PROPERTIES AND NATURE OF SOME BI-CONTAINING PHOSPHATE/MOLYBDATE COMPOUNDS LUMINESCEENCE AND ITS POSSIBLE APPLICATIONS

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Abstract
Bismuth phosphates/molybdates and alkali metal both undoped and doped with luminescent ions have attracted much attention last decade due to their practical applications as effective components for white light emission diodes and laser materials [1, 2]. Due to close ionic radii, the Bi$^{3+}$ cations can be easily substituted by the RE$^{3+}$ dopants, so a lot of types of RE-doped compounds from the mentioned families were synthesized so far (particularly, in form of micro and nano-sized powders) and studied by spectroscopic methods. While the luminescence properties of the RE-doped Bi-containing oxide compounds were studied intensively, lesser attention was paid to study their electronic structure, origin of intrinsic luminescence and mechanisms of excitation energy transfer. However understanding of the luminescence mechanisms of undoped hosts is an indispensable condition for elaboration of effective luminophores on the base of the RE-doped crystals. In this work we used the luminescent and optical spectroscopy studies under various types of excitations together with electronic structures calculations for pure and RE-doped Bi-containing compounds in order to establish the origin of intrinsic emission centers in mentioned compounds. The polycrystalline samples of undoped and RE-doped BiPO$_4$, K$_3$Bi$_5$(PO$_4$)$_6$, K$_2$Bi(PO$_4$)(MoO$_4$), K$_2$Bi(PO$_4$)(WO$_4$) and K$_5$Bi(MoO$_4$)$_4$ (RE = Eu, Tb, Pr, Tm, Ce) crystals were synthesized by spontaneous crystallization method. The PL emission and excitation spectra were measured under excitation with synchrotron radiation (4 – 25 eV) at SUPERLUMI station at HASYLAB (DESY), Hamburg, Germany. Dependencies of luminescence intensities and decay times on temperature were obtained under N$_2$-laser excitation ($\lambda_{exc}$ =337.1nm) in 4.2 – 300 K temperature region. Diffuse reflectance spectra of fine-grained powdered samples were measured at 300 K using double-beam spectrophotometer. Absorbance spectra were calculated from the diffuse reflectance using the Kubelka-Munk relation. The electronic structures of the perfect crystals were calculated by the FLAPW method realized in Wien2k program package [3]. PL emission spectra of all undoped compounds obtained under synchrotron excitation are characterized by complex emission bands in 400-850 nm spectral region. The temperature quenching of emission intensity occurs well below 300 K for all these samples. Luminescence excitation spectra of all studied RE-doped samples registered in emission bands inherent to corresponding RE$^{3+}$ ion, reveal excitation bands clearly identified as the band-to-band excitations. Calculated partial densities of states indicate that the Bi cations, as well as MoO$_4$ groups in the molybdate hosts, play a dominant role of in the processes of luminescence excitation. Analysis of diffuse reflectance and luminescence excitation spectra allows estimation of the energy gap ($E_g$)
parameters of the studied compounds. Temperature dependencies of decay time constants and emission intensities show that “blue-violet” emission components have the Bi^{3+}-related origin whereas emission components of the molybdate crystals in the red spectral region are related to transitions in MoO$_4$ groups.

Obtained data were used to observe possibility to develop new tips for luminescent nano thermometers, especially concerning scanning nano resolution thermal imaging.