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A computational and spectroscopic study of Dy^{3+} doped $BaAl_2O_4$ phosphors

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ABSTRACT

Computational and experimental methods are employed to study the optical properties of Dy-doped $BaAl_2O_4$ matrix. Atomistic modelling is used to make predictions of Dy doping sites and charge compensation schemes. The symmetry predicts from atomistic modeling was used to calculate crystal field parameters and to obtain the energies of the electronic transitions of the Dy^{3+} ion. Dy-doped $BaAl_2O_4$ was prepared via a sol-gel proteic technique. The optical properties were studied using X-ray excited optical luminescence (XEOL) measurements. The X-ray absorption near-edge structure (XANES) at the Ba and Eu L_{III}-edges exhibits typical absorption spectra. The area under the XEOL spectra increases as the photon energy increases in the region around the Ba and Dy L_{III}-edges. The XEOL spectra showed typical Dy lines. Experimental and calculated values for the transition energies are compared. Computational and experimental methods are employed to study of Dy-doped $BaAl_2O_4$ matrix. Atomistic modelling is used to make predictions of Dy doping sites. The optical properties were studied using XEOL measurements.

1. Introduction

Dysprosium is a rare earth ion widely used as an activator dopant in many different materials. In general, the Dy^{3+} ions act as hole traps in the different aluminates [1] including $SrAl_2O_4$: Eu^{2+}, Dy^{3+} [2], $BaAl_2O_4$: Eu^{2+}, Dy^{3+} [3], $CaAl_2O_4$: Eu^{2+}, Dy^{3+} [4] and $Sr_4Al_{14}O_{25}$: Eu^{2+}, Dy^{3+} [5] and aluminosilicates including $Ca_2Al_2SiO_7$: Eu^{2+}, Dy^{3+}, $Sr_2Al_2SiO_7$: Eu^{2+}, Dy^{3+} [6], $CaAl_2Si_2O_8$: Eu^{2+}, Dy^{3+} [7] to increase the persistence of the luminescence. In other aluminates, and silicates including $CaAl_2O_4$: Dy^{3+} [8] and Gd_2SiO_5: Dy^{3+} [9], Dy^{3+} ions act as luminescence centres, important for solid-state laser applications.

$BaAl_2O_4$:Dy^{3+} [10] $BaAl_2O_4$: Eu^{2+}, Dy^{3+} [3] and $BaAl_2O_4$: Nd^{3+}, Dy^{3+} [11] phosphors show longer luminescence persistence as compared with sulphide phosphors [12]. These materials can be used in a wide range of applications, including luminous paints for highways, airports, buildings and ceramic products [1]. In addition, they can also be used in textiles, dial plates of luminous watches, warning signs, escape routes and other applications [13].

The duration of the persistent emission is increased by co-doping with Dy^{3+} ions. Many studies have been dedicated to understanding the relationship between Dy^{3+} ions and hole traps. However, this relationship is still not fully understood. Some studies proposed that the Dy^{3+} ion traps a hole, e.g. Ref. [14] while others proposed that the Dy^{3+} ions induce the formation of hole traps associated with a charge compensating defect, e.g. Ref. [15]. Knowing the position and the effect of a Dy^{3+} ion on the local structure of the $BaAl_2O_4$ matrix can help clarify the trapping mechanism of carriers in the luminescence process.

Therefore, in order to understand the defect properties generated by Dy^{3+} ions in the $BaAl_2O_4$ matrix, the present study employed atomistic simulation techniques and X-ray Excited Optical Luminescence (XEOL) technique spectroscopy. The minimized energy locations of the Dy dopant ion and its surrounding ions are used to obtain crystal field parameters, based on the simple overlap model (SOM), and the crystal field parameters are in turn used to calculate the energies of the electronic transitions of the Dy ion doped into the $BaAl_2O_4$ matrix. The X-ray Excited Optical Luminescence (XEOL) technique was employed to probe the luminescence properties of Dy^{3+}-doped $BaAl_2O_4$, and the predicted electronic transitions were compared to the XEOL spectrum.

2. Modelling and experimental procedure

2.1. Modelling

Atomistic modelling methods have been widely used in studies of doped materials [16–20]. In these methods, the interactions between

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ions in the solid are described through a set of interatomic potentials. The potential parameters for $BaAl_2O_4$ were obtained by empirical fitting, as described in a previous paper [21] using the GULP code [22]. The experimental and calculated lattice parameters show an agreement of 2% or better.

Defect properties were calculated using the Mott–Littleton [23] method in which a spherical region of lattice surrounding the defect (region I) is treated explicitly, with all interactions being considered, and more distant parts of the lattice (region II) are treated using a continuum approach. Having obtained the positions of the dopant ion, and the relaxed positions of the surrounding ions, these are input into a crystal field calculation based on the Simple Overlap model (SOM) [24]. The energies levels were calculated from the crystal field parameters obtained using relaxed positions of the dopant ions and the surrounding lattice ions are obtained from the atomistic calculations together with the free ion parameters obtained for the LaF_3 system [25] where the La^{3+} ion was substituted by each of the ions in the lanthanide series. The same procedure was used in a previous study of $Sr_3Al_2O_6:Eu^{3+}$ [17] and $BaAl_2O_4:Eu^{3+}$ phosphors [26].

2.2. Experimental procedure

$Ba_{0.97}Dy_{0.03}Al_2O_4$ samples were produced using a sol-gel proteic route [27]. In this route, the reagent was mixed with coconut water (*Cocos nucifera*) forming the starting gel and then dried at 100 °C for 24 h, forming a xerogel. In the next step the xerogel is calcined at 1100 °C for 2 h. More details of the procedure can be found in a previous reference [28]. The existence of a single crystalline phase was confirmed by X-ray diffraction measurements. The X-ray Absorption Spectroscopy (XAS) measurements were collected using the XAFS2 beamline at the LNLS (Brazilian Synchrotron Light Laboratory, Campinas, Brazil) around the Ba and Dy L_{III}-edge at room temperature in transmission mode. XEOL spectra were measured simultaneously with the XAS spectra using an Ocean Optics HR2000 spectrometer and an optical fibre.

3. Discussion

$BaAl_2O_4$ has a hexagonal structure with a ferroelectric phase transition at T = 396 K [29]. It belongs to the family of stuffed tridymites which are derived from the structure of SiO_2 β-tridymite. The structure has a three-dimensional network of corner-sharing AlO_4 tetrahedra, with hexagonal channels occupied by Ba^{2+} ions. There are two non-equivalent Ba^{2+} sites having different coordination numbers (8 and 9) and similar average Ba-O distances (2.85 Å and 2.87 Å). There are four non-equivalent Al^{3+} sites which have similar average Al-O distances (1.73, 1.75, 1.77 and 1.81 Å).

In principle, a Dy^{3+} ion can substitute at either an Al^{3+} or a Ba^{2+} site. The ionic radius and oxidation numbers are the two parameters which determine the localisation of the Dy^{3+} ion. The capability of $BaAl_2O_4$ to accommodate a Dy^{3+} ion is of fundamental importance for its optical properties. The influence of the Dy^{3+} ion depends on the substitution site (Al^{3+} or Ba^{2+}) as well as the defects required for charge compensation. When the Dy^{3+} ion is substituted at the Al^{3+} site, no charge compensation is needed. On the other hand, charge compensation is required when the Ba^{2+} ion is the host site. Charge compensation can occur by Ba^{2+} vacancies, anti-site defects, interstitial O^{2-} ions or Al^{3+} vacancies. In order to model the different charge compensation mechanisms, a range of reactions schemes have been developed, as shown in Table 1. Scheme (i) represents substitution at the Al^{3+} site, while schemes (ii) to (v) are for reactions involving substitution at the Ba^{2+} site with a range of charge compensation mechanisms.

Table 1
Reaction schemes for solution of rare-earth dopants.

Reactions schemes
$(i)0.5Dy_2O_3 + Al_{Al} \rightarrow Dy_{Al} + 0.5Al_2O_3$
$(ii)Dy_2O_3 + 3Ba_{Ba} \rightarrow (2Dy^{\bullet}_{Ba} + V''_{Ba}) + 3BaO$
$(iii)0.5Dy_2O_3 + Ba_{Ba} + Al_{Al} \rightarrow (Dy^{\bullet}_{Ba} + Ba'_{Al}) + 0.5Al_2O_3$
$(iv)Dy_2O_3 + 2Ba_{Ba} \rightarrow (2Dy^{\bullet}_{Ba} + O''_i) + 2BaO$
$(v)0.5Dy_2O_3 + 3Ba_{Ba} + Al_{Al} \rightarrow (3Dy^{\bullet}_{Ba} + V'''_{Al}) + 3BaO + 0.5Al_2O_3$

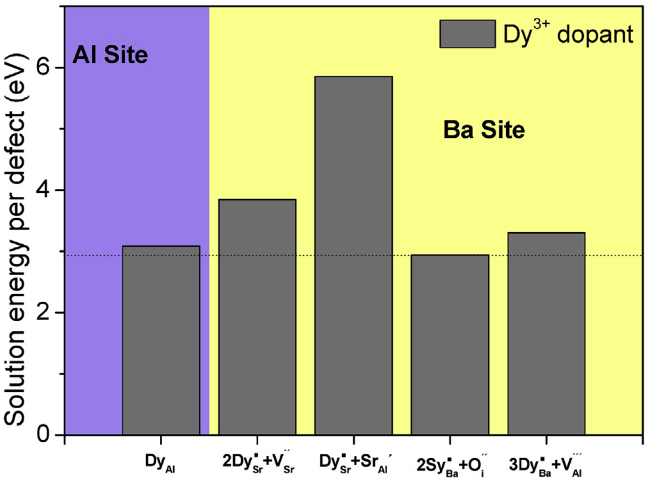

Fig. 1. Solution energy for europium ion in the $BaAl_2O_4$ structure.

The solution energies were calculated by combining the incorporation of Dy dopant in the host site with the appropriate defect and lattice energy terms for each reaction scheme showed in Table 1. These are defined as the total energy involved in the doping process, including charge compensation if needed. Since there is more than one non-equivalent Al^{3+} or Ba^{2+} site, all the defects have more than one possible symmetry configuration and the more provable was showed in Fig. 1.

The results show that the reaction scheme (iv), involving the substitution of Dy^{3+} at the Ba^{2+} site with the oxygen interstitial compensation is more energetically favourable, with a solution energy of 2.94 eV. The second most favourable defect involves the substitution of a Dy^{3+} ion at the Al^{3+} site, with solution energy of 3.08 eV. The relatively small solution energies difference between schemes (i) and (iv), 0.14 eV, indicates a possibility of a Dy^{3+} ion substituting at both cationic host sites. This can be explained in terms of the size difference between the Dy^{3+} ion and the host sites. The ionic radius of Dy^{3+} (0.912 Å) is greater than the radius of Al^{3+} (0.39 Å), and is smaller than the radius of Ba^{2+} (1.47 Å) [30]. When Dy^{3+} ions substitute at the Al^{3+} site, the relative ionic radius difference (0.522 Å) is very similar to when Dy^{3+} ions substitute at the Ba^{2+} site (0.558 Å). In both cases it is possible that large distortions are caused by the expansion or contraction of the first nearest neighbours. Schemes (ii) and (v), which involve charge compensation by a Ba^{2+} or Al^{3+} vacancies respectively, have large solution energies due to the large deformation caused by the creation of a cationic vacancy. For scheme (iii), the large solution energy can be explained by the size difference of the Ba^{2+} and Al^{3+} ions, which causes a distortion of the oxygen tetrahedron.

The persistent luminescence mechanism of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} proposed by Clabau et al. [1] can also be applied to $BaAl_2O_4:Eu^{2+}$, Dy^{3+} and it suggests that Ba^{2+} and O^{2-} vacancies act as electron traps. TL (thermoluminescence) experimental results from Beauger [31] showed that the Dy^{3+} ion increases the number and the depth of the electron traps, but from atomistic simulations it can be seen that Dy^{3+} substitution in the host site (Al^{3+} or Ba^{2+}) does not contribute to the increase in the number of Ba^{2+} or O^{2-} vacancies. The solution energies clearly show that the most stable defects are those that do not involve vacancy formation as charge compensating defects.