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Abstract

Influence of high pressure on luminescent properties of RAlO$_3$ and CsPbBr$_3$ perovskites

This study provides a comprehensive analysis of the luminescent properties of two different types of perovskites: rare-earth aluminum oxide perovskites (RAlO$_3$, where R represents Gd, Tb, Lu, Y, or a mixture) doped with Eu^{3+} and Ce^{3+} ions and cesium lead bromide (CsPbBr$_3$). Spectroscopic techniques were employed to investigate the luminescence centers and band gap properties of the materials, with a focus on high-pressure spectroscopic studies using a diamond anvil cell (DAC).

One part of the study focuses on the luminescent properties of Eu^{3+}-doped RAP (R = Gd, Tb, Y, Lu, or a mixture), which have applications in scintillation detectors. The K-value, which represents the ratio of the intensities of the $^5D_0$ -> $^7F_2$ and $^5D_0$ -> $^7F_1$ transitions of Eu^{3+}, is studied as a function of pressure. The results show that YAP exhibits an atypical shift towards higher energy for some lines with increasing pressure, and the K-value of YAP is smaller compared to the other studied samples. In LuAP, the K-value's behavior on pressure is affected by the interaction of Eu^{3+} centers with defects, which manifest in luminescence as broadband and are attributed to Pb^{2+} dimers. The study concludes that the K-value parameter depends on several factors, including the lattice parameters of the perovskites, the symmetry of the local structure, the concentration of defects, and the strength of the interaction between defects and Eu^{3+} centers.

Another part of the study investigates the luminescent properties of Ce^{3+}-doped LuAP and YAP. The direct bandgap values of YAP and LuAP are determined to be 7.63 eV and 7.86 eV, respectively, through absorption measurements in the near-UV region. The luminescence of both YAP:Ce and LuAP:Ce is studied as a function of temperature up to 873 K, enabling the estimation of the position of the lowest excited *5d* level of Ce^{3+} relative to the bottom of the conduction band. The position of the *4f* levels is found to be consistent with the predictions of Dorenbos theory and DFT calculations. However, the pressure downshift of the *5d* energy levels of Ce^{3+} relative to the free Ce^{3+} ion, as calculated according to the Dorenbos theory, does not agree with experimental data. This disagreement is resolved by calculating the downshift relative to the bandgap energy of YAP and LuAP, which also allows for the correlation of the observed changes in the *5d* state energies under pressure in LuAP with the pressure-induced changes in the average cation-anion distances. Additionally, alternative hypotheses are considered. The high-pressure Raman experiment identifies a soft mode with an energy of 455.4 cm^{-1} at ambient pressure, the energy of which decreases with increasing pressure.

The study also investigates the photoluminescence properties of CsPbBr$_3$, a promising material for use in photovoltaic devices. Low-temperature and high-pressure photoluminescence measurements are conducted, revealing a complex

luminescence spectrum with three main groups of lines: (i) direct (free) and indirect (Rashba) excitons and their phonon replicas, (ii) a broad defect band, and (iii) an unknown line at around 540 nm. The study shows that the sample's structure fluctuation affects its luminescent properties, with fluctuations responsible for the increase in Rashba splitting and the quenching of defect luminescence with the temperature increase from cryogenic to room temperature. For the first time, low-temperature high-pressure luminescence was measured, which allowed for the resolution of free and Rashba excitons under high pressure. The analysis of the results shows that the free and Rashba excitons are competing deexcitation paths. Additionally, the study revealed blue emission from the bulk $CsPbBr_3$ under high pressure, which was explained by the rapid expansion of the $CsPbBr_3$ band gap at high pressures.

The work comprises ten sections, including a Preface, Abstracts, List of publications, Acknowledgements, Introduction, Experimental techniques, Results and discussion, Conclusions, Appendixes, and References. Chapter V. Introduction provides a literature review, while chapter VI. Experimental techniques outlines the experimental techniques employed in the study. Chapter VII. Results and discussion presents and discusses the experimental results, and chapter VIII. Conclusions summarizes the findings and outlines future research directions.

Overall, this work contributes to our understanding of the luminescent properties of perovskite materials and may prove to be a valuable resource for researchers working in scintillation and photovoltaic research.

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