Excitation and emission bands of oxygen vacancies in rare earth bixbyite oxides: experiment and calculations

Andrii Shyichuk#, Joanna Trojan-Piegza, Eugeniusz Zych

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

Cubic oxides of Sc, Y and Lu share the same crystal structure of bixbyite. Y_2O_3 and Lu_2O_3 are well known matrices for lanthanide-based phosphors. Lu_2O_3 is also known for a series of thermoluminescence phosphors of different kinds [1]. Lu_2O_3 is prone to oxygen vacancy formation [2,3]. From both chemical and structural similarities, the other two oxides are also expected to form electron-trapping oxygen vacancies.

From computational standpoint, the three oxides indeed exhibit similar electronic properties. Using periodic density functional theory calculations (DFT) for ground state singlets and triplets, and using the respective optimized geometries in multiconfigurational post-Hartree-Fock calculations, it was possible to obtain configuration coordinate diagrams for the excited levels of trapped electron densities at oxygen vacancy sites, in silico and ab initio.

As a parallel experiment, the three oxides where prepared in a form of pressed ceramic pellets and calcined at high temperature in a reducing atmosphere. Such is the typical procedure for a thermoluminescence (energy storage) phosphors preparation [1], although no dopants were now added: the oxides were processed as purchased. Photoluminescence spectroscopy was then applied, with double-grating monochromators at both excitation and emission channels ensuring the lack of stray light artifacts. Albeit not intense, distinct broad excitation and emission bands where observed at energies very close to those obtained in calculations. Discussion of these data will be presented.

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corresponding author: andrii.shyichuk@uwr.edu.pl