**Article Title**

**Optical spectroscopy study of Eu-doped ions in BaAl2O4 phosphors**

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**Abstract**

Computational and experimental methodology is employed to study optical properties in Eu-doped BaAl2O4 phosphors. The symmetry and detailed geometry of the Eu-dopant site, predicted by atomistic simulation, are used to calculate the crystal field parameters and the intensity parameters (Ω2 and Ω4) based on a Judd-Ofelt approach to the Eu3+ ion. The phenomenological intensity parameters are obtained from the emission spectra of the Eu-doped BaAl2O4 and compared to the theoretical results. Experimental and calculated values for the 7F1 energy sub-levels of the Eu3+ and maximum Stark splittings (ΔEmax) are also obtained.

**Keywords**

Intensity parameters, Simple overlap model, optical properties

**Specifications Table**

|  |  |
| --- | --- |
| **Subject** | Condensed Matter Physics |
| **Specific subject area** | The most specific area is spectrocopy, as we are studying the relationship between spectrocopic properties and crystallite sizes of barium aluminate |
| **Type of data** | Table - Ligand coordinates for site one (R in units of 10-8 cm and angles of π/180), the polarisability (α in units of 10-24 cm3) and their charge factor; Ligand coordinates for site one (R in units of 10-8 cm and angles of π/180), the polarisability (α in units of 10-24 cm3) and their charge factor; Experimental and theoretical values of Ω2 and Ω4 (1020 cm2)  Figure - The result of refinement of BaAl2O4:Eu3+ via Powdercell program; The Williamson-Hall plot of BaAl2O4:Eu3+; Emission spectrum of BaAl2O4:Eu3+ at room temperature; Bar chart of experimental and theoretical values of ΔE0-1(cm-1), Ω2 and Ω4 (1020 cm2); Calculation of area to transition 5D0-7F4. |
| **How data were acquired** | Instruments: GULP, Powdercell, Microcal ORIGIN, MATHCAD programs |
| **Data format** | Raw - spectrum of the Eu3+ doped sample and 2Theta obtained of DRX  Analyzed - intensity parameters and crystallite sizes |
| **Parameters for data collection** | data collection was carried out under ambient conditions and simulations also record such situations. |
| **Description of data collection** | XRD data were collected using the intensity graph (a. u.) as a function of 2 theta. However, spectroscopic data were obtained through the spectrum of the europium doped sample. |
| **Data source location** | Institution: Federal University of Sergipe  City/Town/Region: Aracaju/Sergipe  Country: Brazil |
| **Data accessibility** | With the article  Repository name: Mendeley Data  Data identification number: 10.17632/w77bjtr92t.2  Direct URL to data: <https://data.mendeley.com/drafts/w77bjtr92t> |
| **Related research article** | Authors’ names Romel M. Araujo,, Emanuel Felipe dos Santos Mattos, Bento Francisco dos Santos Júnior, Marcos V. dos S. Rezende,Mário E.G. Valerioand Robert A. Jackson  Title **Optical spectroscopy study of Eu-doped ions in BaAl2O4 phosphors** |

**Value of the Data**

The data obtained are important for the technology industry, as the sample we analyzed is widely used in electronic devices. With this, in the future, society will be able to benefit from this information, as it will have more efficient electronic devices. In addition, the information in this article can be used for the development of new research in spectroscopy.

**Data Description**

**1-INTRODUCTION**

The crystalline barium aluminates have attracted intense research, since they have interesting optical properties. For example, when doped with europium they show luminescence, emitting radiation in 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.

This luminescence was observed by Katsumata et al. [1] and Qiu et al.[2]. The emission band due to Eu2+ doped in BaAl2O4 was reported by Blasse et al. [3], Pallila 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 hours for 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]).

The objective of the present paper is to report the results of experimental and theoretical studies of optical properties of Eu-doped doping in BaAl2O4 phosphors. Therefore, the study is divided in two parts. In the first part, the phenomenological intensity parameters and  were obtained from photoluminescence (PL) spectra of Eu3+ of BaAl2O4 phosphors prepared using a sol-gel proteic method. In the second part, the symmetry and the detailed geometry of the Eu3+ site obtained from simulation was then used to predict the 5D0-7F1 transition splitting (ΔE0-1) and intensity parameters of Eu3+ ions. The combination of experimental and modelling techniques was helpful in revealing some of the important features that contribute to the understanding of specific mechanisms relevant to their application in the light-emission processes in this material.

**2 – METHODOLOGY**

**2.1 Experimental part**

Eu-doped BaAl2O4 nanopowders were produced via a new sol–gel route described in Ref.[14] and the photoluminescence (PL) spectroscopy were recorded using an ISS PC1 spectrofluorimeter at room temperature. Concentration of incorporated Eu3+ species in BaAl2O4 hosts is 3 at%. From emission spectra, the phenomenological intensity parameters were obtained. The emission intensity, *I*, of a given transition is proportional to the area, S, under the emission curve is:

 (1)

where  is the transition energy, N is the population of the emission level (5D0) and  is spontaneous emission coefficient that can to be calculated using the  transition as a reference. Thus  values can be evaluated using the expression:

 (2)

where is the area under of the emission and is the transition barycenter.

The transition is used as reference, because it is an allowed transition via a magnetic dipole mechanism, thus making  quite independent on the crystal field.  can be related to the transition barycenter and the refraction index *n* via:

 (3)

The phenomenological maximum Stark splitting, ΔE is obtained from emission spectra of Eu3+ using the following expression:

 (4)

where α is an expansion factor and Nv is the ligand field strength parameter, defined by

 (5)

The phenomenological intensity parameters and  are obtained from emission spectra of Eu3+ using the following expressions:

 (6)

and

 (7)

where  is the Lorentz factor.

1. **Theoretical part**

The computer modeling techniques used is based on the Born model of solids where the interactions between the ions present in the BaAl2O4 structure are parameterised via long-ranged Coulombic interactions and short range terms described by the Buckingham potential, and the electronic polarizability of the oxygen is included via the shell model of Dick and Overhauser [15]. Defect energies and final relaxed configuration were performed using the Mott-Littleton method [16]. The coordinates of the dopant and the surrounding ions, obtained after relaxation of the dopant in the matrix using the atomistic simulation technique described in detail elsewhere [14], are used to calculate the Bkq parameters using the simple overlap model (SOM) [17]. The intensity parameters and  was calculated using the Bkq parameters using the equation:

 (8)

with

 (9)

where = 2, 4 and t=1, 3, 5, 7 and p= 0,4 (the allowed values of p depend on the symmetry around the rare earth ion) are the intensity parameters coefficient, and  are the contributions of the forced electric dipole mechanism  of the dynamic accompanying mechanism .

The F1 energy sublevels of Eu3+ can be obtained through diagonalisation of the crystal field matrix within the 7F1 manifold. Thus,

 (10)

 (11)

 (12)

where 𝐸0, 𝐸 ― , and 𝐸 + are energy sublevels for J=1, measured in relation to the barycentre. 𝑈2 is the reduced matrix element.

1. **Results and discussion**

Previous calculations of Eu3+ doping in BaAl2O4 have reported the information about the Eu3+ ions localization [14]. These results suggest that the Eu3+ ions prefer to be substituted at the two nonequivalent Ba2+ sites, compensated by interstitial oxygen formation. In this case, the charge compensation needed to neutralise the charge contributes to lattice distortion close to the Eu ions. The relaxed positions of the Eu3+ ions (Eu1 and Eu2) and the surrounding lattice ions were obtained from previous work [14] and used to calculate the crystal field parameters, *Bkq*, which are given in Table 1 and 2, respectively. The results reveal that all *Bkq* parameters are zero, indicating that a site symmetry involving a C1 element is the most probable one. This means that the deformation caused for Eu incorporation in the Ba site is large. From Figure 1(a) and 1(b), the nearest neighbour interaction of the two Eu site ions can be seen.

According to SOM [17], the load factor g must be equal or less than 3, which is the rare earth ion charge. The problem is having to take into consideration that the rare earth ion is immersed in a chemical environment where the charge is neutral (zero), which has not been taken in the (SOM) [17] and in the theory of electrostatic equilibrium [18]. Also using electrostatic arguments and ab initio calculations, Batista and Longo [19] have proposed an improved model that describes the ion as an effective charge *q*(*r*), whose value has the following radial dependence and this equation has then been used to adjust a one parameter Gaussian-type function:

 (13)

As discussed earlier this is true for the free ion. We made an adjustment in the equation considering that the charge is zero for the ion immersed in a chemical environment so that the equation can be written as:

 (14)

This function was not used an effective charge density model, but an effective point charge model in a BaAl2O4 matrix in relation to the positions of the atoms in the ligands.

**Table 1 –** Ligand coordinates for site one (R in units of 10-8 cm and angles of π/180), the polarisability (α in units of 10-24 cm3) and their charge factor.

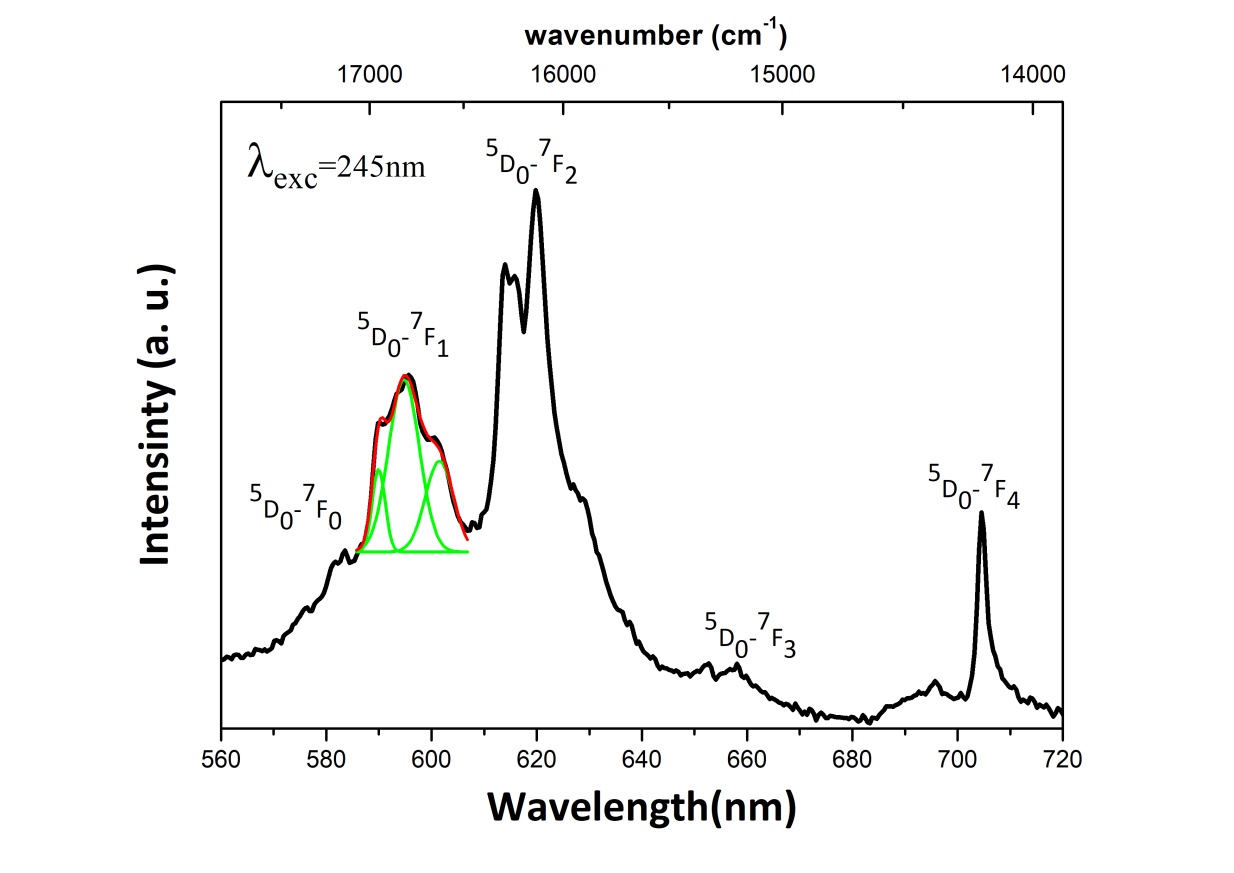
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R | θ | φ | α | g |
| 2.1862 | 50.8142 | 53.4527 | 2.95 | 0.44 |
| 2.4844 | 135.2093 | -0.6044 | 3.97 | 0.42 |
| 2.5740 | 46.4994 | -64.138 | 4.34 | 0.41 |
| 2.3899 | 86.4589 | 23.981+180 | 3.19 | 0.43 |
| 2.7136 | 137.0984 | 59.6874+180 | 4.68 | 0.73 |
| 2.7796 | 88.3351 | -76.2933+180 | 3.11 | 0.57 |

**Table 2 –** Ligand coordinates for site one (R in units of 10-8 cm and angles of π/180), the polarisability (α in units of 10-24 cm3) and their charge factor.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R | θ | φ | α | g |
| 2.3080 | 70.6642 | -6.8653 | 2.86 | 0.72 |
| 2.4349 | 156.0441 | 7.6744 | 2.47 | 0.49 |
| 2.7742 | 48.4661 | 44.161 | 2.44 | 0.31 |
| 2.3488 | 115.1548 | 78.5199+180 | 2.21 | 0.73 |
| 2.5178 | 48.4661 | -65.0518+180 | 3.38 | 0.43 |
| 2.3488 | 113.5996 | -98.5199+180 | 2.99 | 0.32 |

|  |  |
| --- | --- |
|  |  |
|  |  |
| **Figure 1(a) –** Eu1 ions and the surrounding lattice ions. | **Figure 1(b) –** Eu2 ions and the surrounding lattice ions. |

The integrated areas of the emission spectrum showed in Fig. 2 have been used to calculate the intensity parameters, which allow a prediction of the emission characteristics of the RE3+ ion in a particular host [20]. Using equations (1)-(7), the experimental or phenomenological 5D0-7F1 transition splitting (ΔE0-1) and the intensity parameters  and  could be evaluated. The areas used in equations 2 and 3 were calculated by convolving the peaks corresponding to the transitions by integrating the Eu transition. The absolute values of the Ω2 and Ω4 intensity parameters and other values for the other oxides are showed in Table 3. The intensity parameter  was not included in this study since the 5D0-7F6 transition could not be observed and this transition presents, in general, an extremely low intensity [27]. In addition,  and  were also calculated using the modelling approach described via equation (1) and the crystal field parameters obtained for each one of the Eu3+ sites in the matrix. This is the second time that the absolute values of the intensity parameters (,) are reported for aluminate and vanadium crystals. The  intensity parameters reflect covalence between Eu ions and the surrounding oxygen and provide information about the asymmetry of the local environment of the Eu3+ site [41]. The experimental values, obtained from the PL spectrum, and the theoretical intensity parameters obtained by SOM [26,27] and electrostatic equilibrium theory [31] shows high values of the  intensity parameters, reflecting the hypersensitive behaviour of the 5D0-7F2 transition and indicating that the rare earth ion is in a highly polarised chemical environment. This result suggests that the short distance effects are dominant. The  in SrAl2O4 and YVO4 is larger than those of other materials quoted in Table 3 and for BaAl2O4 calculated in the present work. The  values for the BaAl2O4:Eu system, on the other hand, have roughly the same values as the other materials, except for the LaF3 matrix and the Sr(PO3)2 glass. An interesting result is that the experimental intensity parameters obtained from the emission spectra agreed quite well with the values obtained in the modelling part, with a difference around 0.3% and 0.5% for and , respectively. For 5D0-7F1 transition splitting (ΔE0-1) in BaAl2O4 there is a difference of around 0.3%. Table 4 shows predicted 7F1 state energy sublevels and splittings compared with experimental results. The energy sublevels are measured with respect to the barycentre of the 7F1 level and carried for comparison.



**Figure 2 –** Spectrum of the emission of BaAl2O4:Eu (excited at 266 nm).

**Table 3 –** Experimental and theoretical values of Ω2 and Ω4 (1020 cm2).

|  |  |  |  |
| --- | --- | --- | --- |
| Parameters | Ω2(10-20cm2) | Ω4(10-20cm2) | Refs. |
| Fluorite glasses | 0.51 | 4.19 | [20] |
| LaF3:Eu3+ crystal | 1.19 | 1.16 | [21] |
| Sr(PO3)2glasses | 5.90 | 1.40 | [22] |
| Phosphate glasses | 6.91 | 5.01 | [23] |
| Silicate glasses | 9.65 | 6.58 | [24] |
| Y2O3:Eu3+ | 9.90 | 3.60 | [25] |
| Y2O3:Eu3+ | 6.31 |  | [26] |
| Ba5Gd8Zn4O21 | 12.7 | 4.5 | [27] |
| Ca8ZnLa0.5Eu0.5(PO4)7 | 6.93 | 0.22 | [28] |
| SrAl2O4:Eu3+(Exp.) | 26.592 | 5.7548 | [29] |
| SrAl2O4:Eu3+(SOM) site 1 | 26.400 | 5.7411 | [29] |
| SrAl2O4:Eu3+(SOM) site 2 | 29.204 | 5.7735 | [29] |
| YVO4: Eu3+ (Exp)(PL) | 26.177 | 8.8901 | [30] |
| YVO4: Eu3+ (Exp)(RL) | 26.651 | 8.6172 | [30] |
| YVO4:Eu3+(SOM) | 26.129 | 8.8256 | [30] |
| BaAl2O4:Eu3+(Exp)(PL) | 23.865 | 3.342 | present work |
| BaAl2O4:Eu3+(SOM) site 1 | 23.935 | 3.709 | present work |
| BaAl2O4:Eu3+(SOM) site 2 | 23.896 | 3.364 | present work |

**Table 4 –** Experimental and theoretical values of ΔE0-1, E0, E-1, E+1 measured in relation to the barycenter.

|  |  |  |  |
| --- | --- | --- | --- |
| E(cm-1) | Site 1 (nm) | Site 2 (nm) | EExp­(nm) |
| E0 | 586.5 | 595.2 | 590.0 |
| E-1 | 563.3 | 588.0 | 594.7 |
| E+1 | 587.5 | 575.7 | 601.1 |
| ΔE | 133.5 | 133.5 | 133.9 |

1. **Conclusion**

The 5D0-7F1 transition splitting (ΔE0-1) and intensity parameters  and  have been derived from the emission spectrum and from theoretical modelling based on electrostatic equilibrium theory and the agreement between the experimental and the predicted values are very good. As an overall conclusion, the combination of different modelling techniques with experimental results revealed interesting aspects of the optical activity of Eu3+ ions in the BaAl2O4 matrix that could not be accessible separately. The same strategy will continue to be used for a number of other systems where samples are readily available. The Judd-Ofelt parameters results will serve to determine the quantum efficiency and the radiative lifetime that can influence the luminescent properties of BaAl2O4:Eu3+. In addition, this paper has also reformulated the SOM model, making these parameters better determined.

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**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

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