
Luminescence spectroscopy and electronic structure of Zr- and Bi-containing phosphate crystals

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Abstract. Intrinsic photoluminescence (PL) properties of ZrP_2O_7 , $\text{KZr}_2(\text{PO}_4)_3$, $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ and BiPO_4 phosphate crystals are studied in the excitation photon-energy range 3.7–20 eV. The electronic band structures of these crystals are calculated using a full-potential linear augmented plane-wave method. The origins of the intrinsic luminescence in phosphate compounds under study are analyzed basing on the experimental and computational results. It is found that the short-wavelength PL components for the $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ compound located at 380–420 nm should be associated with the emission of Zr-related centres. The long-wavelength emission component for this crystal located near 480 nm should be attributed to the emission of Bi-related centres. The bands in the PL excitation spectra of $\text{K}_2\text{BiZr}(\text{PO}_4)_3$, which are located near 4.9 and 5.5 eV, have a Bi-related nature, whereas the bands observed above 6.5 eV are associated with Zr.

Keywords: luminescence, phosphates, electronic structure, bismuth, zirconium

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1. Introduction

Zr-containing phosphate crystals doped with luminescent rare-earth ions have been attracting much attention due to their potential applications in mercury-free lamps [1, 2], plasma display panels [2] and white-light emitting diodes [3–5]. Bi-containing phosphate compounds have also been actively studied as promising hosts for luminescent rare-earth ions [6–11]. In spite of intense earlier studies, the origin of the intrinsic luminescence and the peculiarities of excitation energy transfer in the Zr- and Bi-containing phosphate crystals are still an important subject of current disputes.

In our previous studies, the photoluminescence (PL) properties and the electronic structures of a number of Zr-containing [12–14] and Bi-containing [6, 15] phosphate crystals have been studied and several assumptions on the origin of their intrinsic luminescence have been made. The present work continues comprehensive experimental and computational studies on the subject. It is focused on comparative analysis of the PL emission and the excitation spectra of different phosphate compounds in the VUV region of excitation photon energies. Namely, we study two Zr-containing (ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$) and one Bi-containing (BiPO_4) compounds, along with the phosphate crystal containing the both cations, $\text{K}_2\text{BiZr}(\text{PO}_4)_3$. The experimental data are analyzed in combination with the calculations of partial densities of electronic states (PDOSes) performed for all of the crystals. One of the primary aims of the present analysis of the experimental and computational results is to ascertain that the intrinsic luminescence spectra of $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ crystals are formed by both Bi- and Zr-related centres.

2. Experimental technique and calculation details

All of the crystals studied by us were synthesized using crystallization from melt. The details of the relevant procedures may be found in our previous studies reported for ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ [13], $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ [14] and BiPO_4 [15]. PL spectroscopic experiments were carried out at the SUPERLUMI station, HASYLAB (DESY), Hamburg, Germany [16]. The PL spectra were obtained in the region 3.7–20 eV of excitation energies at the temperature 8–300 K. The measured PL emission and excitation spectra were corrected by the system response.

The electronic structures of our crystals were calculated using a WIEN2k program package [17], in which a full-potential linear augmented plane-wave method was implemented in the framework of density-functional theory. We refer the reader to Refs. [13–15] for the details of the calculation procedures. The partial densities of states were calculated using conventional approximations and a default set of calculation parameters of the WIEN2k package. The crystalline structures of ZrP_2O_7 , $\text{KZr}_2(\text{PO}_4)_3$, $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ and BiPO_4 compounds used in our calculations were taken from Refs. [18], [19], [14] and [20], respectively.

3. Results and discussion

The PL emission spectra for the crystals under study are shown in Fig. 1. For a convenience of comparison, the spectral intensities are given in arbitrary scales. The PL excitation spectra for all of the crystalline compounds are displayed in Fig. 2. Notice that the vertical arrows in Fig. 1 indicate the wavelength λ_{em} at which the PL excitation spectra are measured, while the arrows in Fig. 2 indicate the excitation energies E_{ex} for the PL emission spectra presented in Fig. 1.

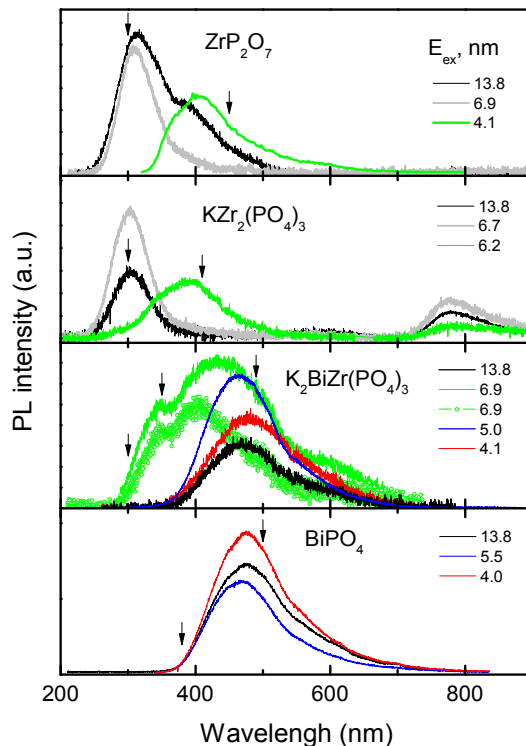


Fig. 1. PL emission spectra obtained at the temperatures 8 K (solid lines) and 300 K (line with circles). Excitation photon energies E_{ex} are indicated in the legend.

The PL emission spectra for both the ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ crystals reveal a short-wavelength component near 300 nm. This component is accompanied by less intense components located at 350–420 nm. The latter components dominate at lower excitation energies, when the

main peaks are observed near 400 nm (see Fig. 1). The spectra obtained for $\text{KZr}_2(\text{PO}_4)_3$ reveal an additional band located in the IR region. The short-wavelength component for the both compounds is also observed at 300 K (the corresponding spectra can be found in Ref. [12]).

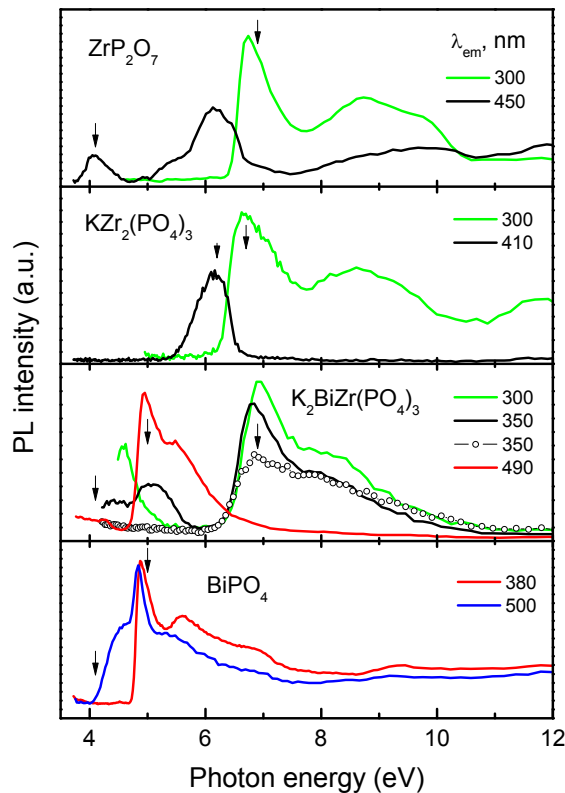


Fig. 2. PL excitation spectra obtained at the temperatures 8 K (solid lines) and 300 K (line with circles). λ_{em} 's (see the text) are indicated in the legend.

As seen from Fig. 2, the short-wavelength PL emission components for the ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ crystals are efficiently excited at the energies higher than 6.5 eV. Two peaks near 6.8 and 8.5 eV are observed in the spectra of these crystals at $\lambda_{em} = 300$ nm. These peaks lie in the energy region of band-to-band electronic transitions, since the dielectric energy gaps E_g for ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ are known to be ~ 6.7 and ~ 6.6 eV, respectively [13]. The PL excitation spectra of the short-wavelength emission components peculiar for ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ are similar, as seen after comparing the corresponding curves in Fig. 2 taken at $\lambda_{em} = 300$ nm.

The calculated PDOS distributions for our crystals are displayed in Fig. 3, where the origin of the energy scale is chosen at the Fermi level E_F . The energy gaps E_g between the valence and conduction bands are presented in Fig. 3 without additional corrections to the experimental data. For convenience of further analysis, we present only the states that reveal notable contributions inside the range $-12 \div 12$ eV. The states that provide less than 1% of the total electron charge in this region have been omitted. As Fig. 3 testifies, the tops of the valence band for ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ are formed by O $2p$ states, whereas Zr $4d$ states evidently dominate at the bottoms of the conduction band. So, the lowest-energy band-to-band transitions in the both compounds have a character of O $2p - \text{Zr } 4d$ charge transfer.

Earlier, the luminescence properties of ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ have been compared to the properties of some other Zr-containing crystals known from the literature and their electronic band structures have been analyzed [13]. As a result, it has been assumed that the short-wavelength emission components observed near 300 nm and the corresponding excitation bands above the

fundamental absorption edges are related to $O^{2-} - Zr^{4+}$ charge-transfer transitions in ZrO_6 polyhedra (notice that Zr^{4+} ions are coordinated by six oxygen atoms in the both compounds). On the other hand, the long-wavelength PL components for the ZrP_2O_7 and $KZr_2(PO_4)_3$ crystals observed near 400 nm and the corresponding excitation bands observed below E_g (see the curves at $\lambda_{em} = 450$ and 410 nm in Fig. 2) have been attributed to ZrO_6 groups that include (or are situated close to) some point defects or impurities of the crystal lattice [13].

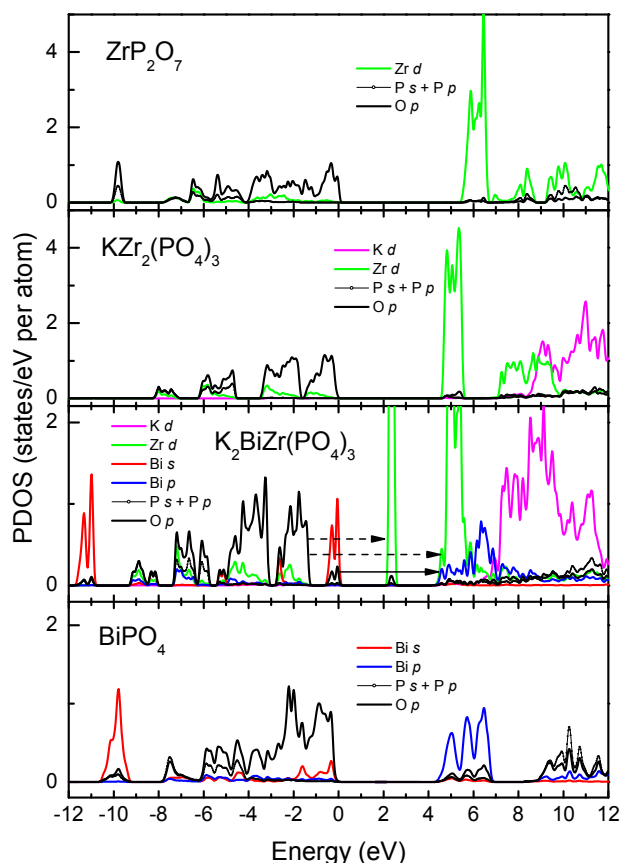


Fig. 3. Partial densities of states calculated for the crystals under study.

As seen from Fig. 1, the $BiPO_4$ crystal is characterized by a complex PL emission band consisting of at least two components, with the main peak located near 480 nm. The excitation spectrum of the short-wavelength component of this band (see the curve at $\lambda_{em} = 380$ nm in Fig. 2) has two peaks located at ~ 4.9 and ~ 5.5 eV. Both of the peaks lie in the energy region of the band-to-band electronic transitions of the crystal host, since the E_g value for $BiPO_4$ is known to be about 4.7 eV [15]. The intrinsic luminescence in $BiPO_4$ is not observed at 300 K due to temperature quenching which is essential already at 100–250 K [15]. As seen from Fig. 3, the PDOSes calculated for $BiPO_4$ reveal domination of O $2p$ states at the top of the valence band, while Bi $6p$ states prevail at the bottom of the conduction band. The states Bi $6s$ are also present at the top of the valence band, but their contribution is small when compared to the oxygen states. It has been supposed in Ref. [15] that the intrinsic PL emission components in $BiPO_4$ are related to the intra-centre transitions occurring in Bi^{3+} ions.

Taking into account the origins of the intrinsic PL emission and the excitation bands described above for the Zr- and Bi-containing phosphates, now we will analyze formation of the intrinsic PL spectra for the $K_2BiZr(PO_4)_3$ compound containing the two cations. Fig. 1 illustrates

clearly that the PL emission spectra of $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ represent a superposition of Zr- and Bi-related emission bands. At the high-energy excitation ($E_{ex} \geq 7$ eV), one can see the spectral components located in the same energy region (330–420 nm) where the defect-related components typical for ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ are observed (compare the relevant curves in Fig. 1). These short-wavelength components are in fact not observed at the low-energy excitation ($E_{ex} \leq 5$ eV), though another band appears near 480 nm. Following from its peak position and spectral half-width, this band is very similar to the intrinsic PL band observed for the BiPO_4 crystal (see Fig. 1).

Issuing from such close similarity of the spectra, we can attribute the short-wavelength PL components observed in $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ at 380–420 nm to the emission of Zr-related centres, whereas the long-wavelength emission component at 480 nm should be ascribed to the emission of Bi-related centres. As seen from Fig. 1, only the short-wavelength components peaked at ~350 and ~400 nm remain in the spectra for $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ at 300 K (as noted above, the intrinsic PL for the ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ crystals is not quenched at the room temperature), while the component located at 480 nm disappears, in much the same way as the intrinsic emission in BiPO_4 . So, the temperature behaviour of the intrinsic luminescence observed in $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ confirms the attribution of the PL components assumed above.

The above attribution is also verified by the PL excitation spectra. Indeed, Fig. 2 shows that the excitation spectra for the short-wavelength emission component in $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ at both 8 K and 300 K are similar to the excitation spectra corresponding to the short-wavelength emission components observed for the ZrP_2O_7 and $\text{KZr}_2(\text{PO}_4)_3$ crystals. The excitation spectrum of the long-wavelength emission component for $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ (see curve at $\lambda_{em} = 490$ nm in Fig. 2) is similar to the excitation spectrum for BiPO_4 measured at $\lambda_{em} = 380$ nm. In other words, the excitation spectra typical for $\text{K}_2\text{BiZr}(\text{PO}_4)_3$ reveal the two groups of bands whose origins are different. The origin of the excitation bands located at 4.9 and 5.5 eV is related to Bi, whereas the bands above 6.5 eV should be attributed to Zr-related excitations.

The calculated PDOS distributions confirm possible participation of the electronic states of both Zr and Bi ions in the processes associated with the intrinsic luminescence in $\text{K}_2\text{BiZr}(\text{PO}_4)_3$. The top of the valence band of this crystal is formed mainly by Bi $6s$ states, while Zr $4d$ states dominate at the bottom of the conduction band (see Fig. 3). The PDOS data indicates that the electronic bands with predominantly O $2p$ character are located well below the top of the valence band: the group of intense peaks related to O p density in the region -2.8 – -1.3 eV is separated from the upper part of the valence band by ~1 eV-wide unoccupied region. The lower part of the conduction band, which is represented by the peaks at 2.1–2.6 eV related to Zr d density, is separated from the upper part of the conduction band by the empty region ~2 eV. The contribution from the Bi $6p$ states becomes notable only in the upper part of the conduction band. Therefore the lowest-energy transitions of the type Bi $6s$ – Bi $6p$ in $\text{K}_2\text{BiZr}(\text{PO}_4)_3$, which are indicated by a solid horizontal arrow in Fig. 3, should have the energies located in the region 4–4.5 eV. The availability of Bi states in the vicinity of the band edges speaks in favour of possible participation of Bi ions in the luminescence processes and, in particular, the existence of Bi-related centres of the luminescence emission in $\text{K}_2\text{BiZr}(\text{PO}_4)_3$. The presence of Bi s and Bi p states in the vicinity of the band edges (see the lower plot in Fig. 3) is an inherent property of BiPO_4 and the other Bi-containing crystals in which the intrinsic luminescence is related to Bi^{3+} ions (see the study [15] and references therein).

The general pattern of the PDOS indicates that the transitions with a definitely established nature O $2p$ – Zr $4d$ can take place only from the lower sub-band of the valence band located in the

region $-2.8 \div -1.3$ eV, where the $O p$ density clearly dominates. The energies of transitions from this sub-band (indicated by dashed arrows in Fig. 3) to the lower sub-band of the conduction band ($2.1 \div 2.6$ eV) and to the upper part of the conduction band, where $Zr d$ states also dominate ($4.5 \div 6$ eV), can be estimated as $3.5 \div 4$ eV and $6 \div 7$ eV, respectively. This indicates that Zr ions can also actively participate in the luminescence processes and can form the luminescence emission centres in $K_2BiZr(PO_4)_3$. This possibility is supported by the fact that $Zr d$ and $O p$ states are also present in the vicinities of the band edges in ZrP_2O_7 and $KZr_2(PO_4)_3$ (see the two upper plots in Fig. 3), where Zr-related luminescence centres surely exist [13].

As a result, the calculation results obtained by us point to possible participation of both Bi and Zr states in the formation of intrinsic PL excitation spectra for the $K_2BiZr(PO_4)_3$ crystals. Clarification of the main features of this participation requires additional studies, which will be a subject of our further work.

4. Conclusions

The comparative analysis of the intrinsic PL properties for the ZrP_2O_7 , $KZr_2(PO_4)_3$, $K_2BiZr(PO_4)_3$ and $BiPO_4$ phosphate crystals performed in this work and the calculations of their electronic structures have resulted in the following conclusions.

1. The short-wavelength PL emission components for $K_2BiZr(PO_4)_3$, which are peaked at 380–420 nm, should be associated with the emission of Zr-related centres, whereas the long-wavelength emission component for this crystal located near 480 nm should be attributed to the emission of Bi-related centres.
2. The origin of the bands located near 4.9 and 5.5 eV in the PL excitation spectra of $K_2BiZr(PO_4)_3$ are related to Bi, whereas the bands observed above 6.5 eV have a Zr-related nature.
3. The electronic transitions of the types $O 2p - Zr 4d$ and $Bi 6s - Bi 6p$ can participate in the formation of intrinsic PL excitation spectra for the $K_2BiZr(PO_4)_3$ crystals.

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Анотація. Вивчено власну фотолюмінесценцію (ФЛ) фосфатних кристалів ZrP₂O₇, KZr₂(PO₄)₃, K₂BiZr(PO₄)₃ і BiPO₄ у діапазоні фотонних енергій збудження 3,7÷20 eV. Зонну структуру цих кристалів розраховано з використанням лінеаризованого методу приєднаних плоских хвиль. Походження власної люмінесценції фосфатних сполук проаналізовано на основі одержаних експериментальних і розрахункових результатів. Встановлено, що короткохвильові компоненти ФЛ для сполуки K₂BiZr(PO₄)₃, розташовані при 380 ÷ 420 нм, слід приписувати випромінюванню центрів, пов'язаних із Zr. Довгохвильову емісійну компоненту для цих кристалів, пік якої розташований поблизу 480 нм, слід відносити до випромінювання центрів, пов'язаних із Bi. Смуги в спектрах збудження ФЛ K₂BiZr(PO₄)₃, розташовані поблизу 4,9 і 5,5 eV, мають природу, пов'язану з Bi, тоді як смуги, спостережувані вище за 6,5 eV, пов'язані з Zr.