Excitation and emission bands of oxygen vacancies in rare earth bixbyite oxides: technical details

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The computational model for an oxygen vacancy in a bixbyite oxide was developed as follows. The experimental crystal structure was used to prepare ab initio model potentials (AIMPs) for RE and O in a pure RE_2O_3 crystal (RE = Sc, Y, Lu), as described in [1]. These AIMPs represent the "non-chemical" part of the system and surround the embedded cluster. The cluster is constructed from the RE_4O17 moiety of the crystal, which includes the four Lu atoms surrounding an oxygen site and the oxygen atoms surrounding those four Lu atoms. The central oxygen atom is replaced by a ghost atom with a modified, more spatially extended basis set. The total charge of this cluster is 22, corresponding to two trapped electrons at the ghost atom (vacancy) site. The system is then subjected to multiconfigurational calculations for singlets using DFT, RASSCF, CASPT2, and RASSI-SO methods in a sequence.

To achieve the experimentally observed broad spectroscopic bands, a (pseudo)vibrational deformation must be applied to the cluster. In this study, it was assumed that the system "slowly" oscillates between two geometries corresponding to singlet and triplet states of the vacancy's two-electron density. These geometries were obtained using DFT PAW calculations on a single $RE_{32}O_{47}$ cell, with the cell size fixed to the experimental value while optimizing the atomic positions. Interpolating between the two cluster geometries resulted in a set of cluster geometries. The respective clusters were placed in the pristine-crystal embedding lattice, the calculations described above followed.

The calculations produced a set of energy levels that were interpolated to achieve smooth E(R) curves, where E represents energy and R represents the average bond length of the ghost atom. Using these interpolation curves, absorption and emission spectra were simulated. Notably, this methodology can also be applied in experimental spectra analysis: a novel band shape is proposed, allowing for the modeling of an arbitrary Gaussian-like asymmetric band with as few as four parameters plus temperature. This approach assumes that the initial and final level energies are described by E(R) parabolas and that the initial level populations follow a Boltzmann distribution.

[1] L. Seijo, Z. Barandiaran, J. Math. Chem. 10 (1992) 41–56. https://doi.org/10.1007/ BF01169170

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