



The optical properties of Eu³⁺ doped BaAl₂O₄: A computational and spectroscopic study

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ABSTRACT

The optical properties of Eu³⁺ doped BaAl₂O₄ are studied by computational and experimental methods. Atomistic modelling is used to make predictions of doping sites and charge compensation schemes. Crystal field parameters are then calculated and used to obtain the energies of the electronic transitions of the Eu³⁺ ion. The experimental emission spectrum was obtained for BaAl₂O₄:Eu³⁺ prepared via a sol–gel proteic method. Experimental and calculated values for the transition energies are compared.

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1. Introduction

Europium ions exhibit luminescence, emitting radiation from an excited electronic state, the emitted light having sharp lines characteristic of f–f transitions. Such luminescence has been observed when the ions are doped into a wide range of materials, including aluminates and aluminosilicates.

Barium aluminates are an important class of materials that have been investigated recently for long afterglow applications. In general terms, these properties are observed when the materials are doped with europium and other rare earth ions. Katsumata et al. [1] reported this property in single crystals of BaAl₂O₄:Eu²⁺, Dy³⁺ and Qiu et al. [2] observed it in nanoparticles of BaAl₂O₄:Eu²⁺, Nd³⁺. The emission band due to Eu²⁺ doped in BaAl₂O₄ was reported by Blasse et al. [3], Palilla et al. [4] and Poort et al. [5]. BaAl₂O₄ also shows long afterglow when doped with other rare earth ions. Jia et al. [6] observed these properties by eye in darkness for as long as 10 h with BaAl₂O₄:Ce³⁺ and BaAl₂O₄:Ce³⁺, Dy³⁺. Ca₂Al₂SiO₇:Eu²⁺, Dy³⁺ and Sr₂Al₂SiO₇:Eu²⁺, Dy³⁺ [7] are examples of aluminosilicates that show luminescence properties when doped with Eu ions. Other aluminates have applications in optical devices, including the strontium aluminates (SrAl₂O₄:Eu²⁺, Dy³⁺, B³⁺ [8], Sr₄Al₁₄O₂₅:Eu²⁺, Dy³⁺, B³⁺ [9], SrAl₄O₇:Eu²⁺, Dy³⁺ [10], SrAl₁₂O₁₉:Eu²⁺, Sr₂Al₆O₁₁:Eu²⁺ [11]) and calcium aluminates (CaAl₂O₄:Eu²⁺, Nd³⁺, B³⁺ [12] and Ca₁₂Al₁₄O₃₃:Eu²⁺, Nd³⁺ [13]).

This paper makes use of computer modelling methods, using a combination of lattice energy minimisation and crystal field calculations. The minimised energy locations of the dopant ion and its surrounding ions are used to obtain crystal field parameters, and the crystal field parameters are in turn used to calculate the energies of the electronic transitions of the europium ion doped into the BaAl₂O₄ matrix. These are then compared with measurements on Eu³⁺ doped BaAl₂O₄ nanopowders prepared via sol–gel proteic methods.

2. Methodology

In this work, computer modelling and experimental analysis were used to study the transition energies resulting from Eu³⁺ doping in BaAl₂O₄. It is noted that BaAl₂O₄ exists in two phases, with space groups P6₃ and P6₃22 respectively [14], and that the calculations presented here have been carried out for the P6₃ (ferroelectric) phase.

Computer modelling was employed in two stages. The first stage involved atomistic modelling based on energy minimisation, with interactions represented by interatomic potentials. Buckingham potentials were used to describe the interactions between ions, and the potential parameters (see Table 1) were obtained as described in a previous paper [14] by empirical fitting to the structure of all known barium aluminate crystalline phases, using the GULP code [15]. The predicted lattice parameters, $a = b$, 10.4490 Å, and c , 8.7930 Å, for BaAl₂O₄ (P6₃ phase) compare well with the experimental values of 10.5831 Å and 8.7594 Å [16], respectively. Overall, it can be concluded that the derived interatomic potentials

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Table 1
Potential parameters obtained by empirical fitting.

Short-range interactions	A (eV)	ρ (Å)	C (eV Å ⁶)	Cutoff (Å)
Ba _{Core} –O _{Shell}	1316.70	0.3658	0.00	10.0
Al _{Core} –O _{Shell}	1398.40	0.3006	0.00	10.0
O _{Shell} –O _{Shell}	22764.0	0.1490	27.88	10.0
Spring O _{Core} –O _{Shell}	70.0	–	–	–
Charge (e)	Z _{Ba}	Z _{Al}	Z _{O_{core}}	Z _{O_{shell}}
	2.00	3.00	0.900	–2.900

reproduce the structure of the barium aluminate compounds studied reasonably well. Defects are modelled using the Mott–Littleton approximation [17] in which a spherical region of lattice surrounding the defect is treated explicitly, with all interactions being considered, and more distant parts of the lattice are treated using a continuum approach.

In the second stage of the modelling, the new set of coordinates of the first neighbour ligand ions, obtained after relaxation of the dopant in the matrix using the atomistic simulation technique described above, are used to calculate the B_q^k parameters using the simple overlap model (SOM) [18]. The B_q^k components provide an unambiguous indication of the local symmetry of the central optically active ion. This means that the crystal field calculations can give crucial information on the optical behaviour of a particular host-dopant system. Then the crystal field theory developed by Judd [19] and Ofelt [20] is used to calculate the Hamiltonian for the crystal field interaction:

$$H_{CF} = \sum_{k,q} B_q^k C_q^k \quad (1)$$

The C_q^k are the Racah spherical tensors, which account for the angular part of the interaction related to the dopant ion. The B_q^k are the crystal field parameters obtained in the second step. The Hamiltonian is then used to calculate the energy transitions of the dopant ion. This methodology has been employed successfully in previous papers [21,22].

In the experimental study, BaAl₂O₄ and Ba_{0.97}Al₂O₄:Eu_{0.03} nanometre phosphors were prepared by a sol–gel proteic method [23]. In a round-bottomed flask, aluminium nitrate Al(NO₃)₃·9H₂O, barium nitrate Ba(NO₃)₂, and europium nitrate EuCl₃·6H₂O were dissolved in coconut water (*Cocos nucifera*). The resultant gel was dried at 100 °C for 24 h (the dried gel, named xerogel). The resultant precursor xerogel powder was heated for 2 h at 1100 °C in air. Crystal structures of samples were checked using a Rigaku RINT 2000/PC diffractometer with Cu K α radiation. The luminescent properties of the samples were measured at room temperature using an ISS PC1 spectrofluorimeter. The excitation (λ_{exc} = 245 nm) source was a xenon lamp.

3. Results

Eu³⁺ dopant ions can, in principle, be incorporated into the lattice at either Ba²⁺ or Al³⁺ sites, and there is more than one possible mode of charge compensation in the case of Ba²⁺ site substitution. In the crystal structure of BaAl₂O₄ [16], there are two types of Ba²⁺ coordinated to nine oxygen atoms, and there are four types of Al³⁺ in [AlO₄] tetrahedra. Five reaction schemes have been considered for the incorporation of the trivalent rare earth ions into the BaAl₂O₄ matrix, as described in Table 2.

In scheme (i) the rare earth ion is considered to substitute at the Al³⁺ site. In schemes (ii), (iii), (iv) and (v), the rare earth ion is considered to substitute at the Ba²⁺ site. For scheme (i), no charge compensation is needed and the main difference between all the other mechanisms is the type of charge compensating defect

involved. Scheme (ii) involves compensation by a Ba vacancy, scheme (iii) considers the possibility of a Ba ion displaced to an Al site, scheme (iv) involves compensation by oxygen interstitials (one interstitial compensating 2 dopants) and in scheme (v) one Al vacancy compensates three trivalent dopants substituting at the Ba site. In addition, each charge-compensation mechanism may have more than one possible configuration symmetry, depending on the way the dopant and the charge compensating defects are arranged in the crystalline matrix. The modes of substitution that are considered for europium ions are shown in Table 2.

In the first stage of the computer simulation calculation, the formation energy for Eu³⁺ doped into the BaAl₂O₄ matrix is calculated, using the lattice energies in Table 3; the energies are summarised in Table 4. The notation used in Table 4 for the different symmetries is explained in the appendix (Table A.1). Kroger–Vink notation [24] is employed to identify the defects. The effect of temperature was included in the modelling using the harmonic approximation, and two temperatures (0 and 293 K) were considered.

Using the formation energy of each configuration, the solution energy for the substitution of Eu³⁺ in BaAl₂O₄ has been calculated. This is defined as the total energy involved in the doping process, including charge compensation mechanisms if needed. The reaction schemes considered are given in Table 2. For reaction (i), for example, the solution energy (E_{sol}) is calculated as follows:

$$E_{sol} = E[Eu_{Al}] + \frac{1}{2}E_{latt}[Al_2O_3] - \frac{1}{2}E_{latt}[Eu_2O_3] \quad (2)$$

In Eq. (2), $E_{latt}[Al_2O_3]$ and $E_{latt}[Eu_2O_3]$ terms are lattice energies, and $E[Eu_{Al}]$ is the defect formation energy for a Eu ion substituting at an Al site. Each one of the terms in the equation, and in the other similar equations for all five mechanisms, is calculated separately. For reaction (iv) in Table 2, the oxygen interstitial site used was (2/3, 1/3, 0.7594).

At 0 K (see Table 4), it can be seen that scheme (iv), involving the substitution of a Eu ion at the Ba site with interstitial oxygen compensation (D2), has the lowest solution energy (3.01 eV). The D2 configurations involve two Eu ions entering at the Ba2 sites with oxygen interstitial compensation (2M_{Ba2}–O_i). The second lowest energy configuration (E14), with solution energy of 3.03 eV, involves the substitution of three Eu ions at Ba2 sites with Al2 vacancy compensation (3M_{Ba2}–V_{Al2}). Also at 0 K, the solution energy for substitution of Eu at the Al site is higher in comparison with substitution at the Ba site. Despite the host ions and Al site having the same oxidation number, the distortion caused by the large difference between the ionic radii of the host ion and the aluminium site, 0.947 Å and 0.39 Å, respectively, is large. Thus it is less likely that Eu will substitute at the Al site at this temperature.

At 293 K (see Table 4), Eu³⁺ ions are more likely to substitute at the aluminium site. Despite the smaller ionic radius of the aluminium ion compared with the europium ion, the increase in temperature leads to an increase in the Al–O distance, thus increasing the available space at the aluminium site, facilitating the incorporation of europium. However, the most energetically feasible configurations involve the substitution of europium at the barium site with charge compensation by interstitial oxygen (D1 and D2). In D1 (2M_{Ba1}–O_i), two dopant ions substitute at Ba1 sites and, in D2 (2M_{Ba2}–O_i), the two substitutions occur at the Ba2 site. This means that the europium dopant can be found at both barium sites in the BaAl₂O₄ matrix.

Possible explanations for the preference for scheme (iv) are as follows: (i) similar ionic radii of the europium ion and the barium site (0.947 Å and 1.47 Å, respectively); (ii) the second most energetically favourable intrinsic defect in the BaAl₂O₄ lattice, see [14], is an oxygen Frenkel defect, indicating that the occurrence of oxygen interstitials in the lattice is favoured; and (iii) the structure of

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