Figure 1: Calculated (GGA+U) band structure of MA_2O_4:Eu^3+ (M: Ca, Sr, Ba).

Character: While the CB consists mostly of the 4P (3 5/2) and 4A (5/2, 11/2) bands, the VB is mainly of the 0 ZP emission bands at least at low (e.g., 1 meV) doping levels. The VB is more than 1 eV above the Fermi level, which may result in only one ZP conduction band at least at low (e.g., 1 meV) doping levels. The VB is more than 1 eV above the Fermi level. The band gap is increased by the introduction of more Eu-O distances. In addition, the difference in the Eu-O bonds decreases, as witnessed by the band gap increase.

Synchrotron radiation (SR) VUV-VIS spectroscopy

Synchrotron radiation provides information about the electronic structure of the compounds. The different energy schemes were compared with the experimental methods to study the Eu-doped samples. The results show that the Eu-doped samples exhibit similar electronic structures as the undoped samples. The conduction band (CB) composition of Eu^2+ and Eu^3+ ions was replaced with Eu^2+ and Eu^3+ ions. The distortions resulting from the charge size mismatch between the R^3+ and M^2+ ions. The defects distortions resulting from the change in size mismatch between the R^3+ and M^2+ ions. The defects in the alkali materials are more effective than the alkali elements. Persistent luminescence materials release stored energy at light frequencies at room temperature.

Keywords: DFT calculations, electronic structure, persistent luminescence, blue light.
Only fair agreement was found between the calculated (5.7) and experimental (6.5 eV) band gap energy. This may be due to the covalent character in BaAl₂O₄. The increasing lattice covalency in the MAI₂O₄ (Ca→Sr→Ba) series moves the Eu²⁺ 4f⁷ ground level towards VB (Figure 1). After the optimization of the crystal structure, the 4f⁵5d⁴→4f⁷ energy difference was 4.3 eV for both Ba sites. This suggests that the emission energy is the same irrespective of the Ba site occupied by Eu²⁺.

The experimental band gap energy decreased slightly (with 0.1 eV from 10 to 300 K) with increasing temperature. This is in agreement with the conventional behaviour found for the semiconducting materials [3]. The SR emission spectrum consists of two bands (2.4 and 2.8 eV) which may be due to the 4f⁵5d⁴→4f⁰ emission of Eu²⁺ in both Ba sites (Figure 2). However, this is not directly indicated by the electronic structure calculations (see above). The weak additional luminescence band may thus also originate from the possible creation of a new Ba²⁺ site due to the effect of water exposure on BaAl₂O₄:Eu²⁺ [4].

![Figure 2: The synchrotron radiation excited (λexc: 92 nm) emission spectra of BaAl₂O₄:Eu²⁺,Dy³⁺ at selected temperatures between 10 and 300 K (SUPERLUMI, HASYLAB).](image)

The DFT results show that the calculations are an excellent tool to probe the crystal and electronic structure of the Eu²⁺ doped persistent luminescence materials especially when difficult or impossible to study experimentally. Trap states induced by the isolated defects and defect aggregates present in the BaAl₂O₄:Eu²⁺,R³⁺ materials should still be studied in detail since they are expected to have a crucial effect on the persistent luminescence efficiency of these materials.

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