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Electron band structure calculations for $PbWO_4$ crystals

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Results of semiempirical calculation of partial densities of the electron states and the imaginary part of dielectric constant $\varepsilon_2(\omega)$ are presented for tetragonal and monoclinic modifications of lead tungstate $PbWO_4$ crystals. Calculated $\varepsilon_2(\omega)$ distributions are compared with experimental reflection data. The role of the regular constituents of crystal lattice — Pb^{2+} lead ions and WO_4^{2-} molecular anion complexes in the luminescence excitation process is examined.

Приведены результаты расчетов полуэмпирическим методом плотностей электронных состояний и мнимой части комплексной диэлектрической проницаемости $\varepsilon_2(\omega)$ для тетрагональной и моноклинной модификаций кристаллов вольфрамата свинца $PbWO_4$. Рассчитанные зависимости сопоставлены с экспериментальными данными по спектрам отражения. По результатам анализа распределений парциальных плотностей состояний оценена роль в процессах возбуждения люминесценции регулярных составных элементов кристаллической решетки вольфрамата свинца — ионов Pb^{2+} и анионных комплексов WO_4^{2-}.

Among other scintillators, the crystal of lead tungstate $PbWO_4$, is a probable working material for use in detectors of high-energy particles [1]. Therefore, when investigating its optical properties, a great attention is paid to luminescence in 350–550 nm region. The majority of both laboratory and industrial samples of $PbWO_4$ shows two luminescence bands in this spectral region. One of them, so called blue band, has a maximal value λ_m near 420 nm, while another one, denoted often as the green band, has λ_m about 500 nm. The intensity ratio of these bands depends on the excitation method, temperature, and the sample growth conditions [2, 3]. At room temperature (RT), the blue band is excited in 310–330 nm spectral range while the excitation maximum for green luminescence is about 330 nm [3].

Today, the main spectral and luminescence properties and their temperature dependence for "pure" and defect lead tungstate crystals have been studied more or less completely [3–6]. But the problem of the luminescence centers origin remained still unresolved. As for the blue band, there are two prevalent viewpoints. One of them associates the band with transitions in regular tungstate group WO_4^{2-} [7] while another ascribes this luminescence mainly to electronic states of lead ion Pb^{2+} [2]. According to the generally adopted concept, the green band has a defect nature, but the proposed models of its luminescence centers are different. The green luminescence is ascribed to transitions in a defect anion group WO_3 [8], or to inclusions of the monoclinic $PbWO_4$ crystal phase (raspite) in the bulk of the main tetragonal lead tungstate crystal type (sheelite) [9]. All artificially grown samples of lead tungstate are accounted to have the sheelite structure [10], but another structural modification of $PbWO_4$, raspite, also exists in nature [11]. In the present work, we intend to explore the role of the lead ion Pb^{2+} electron states and monoclinic phase inclusions in the $PbWO_4$