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Luminescence spectroscopy of Ln-doped Bi-containing phosphates and molybdates

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HIGHLIGHTS

- PL excitation of $K_3Bi_5(PO_4)_6$ and $K_2Bi(PO_4)(MoO_4)$ is related to Bi^{3+} ions.
- Energy transfer from Bi^{3+} to Eu^{3+} exists in $K_3Bi_5(PO_4)_6$:Eu and $K_2Bi(PO_4)(MoO_4)$:Eu.
- PL excitation spectra of $K_2Eu(PO_4)(MoO_4)$ are formed by O − Eu CT transitions.

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ABSTRACT

The photoluminescence (PL) emission and excitation spectra of undoped and doped with rare-earth (RE = Eu, Tb) ions $K_3Bi_5(PO_4)_6$ and $K_2Bi(PO_4)(MoO_4)$ crystals are studied in 3.7–14 eV region of the excitation photon energies at T = 8 and 300 K. The mechanisms of the host-related and RE-related luminescence in 3.7–7 eV region of the excitation photon energies are revealed in comparative analysis of the PL spectra of studied compounds. It is assumed that the excitation mechanisms of host luminescence of $K_3Bi_5(PO_4)_6$ and $K_2Bi(PO_4)$ (MoO_4) crystals below 4.8 eV are related to Bi^{3+} ions in oxygen surrounding. An efficient energy transfer from the Bi^{3+}-related luminescence centers to the emitting RE centers exists in crystals with low concentration of the RE dopants (1%). The PL excitation spectra of $K_3Bi_5(PO_4)_6$ crystals with high concentration of Eu dopants are formed by O − Eu CT transitions.

1. Introduction

The bismuth-containing compounds can be easily doped with luminescent rare-earth ions since the Bi^{3+} ionic radius is close to ionic radii of the lanthanides. The photo-luminescence properties of the RE-doped Bi-containing phosphates and molybdates are intensively studied at present from viewpoint of potential application of these materials as the components of white light emission diodes, phosphor and laser host materials (Huang et al., 2014; Sanyasi Naidu et al., 2012; He et al., 2010; Voda et al., 1998, 2001; Canibano et al., 2003; Reshak et al., 2008a, 2008b). The origin of PL emission components of the set of undoped Bi-containing phosphate and molybdate hosts was revealed in our recent papers (Nedilko et al., 2013; Hizhnyi et al., 2014, 2013). However, a mechanisms of the PL excitation for these compounds was not analyzed yet. In this paper, we study the PL properties of two crystals from this set, $K_2Bi(PO_4)(MoO_4)$ and $K_3Bi_5(PO_4)_6$. We consider the influence of RE-doping on the PL spectra of these crystals at different temperatures aiming to clarify the origin of luminescence of the crystal hosts, in particular, formation of peculiarities in the PL excitation spectra.

It is a well known phenomenon that doping with RE ions usually suppresses host PL emission of oxide compounds. The RE^{3+} dopants can create new “channels” the excitation energy relaxation which compete with host-related PL emission. The RE^{3+} ions can be excited by intra-center excitations, either by inner-shell f-f transitions or by charge-transfer (CT) O − RE transitions. At the same time, the excitation energy can be transferred to the RE^{3+} ions after band-to-band excitations of the crystal host. Comparison of the

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excitation spectra of undoped and RE-doped oxide compounds can provide much information on the excitation mechanisms as for the host-related as well as for the RE^{3+}-related luminescence. In this paper, we consider only those RE dopants in $K_2Bi(PO_4)(MoO_4)$ and $K_3Bi_5(PO_4)_6$ hosts which provide the most relevant information for clarification of the excitation mechanisms in these compounds.

2. Synthesis and experimental methods

Two synthetic pathways have been applied for samples preparation. A flux growth has been used for undoped samples and for doped with small amount of activator. The synthetic procedures for $K_2Bi(PO_4)(MoO_4)$, $K_2Bi(PO_4)(MoO_4)$:Eu(0.1, 1%), $K_3Bi_5(PO_4)_6$, $K_3Bi_5(PO_4)_6$:Eu (1%+) are described in detail in (Nedilko et al., 2013). In case of $K_2Bi(PO_4)(MoO_4)$:Tb(1%) the same procedure has been applied with addition of Tb_4O_7 in amount of 0.25 mol. % in the initial melt. For samples with high europium content ($K_2Eu(PO_4)(MoO_4)$, $K_3Bi_4Eu(PO_4)_6$, $K_3Bi_{2.5}Eu_{2.5}(PO_4)_6$) the solid state approach has been chosen. The reagent-grade raw materials were Bi_2O_3, Eu_2O_3, K_2MoO_4, KPO_3 and $(NH_4)_2HPO_4$ powders with purity of more than 99.99%. Stoichiometric amounts of reagents have been thoroughly mixed with an agate mortar and pestle into fine powders at the first stage. The mixture for $K_2Eu(PO_4)(MoO_4)$ in an alumina crucible was gradually heated to 700 °C for 8 h, 850 °C for 12 h. For $K_3Bi_4Eu(PO_4)_6$ and $K_3Bi_{2.5}Eu_{2.5}(PO_4)_6$ synthesis, the mixtures of the stoichiometric reagents have been preheated at 500 °C for 2 h to get rid of gaseous co-products, and then they were annealed at 750 °C for 6 h, 850 °C and 950 °C for 12 h with intermediate regrinding. The X-Ray powder diffraction (XRD) data were collected on a SHIMADZU XRD-6000 diffractometer with a linear detector and Cu Kα radiation (λ = 1.5418Å). Data were collected over the 2θ range of 5–90^O with the step 0.02^O and 1sec exposition per step. The patterns obtained match well with reference data for $K_2Bi(PO_4)(MoO_4)$ (Zatovsky et al., 2006; Daub et al., 2012) and $K_3Bi_5(PO_4)_6$ (Terebilenko et al., 2007).

The PL properties under the VUV synchrotron excitations were studied on SUPERLUMI station at HASYLAB (DESY), Hamburg, Germany (Zimmerer, 2007). The PL spectra were obtained for 3.7–14 eV region of excitation photon energies in 8–300 K temperature range. All PL emission and excitation spectra were corrected on instrumental response.

3. Results and discussion

The PL emission spectra of undoped, Eu- and Tb-doped $K_2Bi(PO_4)(MoO_4)$ crystals measured at T = 8 K are presented in Fig. 1. The spectra of undoped crystal reveal several components peaking in the blue–green and red spectral regions. In our previous studies, we attributed the blue–green emission components of undoped $K_2Bi(PO_4)(MoO_4)$ to radiative transitions in Bi^{3+} ions, whereas the red component was related to transitions in MoO_4^{2-} groups of the crystal (Hizhnyi et al., 2014). As the Figure shows, doping with europium leads to suppression of host emission and only Eu^{3+}-related spectral bands are observed in spectra starting from C_{Eu} = 1%. These bands are generated by the inner-shell f-f transitions in Eu^{3+} ions (their detailed assignment can be found in Nedilko et al. (2013). The spectra of Tb-doped samples reveal Tb^{3+}-related narrow spectral bands which are observed against a "background" of the low-intensity host luminescence band. These narrow bands originate from the inner-shell f-f transitions in Tb^{3+} ions (the band assignment can be found e.g. in Souza et al. (2010)). Intensity of the most intense Tb^{3+}-related band observed near 550 nm exceeds intensity of the host emission at this wavelength almost by a decade.

The PL excitation spectra of undoped, Eu- and Tb-doped $K_2Bi(PO_4)(MoO_4)$ crystals are presented in Fig. 2. Vertical dashed line in the upper plot represent the value of the energy gap E_g of $K_2Bi(PO_4)(MoO_4)$ crystal estimated in our earlier paper (Hizhnyi et al., 2014). The excitation spectra of the blue–green and red PL components of undoped $K_2Bi(PO_4)(MoO_4)$ are alike and reveal four well-distinctive components at energies indicated by arrows with corresponding notations. The same components are manifested in

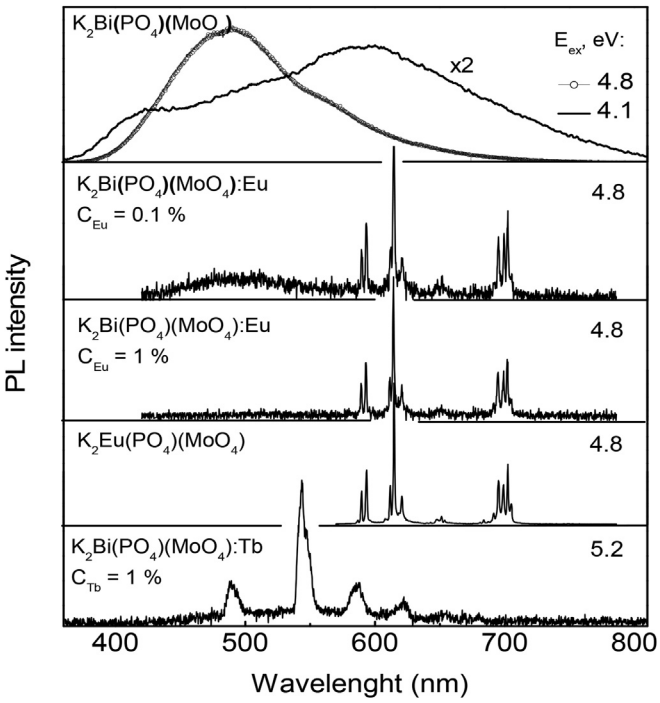

Fig. 1. The PL emission spectra of undoped, Eu- and Tb-doped $K_2Bi(PO_4)(MoO_4)$ crystals, T = 8 K, excitation photon energies E_{ex} are indicated in the figure.

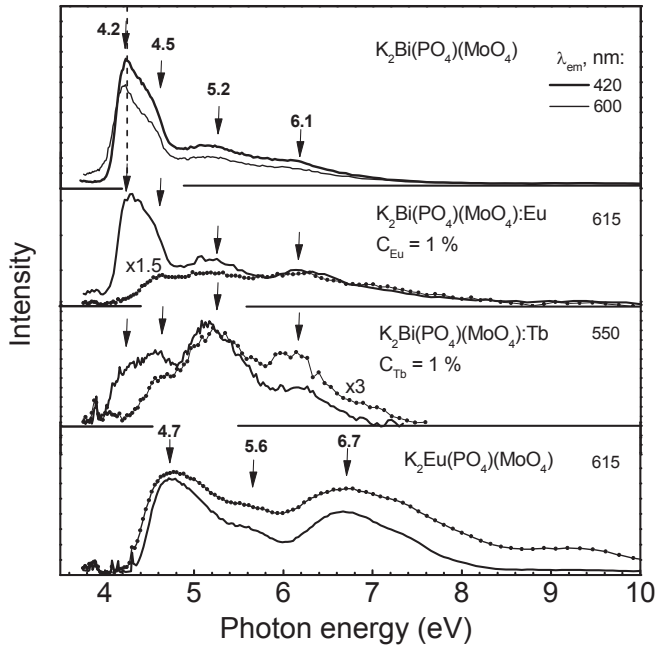

Fig. 2. The PL excitation spectra of undoped, Eu- and Tb-doped $K_2Bi(PO_4)(MoO_4)$ crystals. For undoped samples: T = 8 K; for Eu- and Tb-doped: T = 8 (lines) and 300 K (lines with circles), λ_{em} are indicated in the figure.