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Electronic structure and some optical properties of $PbWO_4$ crystals with defects: cluster approach

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Electronic structure of molecular clusters selected in perfect lead tungstate crystals $PbWO_4$ and in the crystals with molybdenum impurity defects and oxygen vacancies V_O has been *ab-initio* calculated. Densities of one-electron states, partial densities of states and joint density of states are analyzed for clusters corresponding to perfect and defect crystals. Lead ions Pb 6*p*-states have been found to dominate at the conductive band bottom in perfect lead tungstate crystal. Conclusions concerning change in charge localization under interband electron transitions with transition energies ranging from 4 to 6 eV have been drawn. The influence of defects on the electron structure and optical properties of crystals is investigated. Possible involvement of two closest to V_O tungstate groups — defective WO_3 and the perfect WO_4 in optical processes associated with interband electron transitions in the crystals with oxygen vacancies is revealed by calculations.

Рассчитана электронная структура молекулярных кластеров, выделенных в регулярных кристаллах вольфрамата свинца $PbWO_4$ и в кристаллах с дефектами примеси молибдена и вакансии кислорода V_O. Проанализированы плотности электронных состояний, парциальные плотности состояний и комбинированная межзонная плотность состояний кластеров, которые отвечают идеальному по структуре и дефектным кристаллам $PbWO_4$. В результате расчетов получено доминирование плотности 6*p*-состояний ионов Pb в области дна зоны проводимости кристалла с идеальной структурой. Сделаны выводы относительно изменения локализации электронного заряда при межзонных одноэлектронных переходах с энергией перехода 4–6 эВ. Исследовано влияние дефектов на электронную структуру и оптические свойства кристаллов. Обнаружена возможность участия двух ближайших к вакансии V_O вольфраматных групп — дефектной WO_3 и регулярной WO_4 в оптических процессах, которые связаны с межзонными переходами в кристаллах $PbWO_4$ с кислородными вакансиями.

Lead tungstate ($PbWO_4$) crystal is one of the most effective scintillation materials for calorimetric devices designed to detect the extremely high energy particles [1]. Thus, the interest to its scintillation properties has increased recently noticeably. Radio luminescence as well the other optical features of $PbWO_4$ crystals were studied rather intensively [1–5]. However, the obtained experimental results on $PbWO_4$ properties differ substantially from each other. Some luminescence and corresponding photo-excitation bands differ in relative intensity and position in the energy scale for crystals grown in different conditions. Such a discrepancy results in that up to now, there are no generally accepted explanations for the luminescence centers in lead tungstate. According to some presumptions (see, for example [3]), the most technologically important green emission band with $\lambda_{max} = 500$ nm is ascribed to transitions in defect tungstate groups WO_3 or, in other words, to the presence of oxygen va-