DFT and synchrotron radiation study of the Eu^{2+} doped $BaAl_2O_4$ O – 02

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Persistent luminescence materials release stored energy as light gradually at room temperature. The alkaline earth aluminates doped with Eu^{2+} and R^{3+} ($MAl_2O_4:Eu^{2+},R^{3+}$; M: Ca/Sr/Ba; R: *e.g.* Nd/Dy [1]) are among the most efficient ones. The development of even more efficient materials is hindered by the lack of knowledge on the effect of charge compensation defects and structural distortions resulting from the charge/size mismatch between the R^{3+} and M^{2+} ions. The defects may play either a desired or unwanted role as energy storage or luminescence quenching centers, respectively. Neither it is clear the exact electronic structure (band gap, valence (VB) and conduction band (CB) composition, Eu^{2+}/R^{3+} $4f^7$ and $4f^65d^1$ level positions) of $MAl_2O_4:Eu^{2+},R^{3+}$.

In this work, the *ab initio* density functional theory (DFT) calculations using the WIEN2k program package [2] were employed together with experimental methods to study the Eu^{2+} doped $BaAl_2O_4$. Every eighth of the host's Ba^{2+} ions was replaced with Eu^{2+} and the different energy schemes were calculated. Selected luminescence properties were studied experimentally by using the synchrotron radiation (SR) VUV-UV-vis spectroscopy.

The $BaAl_2O_4$ structure was found less distorted with Eu^{2+} substituting Ba1 than Ba2 as witnessed by the three-fold average decrease in the Eu-O distances for the latter. In addition, the difference (40 eV) in the total energies suggests that Eu^{2+} prefers the Ba1 site which may result in only one emission band, at least at low (*e.g.* 1 mole-%) doping levels. The VB is mainly of the O 2p character, whilst the CB consists mostly of the Ba (5.3 to 13 eV) and Al (13+ eV) levels.

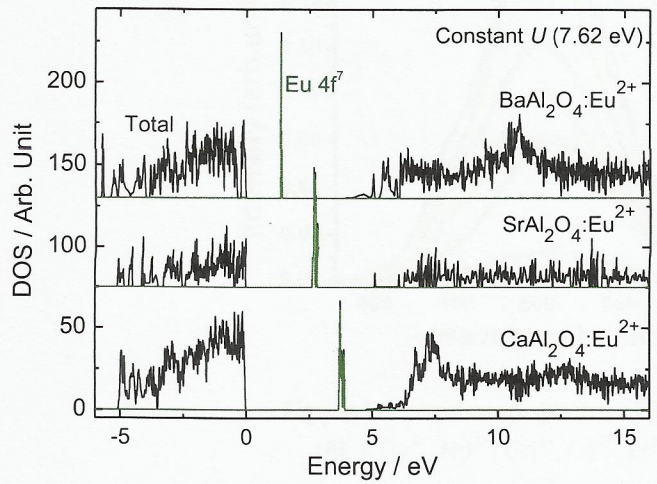

Figure 1: Calculated (GGA+U method) band structure of $MAl_2O_4:Eu^{2+}$ (M: Ca/Sr/Ba).

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 $BaAl_2O_4$. The increasing lattice covalency in the MAl_2O_4 (Ca→Sr→Ba) series moves the Eu^{2+} $4f^7$ ground level towards VB (Figure 1). After the optimization of the crystal structure, the $4f^65d^1$-$4f^7$ 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 Eu^{2+}.

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 $4f^65d^1 \rightarrow 4f^7$ emission of Eu^{2+} 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 Ba^{2+} site due to the effect of water exposure on $BaAl_2O_4:Eu^{2+}$ [4].

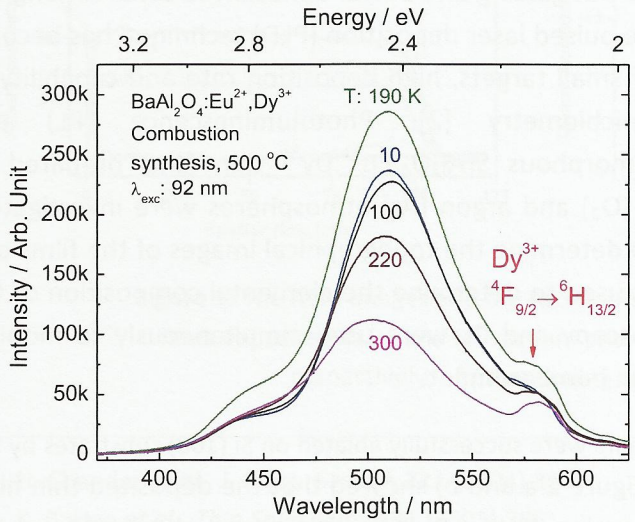

Figure 2: The synchrotron radiation excited (λ_{exc}: 92 nm) emission spectra of $BaAl_2O_4:Eu^{2+},Dy^{3+}$ at selected temperatures between 10 and 300 K (SUPERLUMI, HASYLAB).

The DFT results show that the calculations are an excellent tool to probe the crystal and electronic structure of the Eu^{2+} 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 $BaAl_2O_4:Eu^{2+},R^{3+}$ 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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