K_3Bi_5(PO_4)_6$ substantially differs from the case of $BiPO_4$. Two overlapping components with approximately equal intensity are clearly distinguishable at ~ 500 and ~ 580 nm when $E_{ex} = 6.2$ eV and third component arises in the red spectral region at lower excitation energies. When $E_{ex} = 6.2$ eV, the

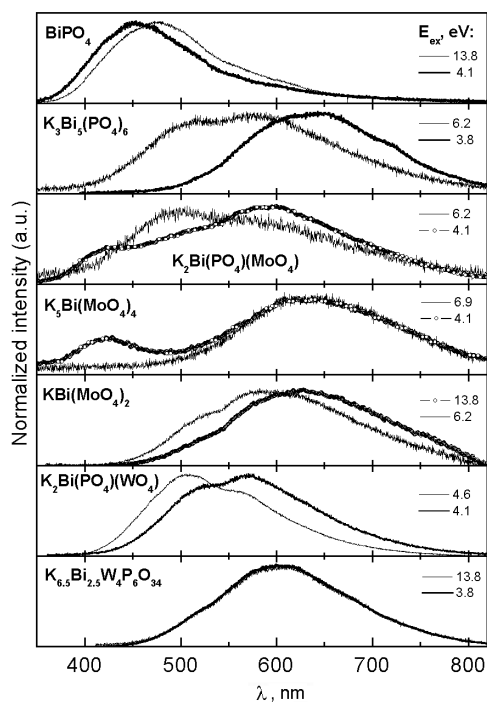


Fig. 1. PL emission spectra of the studied crystals, $T = 8$ K.

PL emission spectrum of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ reveals complex band with the main peak near 500 nm. At lower excitation energy ($E_{ex} = 4.1$ eV), the main peak in the $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ spectrum is observed near 590 nm, while the additional component arises in the violet region (below 440 nm). The PL emission spectrum of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ demonstrates a broad band peaking near 620 nm. When $E_{ex} = 4.1$ eV, the spectrum of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ reveals additional component in the violet region. Both spectra of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ presented in Fig. 1 clearly indicate existence of two components peaking near 510 and 570 nm. The relative intensities of these components depend of the excitation energy (see Fig. 1).

The PL excitation spectra of studied crystals are presented in Fig. 2. As the Figure shows, the excitation spectrum of the violet emission component of BiPO_4 contains an intense band at ~ 4.8 eV. Except this intense band, an additional band is clearly seen in the excitation spectra of BiPO_4 at the lower energies (near ~ 4.5 eV) when $\lambda_{em} = 500$ nm. When $\lambda_{em} = 450$ nm, the excitation spectrum of $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ reveals two intense peaks at ~ 4.6 and ~ 5.7 eV. A low-intensity band also exists in this excitation spectrum in 3.0–3.3 eV region. The excitation spectrum of the red component of

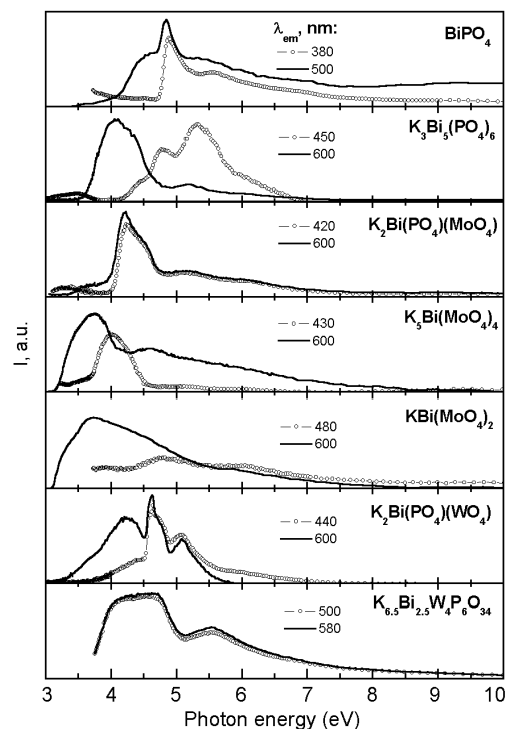


Fig. 2. PL excitation spectra of the studied crystals, $T = 8$ K.

$\text{K}_3\text{Bi}_5(\text{PO}_4)_6$ ($\lambda_{em} = 600$ nm) reveals the intense band peaking at ~ 4.1 eV. Besides the intense excitation band at ~ 4.2 eV, the excitation spectrum of the violet component of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ ($\lambda_{em} = 420$ nm) reveals an additional band with the peak position near ~ 3.3 eV. The excitation spectrum of the red component of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ ($\lambda_{em} = 600$ nm) resembles profile of corresponding spectrum of the violet component when excitation energies are above 4 eV. The excitation spectrum of the violet component of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ ($\lambda_{em} = 430$ nm) reveals intensive band peaking near 4.0 eV. The most intensive excitation band of the red component of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ ($\lambda_{em} = 600$ nm) reaches the peak position near 3.5 eV. The excitation spectra of both PL emission components of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ contain two intensive excitation bands peaking at ~ 4.6 and ~ 5.1 eV. Besides this, the both components are characterized by additional excitation bands at the lower energies, near ~ 4.2 eV.

Calculated PDOSes of the studied crystals are presented in Fig. 3. For convenience of analysis, only these states which have valuable contribution in -8 – 10 eV energy region are presented in the Figure (the states which supply less than 1 % of the total electron charge within this region are omitted).

It is known that DFT-based calculations usually underestimate the values of the energy gaps E_g between the Valence bands (VBs) and the Conduction bands (CBs) of oxide crystals. For this reason, correct estimation of E_g values requires additional analysis. The values of the energy gaps presented in Fig. 3 were estimated in our previous papers: for BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ in [7] and for $\text{KBi}(\text{MoO}_4)_2$ in [9]. We tentatively estimate the E_g value of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ as 4.2 eV taking into account the peak position of the lowest-energy band in the excitation spectrum of this crystal that presented in Fig. 2. More precise estimation of the energy gap of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ will be the subject of our further studies.

The following general features can be distinguished from the PDOS distributions presented in Fig. 3. Mainly O p states form the upper parts of the VBs of all studied crystals. Bi s states have noticeable contribution at the tops of the VBs (TVBs) of all studied compounds. Bi p contribute at the bottoms of the CBs (BCBs) of all crystals except $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$. Mo d (W d) states form the lower parts of the CBs (in particular, the BCBs) of studied molybdates (tungstates). P states are absent at the band edges (neither at TVBs, nor at the BCBs) of all studied phosphate compounds.

So, the calculations indicate that bismuth ions in all studied crystals (except $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$) together with the molybdate (tungstate) groups in the studied molybdates (tungstates) form the lowest-energy band-to-band transitions. The Bi $s \rightarrow$ Bi p , as well as the O $s \rightarrow$ Mo d (W d) transitions form the fundamental absorption edges of the mentioned crystals and consequently, Bi^{3+} ions as well as MoO_4^{2-} (WO_4^{2-}) groups can easily create centers of intrinsic luminescence emission. The Bi p states are absent at TVB of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$, so calculations indicate unlikely participation of Bi^{3+} ions in the intrinsic PL emission processes for this crystal (this question will be discussed below). Detailed analysis of the origin of intrinsic PL emission and excitation bands of BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ and $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ was done in our previous paper based on the electronic structure results [7]. The main inferences on the origin of PL components of these five crystals obtained in the mentioned paper can be formulated briefly as the following. The high-energy PL components of BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$

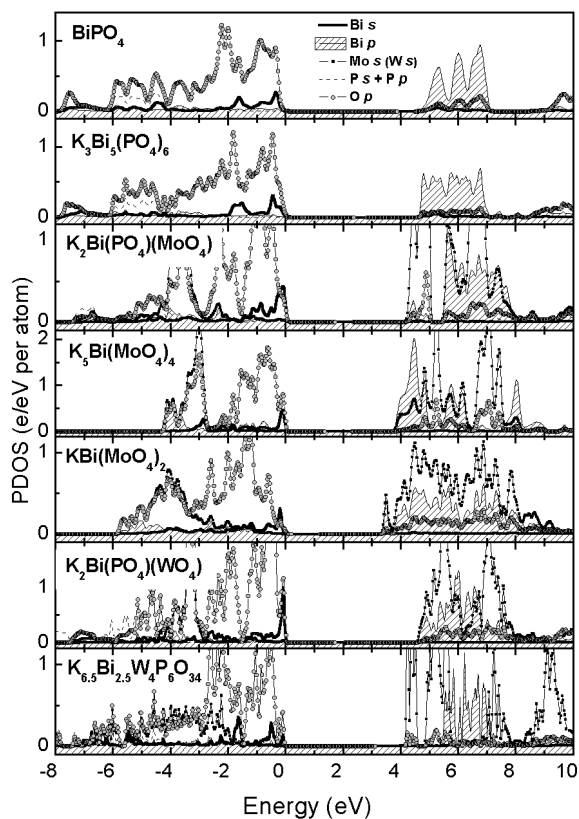


Fig. 3. Calculated partial densities of states (PDOS) of the studied crystals.

and $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ (peaking in the blue and violet regions, see Fig. 1) have the bismuth-related origin ($^3P_1 \rightarrow ^1S_0$ radiative transitions in Bi^{3+} ions). The red PL components of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ have MoO_4^{2-} -related origin. The red PL component of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ presumably originates from the molybdenum impurities which form MoO_4^{2-} emission centers in the tungstate host. The origin of intrinsic luminescence in $\text{KBi}(\text{MoO}_4)_2$ and $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ is analyzed below.

As Fig. 1 shows, spectral position and half-width of the red PL component of $\text{KBi}(\text{MoO}_4)_2$ are very close to corresponding parameters of the red component of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$. The excitation spectra of these red components are also very similar for both crystals (see Fig. 2). For both compounds, the excitation curves taken at $\lambda_{em} = 600$ nm reach the peak position approximately at the same energy (near ~ 3.8 eV), reveal the same shoulders in 3.3–3.5 eV region and demonstrate analogous decrease of intensity with increasing energy above 4 eV. From structural point of view, both $\text{KBi}(\text{MoO}_4)_2$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ contain

molybdate molecular groups MoO_4^{2-} on anionic lattice positions. The electronic states of the molybdate groups form the band edges of both crystals (see Fig. 3 and accompanying text) indicating high probability for MoO_4^{2-} -groups to form centers of the intrinsic PL emission. So, we have full reason to assume that the red PL component of $\text{KBi}(\text{MoO}_4)_2$, analogously to the red component of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ is generated by transitions in MoO_4^{2-} -groups.

When $E_{ex} = 6.2$ eV, the PL emission spectrum $\text{KBi}(\text{MoO}_4)_2$ clearly demonstrates a shoulder in 500–550 nm region indicating existence of additional emission component in the blue-green spectral region. There are no clear analogs of such component in the PL emission spectra of $\text{K}_5\text{Bi}(\text{MoO}_4)_4$. However, the PL emission component in the blue region is observed for another Bi-containing molybdate crystal, namely $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ (see Fig. 1). This component is attributed to radiative transitions in Bi^{3+} ions (see text above). Coordination of Bi^{3+} ions $\text{KBi}(\text{MoO}_4)_2$ and $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ is analogous: in both lattices bismuth ions form BiO_8 polyhedra with the nearest oxygen surrounding (in contrast to $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ where they form BiO_6 polyhedra). So we can presume that analogously to $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ case, the blue-green PL emission component of $\text{KBi}(\text{MoO}_4)_2$ is formed by transitions in Bi^{3+} ions. Additional studies are obviously required to verify this assumption.

The excitation spectrum of the blue-green emission component of $\text{KBi}(\text{MoO}_4)_2$ is similar to the excitation spectrum of the red emission component of this crystal at energies above ~ 5 eV (compare curves for $\lambda_{em} = 480$ and 600 nm in Fig. 2). So most probably, excitation of the both components above 5 eV is mediated by band-to-band excitations of the crystal host. Below 5 eV, the excitation spectra of the two components differ. In addition, the excitation spectrum of the blue-green component of $\text{KBi}(\text{MoO}_4)_2$ does not reveal well distinguished peaks or gaps in this energy region. So formation of this spectrum below 5 eV requires additional studies.

The PL emission spectra of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ reveal a broad band with the peak position near 600 nm (see Fig. 1). The emission spectra are practically independent of the excitation photon energy, whereas the excitation spectra of this crystal also very weakly depend on λ_{em} (see Fig. 2). This feature obviously points to exist-

ence of only single component of intrinsic emission. The peak position of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ emission band is valuably shifted to the longer wavelengths with respect to the peak position of the long-wavelength component of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$. Taking into account this difference in the spectra, we can assume that the centers of intrinsic PL emission in $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ and $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ are different. Such inference is supported by structural data. While $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ contains WO_4^{2-} groups and uncontrolled isovalent impurities of molybdenum can easily form MoO_4^{2-} emission centers in this crystal, $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ crystal contains WO_6 polyhedra and Mo impurities should hardly form MoO_4^{2-} centers in it. So probably, the PL emission of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ is not related to the MoO_4^{2-} centers.

The PL excitation spectra of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ differ substantially from $\text{K}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$ case as well as from the excitation spectra of other crystals studied here (see Fig. 2). In the VUV region of excitation energies, $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ reveal quite intense intrinsic luminescence at the room temperature [10], whereas the intrinsic PL of other crystals undergoes complete temperature quenching well below 300 K (see [7, 9]). This fact points to different centers of the intrinsic emission in $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ with respect to other Bi-containing crystals studied here. At the same time, the calculations indicate that Bi^{3+} ions are unlikely to form the centers of the intrinsic emission in $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ since Bi *p* states are absent at the TVB of the crystal in contrast to all other compounds considered (see Fig. 3 and accompanying text). So, we can presume that the intrinsic emission of $\text{K}_{6.5}\text{Bi}_{2.5}\text{W}_4\text{P}_6\text{O}_{34}$ is not related to transitions in Bi^{3+} ions. This presumption has to be verified in further studies.

4. Conclusions

The origin of intrinsic luminescence in the set of oxide crystals which contain Bi^{3+} ions and PO_4^{3-} , MoO_4^{2-} or WO_4^{2-} molecular anionic groups is clarified in complex experimental and computational studies. It is found that PL emission components of BiPO_4 , $\text{K}_3\text{Bi}_5(\text{PO}_4)_6$, $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$ and $\text{KBi}(\text{MoO}_4)_2$ in the violet-green spectral region are related to radiative transitions in Bi^{3+} ions. The red PL components of $\text{K}_2\text{Bi}(\text{PO}_4)(\text{MoO}_4)$, $\text{KBi}(\text{MoO}_4)_2$ and $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ have MoO_4^{2-} -related origin.

The red emission component of $K_2Bi(PO_4)(WO_4)$ luminescence is related to the molybdenum impurities which form MoO_4^{2-} emission centers. The intrinsic PL emission band of $K_{6.5}Bi_{2.5}W_4P_6O_{34}$ is probably related neither to Bi^{3+} ions nor to MoO_4^{2-} impurity centers.

References

1. N.B.Sanyasi, B.Vishwanadh, V.Sudarsan, V.R.Kumar, *Dalton Trans.*, **41**, 3194 (2012).
2. M.Zhao, L.Li, J.Zheng et al., *Inorg.Chem.*, **52**, 807 (2013).
3. P.Arunkumar, C.Jayajothi, D.Jeyakumar, N.Lakshminarasimhan, *RSC Advances*, **2**, 1477 (2012).
4. M.Roming, C.Feldmann, *J.Mater.Sci.*, **44**, 1412 (2009).
5. X.He, M.Guan, N.Lian et al., *J.Alloys Compd.*, **492**, 452 (2010).
6. Z.Q.Wu, J.F.Tang, J.H.Huang et al., *Opt.Mater.*, **34**, 287 (2011).
7. Yu A.Hizhnyi, S.G.Nedilko, V.P.Chornii et al., *J.Alloys Compd.*, **614**, 420 (2014).
8. S.Nedilko, V.Chornii, Yu.Hizhnyi et al., *Functional Materials.*, **20**, 29 (2013).
9. Yu.Hizhnyi, S.Nedilko, V.Chornii et al., *Sol.St.Phenomena*, **200**, 114 (2013).
10. Yu.Hizhnyi, S.Nedilko, V.Chornii et al., 2014 IEEE Intern. Conf. on Oxide Materials for Electronic Engineering (OMEE), Book of Conf. Proc. 6912395, DOI: 10.1109/OMEE.2014.6912395 (2014), p.170.
11. K.V.Terebilenko, I.V.Zatovsky, N.S.Slobodyanik et al., *J.Sol.St.Chem.*, **180**, 3351 (2007).
12. I.V.Zatovsky, K.V.Terebilenko, N.S.Slobodyanik et al., *J.Sol.St.Chem.*, **179**, 3550 (2006).
13. I.V.Zatovsky, K.V.Terebilenko, N.S.Slobodyanik et al., *Acta Crystallogr.E*, **62**, i193 (2006).
14. K.V.Terebilenko, I.V.Zatovsky, V.N.Baumer et al., *J.Sol.St.Chem.*, **181**, 2393 (2008).
15. G.Zimmerer, *Radiat.Measur.*, **42**, 859 (2007).
16. P.Blaha, K.Schwarz, G.Madsen et al., WIEN2k, An Augmented Plane Wave Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Austria: Techn. Universitadt Wien, ISBN 3-9501031-1-2 (2001).
17. J.P.Perdew, Y.Wang, *Phys.Rev.B*, **45**, 13244 (1992).
18. P.E.Bloch, O.Jepsen, O.K.Andersen, *Phys.Rev.B*, **49**, 16223 (1994).