**Defects and spectroscopic investigation of Eu3+-doping in MgGa2O4**

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**Abstract:** Atomistic simulation was performed to study the defect properties and spectroscopy in the MgGa2O4 structure. The calculations indicate that the most favorable type of intrinsic defect is generated by the cation antisite defect, in which there is an exchange of positions between Mg2+ and Ga3+ ions. The calculation also indicates that the incorporation of Eu3+ dopant at the Ga3+(2) site is the most energetically favorable. According to a spectroscopic study using the crystal field approach, the Eu3+ replaces the Ga3+ site occupying a combination of C4 and C4h symmetries while maintaining the same amount of the non-null crystal field parameters. This result was important for the reproduction of experimental energy sublevels and ∆E (7F1) manifold splitting.

**Keywords.** optical materials; defects; luminescence; crystal field; symmetry.

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1. **Introduction**

Solid state lighting devices, such as Light Emitting Diodes (LEDs), are present in several current technologies related to artificial lighting [1,2], display of information[3]. Spinel oxide compounds are attractive candidates for such applications due to their high optical transparency[4], high temperature resistance and good chemical stability[5], as well as amazing electronic and magnetic properties [6]. Among these spinels, the studies on magnesium gallate (MgGa2O4) spinel have gained a lot of attention for being a promising material for solid-state illumination devices[6–8] and phosphors for various luminescent applications[4].

Trivalent europium (Eu3+) plays an important role as photoluminescent activator ion (PL) in the MgGa2O4 spinel due to its narrow emission bands in the orange region[9]. Recent studies reveal that the combination of orange emission associated with Eu3+ dopants with blue intrinsic emission and green emission of Mn2+ ions allow phosphors in the visible range of the spectrum to be obtained[10]. There is great interest in magnesium gallate spinel in view of its possible applications, questions about the PL mechanisms of Eu3+ ions, its incorporation into the host spinel matrix, and whether defects influence this process is still not quite clear. It is important to note that the Eu3+ is a spectroscopic probe[11] and as such can be used to understand a local structure through its luminescent response. Theoretically, the crystal field models are useful to indicate the local symmetry that Eu3+ itself occupies in a doped crystal structure. In this study, we used the simple overlap model (SOM) and the method of equivalent nearest neighbors (MENN) to perform these spectroscopic studies[12,13]. These models with this method have also been widely used and applied in several studies[14–18].

Atomic scale simulation can be used to develop an understanding of the relationship between intrinsic defects caused by the presence of the Eu and how these defects affect the luminescent properties of the material. Thus, this work consists of computational modeling in order to shed light on the most energetically probable defects and their interaction with the lattice as well as to perform a crystalline field study of MgGa2O4:Eu. This methodology has been successfully applied to a variety of materials to make accurate predictions about defect structures, local structural changes, migration energies, and doping properties[14–16].

**2. Computational methods**

The structure of MgGa2O4 compound[7,8,19–22] was systematically modeled using an lattice energy minimization method performed with the GULP code[23]. To calculate the effects of lattice parameters, as well as structural and defect properties, the Born model[24] was used to describe the ionic crystalline solid in which ions are assigned their formal charges, (*e.g*., oxygen ions with a -2 charge state). In this model, we assume that pairwise interatomic interactions between ions, including a long-range Coulombic potential term (*i.e*., potential term that represents the largest contribution to the share of the total interaction energy of ions in the host lattice), and also, a short-range potential term described by the Buckingham potential[25–28]. The Buckingham potential parameters assumed to be a pairwise potential describing the interionic electrostatic interactions between all the ions in the lattice, indexed and , as Buckingham term, is given by

(1)

In Equation (1), the first term include long-range coulombic interactions, where *rij* is the separation distance between a given pair of ions in the lattice, *Zi* and *Zj* are the charge numbers of the two interacting ions, *e2* is the elementary charge state, is the dielectric constant; the second term determines the short-range repulsion interactions between neighbouring electron clouds with van der Waals attraction forces[29].The effect of polarizability ionic was included in our calculations due the oxygen-ion pair interaction and was represented by the core-shell model[30].

The MgGa2O4 structure was modelled using a new set of potential parameters assigned to the Mg2+–O2- and Ga3+–O2- interactions, and derived by using the ParamGulp code[31], while the potential parameters for O2--O2- interaction were derived by Catlow *et al.* [32]. Interatomic potentials for Eu3+ ions were those corresponding to binary metal oxides a­ccording to[33] and presented in the Table 1. The defect formation energy were calculated using the Mott Littleton approach[30], which involves explicit relaxation structural of a spherical region around the defect, *i.e*., the crystal lattice is divided into two spherical regions: the ions in the inner region around the defect are treated explicitly in order to directly influence the defect formation energy, in the outermost region, the remainder of the crystal lattice is treated using quasi-continuum approximation. To calculated formation energy of defect, the radius of region I and II was optimized. In this work, the radius of region I is chosen as 12 Å (so that there are 1131 atoms) with a 16 Å radius for region II (so that there are 1543 atoms). Our tests show that this choice provides an acceptable convergence of defect energies to ca. 0.1 eV or better with relatively low computational costs.

**Table 1.** Potential parameters for the MgGa2O4 structure.

|  |  |  |  |
| --- | --- | --- | --- |
| **Buckingham potential** | ***Aij (eV)*** | ***ρ*ij*(Å)*** | ***Cij (eV Å6)*** |
| Mg2+ core – O2- shell | 4049.00 | 0.2477 | 0.00 |
| Ga3+ core – O2shell | 1792.74 | 0.2999 | 0.00 |
| O2- shell – O2- shell | 22764.01 | 0.1490 | 27.88 |
| Eu3+ core – O2- shell | 1619.40 | 0.3471 | 0.00 |
| Spring | *k (eV Å-2)* | | |
| O2- core – O2- shel | 98.67 | | |
| Charges (|e|) |  | | |
| Mg2+ core | 2.00 | | |
| Ga3+ core | 3.00 | | |
| Eu3+ core | 3.00 | | |
| O2- core | 0.860 | | |
| O2-shell | -2.860 | | |

In the spectroscopic study, we used the Simple Overlap Model (SOM) in which considers a small contribution of covalence in the Ln3+-NN chemical bonding. From this definition, we have that the crystal field Hamiltonian (*HCF*) is presented in Eq. 2), where is the Racah’s spherical tensor that contains the angular coordinates of the *4f* electrons, *i* standing to the *4f* electrons; is the crystal field parameter that contains the radial integrals associated to the *4f* electrons and the coordinates of the nearest neighbours (NN), *j* standing to the NN, as can be seen in eq. (2).

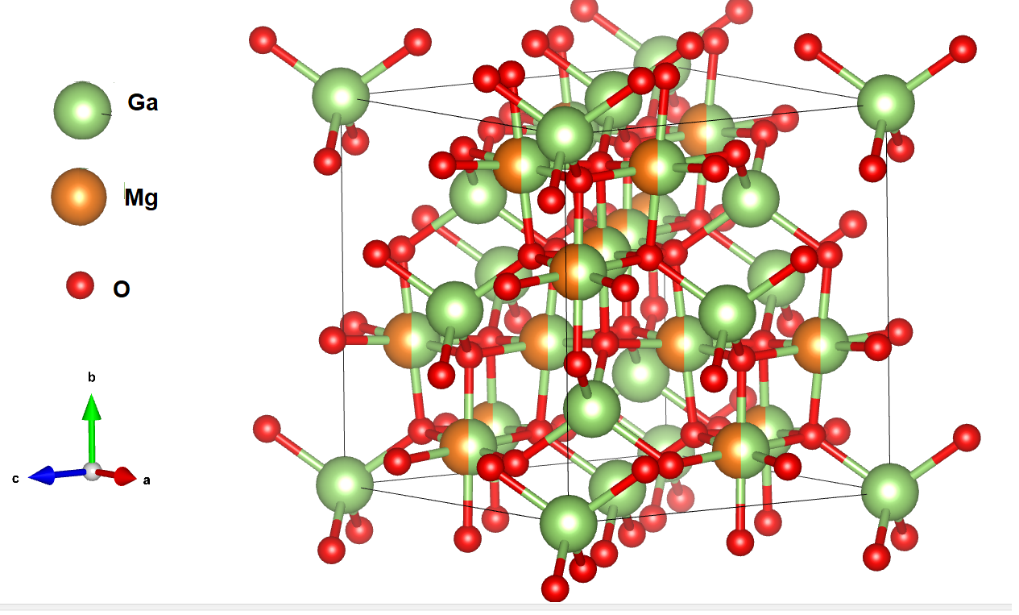
(2)

(3)

The average distance of the <*4f*|NN> overlap in relation to the origin of the RE site is determined by the ratio , where . The overlap integral is defined as , where R0 is the smallest RE-NN distance, *n* = 3.5 and is the maximum overlap between the 4f electrons and the NN electrons[34]. The Method of Equivalent Nearest Neighbours (MENN) is a way of using the SOM and is constituted of three premises: i) equivalent NN are identified through symmetry to define the quantify of degrees of freedom, c; ii) A set of phenomenological gj charge factors are used to reproduce the ∆E experimental splitting and energy sublevels; iii) the sum of the charge factors must be equal the central ion charge[35]. The SOM has been widely used and has showed quite satisfactory results[14,15,36].

1. **Results and discussions**

The starting point of the study was to reproduce the crystalline structures observed experimentally. MgGa2O4 exhibits a cubic crystallographic structure belonging to material family AB2O4 [37] with partial inversion of the A-B [9,38–40] and a Fd3m space group (number 227) with cell parameter a = 8.286 [39] according to the ICSD: 24230 [41] and two possible positions of cations, A2+ and B3+ (see Fig. 1). In normal spinels, the oxygen ions are positioned in a closed, face-centered cubic arrangement with metal ions in the interstices[42]. The unit cell of MgGa2O4 contains 32 oxygen ions with 96 interstices (32 octahedral B3+ sites and 64 tetrahedral coordinate A2+ sites).

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**Figure. 1 –** Crystal structure of the compound MgGa2O4.

In Table 2, it can see the comparison of the calculated and experimental lattice parameters and selected bond lengths of the MgGa2O4 structure. A very satisfactory agreement can be seen with deviations that are less than 1%. These results reveal that the potential model can be successful in calculating defects supporting the validity of the model employed in this work. To simulate the partial occupation of the Ga3+/Mg2+ located in the same crystallography site (50% disorderly occupied), a 2x2x2 supercell was employed for treating this site-disordered, which a random distribution of ions at the sites was considered [43,44].

**Table 2.**  Experimental data (ICSD: 24230) and calculated lattice parameters and selected bond lengths for MgGa2O4 phase.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Lattice parameters** | | | | | | | | |
|  | a *(Å)* | b *(Å)* | | c *(Å)* | | *α= β= γ (º)* | | *V(Å³)* |
| Calc. | 8.260 | 8.260 | | 8.260 | | 90.000 | | 563.560 |
| Exp. | 8.260 | 8.260 | | 8.260 | | 90.000 | | 563.559 |
| **Bond length (Å)** | | | | | | | | |
| Atom pair | Mg/Ga2–O (6x) | |  | | Ga1–O (4x) | |  | |
| Calc. | 1.937 | | 2.033 | |
| Exp. | 1.935 | | 2.032 | |

A deeper insight into the properties of magnesium gallate defects is key to a full understanding of the luminescent properties involved in dopant incorporation. The energies of formation of Frenkel, antisite and Schottky-type defects were determined using a series of single-point defect energies (vacancy and interstitial) which were first calculated (see Table 3) following the equations describing the defect reactions in Krӧger-Vink notation[45] (see Table 4).

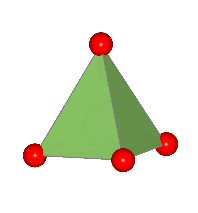
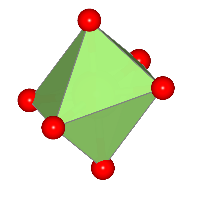
**Table 3 –** Defect formation energy in MgGa2O4 structure and lattice energy of precursor oxides.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **MgGa2O4** | | | | | | | | | |
| **Defect** | **Energy (eV)** | **Defect** | **Positions (Å)** | | | | **Energy (eV)** | **Defect** | **Energy (eV)** | |
| **Vacancy** | | **Interstitial** | | | | | | **Antisite** | | |
|  |  |  | x | y | | z |  |  | |  |
|  | 55,12 |  | 0.2500 | 0.2500 | | 0.5000 | -36,90 |  | | -23,87 |
|  | 57,63 |  | 0.2500 | 0.2500 | | 0,8750 | -38,11 |  | | -23,87 |
|  | 28,50 |  | 0.50495 | 0.51000 | | 0.50000 | -12,57 |  | | 25,04 |
|  | 25,00 |  | 0.5606 | -0.1332 | | -0.0922 | -8,96 |  | | 25,14 |
| **Structure** | | | | | **Lattice energy per ion (eV/ion)** | | | | | |
| MgGa2O4 | | | | | -196,83 | | | | | |
| MgO | | | | | -41,93 | | | | | |
| Ga2O3 | | | | | -154,02 | | | | | |

**Table 4 –** Schemes and solution energies of an intrinsic defect in MgGa2O4 compound.

|  |  |
| --- | --- |
| **Defect type** | **Defect reaction** |
| Mg Frenkel |  |
| Ga Frenkel |  |
| O Frenkel |  |
| MgGa2O4 Schottky |  |
| MgO Schottky |  |
| Ga2O3 Schottky |  |
| MgGa2O4 anti-schottky |  |
| Mg/Ga antisite |  |

Magnesium gallate has more than one non-equivalent Ga site, Ga1 and Ga2, occupying tetrahedral and octahedral positions[46,47], respectively. In this way, the formation energies of all sites non-equivalent ions were calculated. The formation energies of interstitial, vacancy and antisite defects were calculated for more than one position, being position most likely of interstitial located in 0.25, 0.25, 0.50 (see Table 3). Thus, the results in the solution energy of the equations in Table 4 are presented in Figure 2. The results reveal that the most favorable intrinsic defect is the Mg/Ga2 antisite with 0.58 eV. The other defects are highly unfavorable and therefore unlikely to occur at any significant concentration. In fact, the Mg/Ga2 antisite defect is the most dominant in MgGa2O4 and this is quite noticeable in Figure 2 with the sharing of the sites that characterize the spinel inversion process. The possibility of presenting the same coordination number and ionic radius similarity between Mg/Ga2 (0.57 Å / 0.62 Å)[48] facilitates this exchange of sites. As the most likely defect, Mg/Ga2 antisites contribute the most to the native luminescence process of MgGa2O4, which presents bright blue luminescence after vacuum annealing[49]. This antisite leads to the formation of and acting as hole trap and an electron trap, respectively, as presented in Table 4. This provided the necessary mechanisms for the persistent luminescence of this material[21].



**Figure 2 –** Solution energies for different intrinsic disorder mechanisms.

Experimental studies revealed the influence of Eu doping on the photoluminescence properties of MgGa2O4 [9,38,50–52]. Rare earth dopant preferred locations and charge compensation defects are directly related to the luminescence phenomena. Thus, the substitution of Eu3+ ions was investigated at all possible locations *(i.e*. Mg and Ga) in order to obtain the most favorable location and different possible compensation mechanisms, if needed, were investigated and are shown in Table 5, using the Krӧger-Vink notation. Solution energies were evaluated by combining the corresponding defect and lattice energy terms, as shown in Fig. 3. The results reveal that Eu3+ ions are most energetically favorable to be incorporated into the Ga host site. In this case, there is no need for a charge compensation mechanism, as the valence of the dopant is equal to the occupied site. Also it can be note that lowest solution energy for the incorporation at Ga2 is lower than at the Ga1 host site. This is an indicative that Eu3+ ions prefer to be incorporated at octahedral host sites (Ga2 site) than at tetrahedral host sites (Ga1 site). The larger difference of the ionic radius of Eu3+ (0.95 Å)[53] and Ga3+ (0.62 Å)[54] host site results in large lattice deformation and induced non-uniform local deformation in the Eu3+ ions[38,50,51], that could be seen by chance in the X-ray diffraction (XRD) peaks[9]. Experimental results reveal that the Eu3+ dopant is successfully incorporated into the MgGa2O4 structure since X-ray diffraction (XRD) measurements showed that no other products or starting materials were observed, implying that Eu ions entered the MgGa2O4 structure with no effect on the phase composition.

**Table 5 –** Reaction schemes considered due to Eu3+ incorporation in the MgGa2O4 structure.

|  |  |  |
| --- | --- | --- |
| **Site** | **Charge compensation** | **Reaction** |
| **Mg2+** | Mg vacancy |  |
| Ga vacancy |  |
| O interstitial |  |
| Mg/Ga antisite |  |
| **Ga3+** | No charge compensation |  |



**Figure 3** **–** Solution energies for incorporation of Eu3+ ions in the MgGa2O4 compound.

From the atomistic calculations, relaxed positions of the Eu3+ ions at Ga2 site and the surrounding lattice ions are obtained. This information is then used to calculate the crystal field parameters, of s. Table 6 shows the spherical crystallographic coordinates obtained from the atomistic calculations and showed in Fig. 4. From this information, we established the number of equivalent nearest neighbors to define the amount of phenomenological charge factor according to the first premise of the MENN. In Table 7, the crystal field parameters s obtained for the Eu3+ ions at Ga2 site is given, since the atomistic simulations show that Eu3+ ions prefer to be incorporated into at Ga2 site (as confirmed by the solution energies given in Fig. 3). The set of non-null crystal field parameters (CFP) provide an indication of the local symmetry of the central optically of a combination of C4 and C4h symmetries. According to the emission spectrum reported by[20], we have that the 5D0→7F2 transition is more intense than the 5D0→7F1 transition. This indicates that trivalent europium occupies a site in the crystal that does not have an inversion center. However, an important fact to be disregarded is that in addition to the 5D0→7F2 transition, we also have the 5D0→7F4 transition and unfolded by crystal field effects. This reveals a good indication of a combination of C4 and C4h symmetries of Eu3+ in the MgGa2O4.

According to chemical environment equivalence and premise of the MENN, for the ions O1 and O6 we used g1 = 0.769 and for ions O2, O3, O4 e O5, g2 = 0.455. These values resulted in the sum of the charges factors equal to 3.358. The overlap wave functions used was 0.05. An important consideration to be highlighted is that for both symmetries the amount of s are the same, in which maintains the same interactions between the Eu3+ ion and the chemical neighborhood. Due to the distortion caused by the incorporation of the Eu3+ ion in the Ga2 host site, other unexpected parameters are different from zero. However, this does not cause significant changes in the crystal field strength parameter (Nv). This parameter encompasses all parameters in a symmetry. Table 8 shows the 7F1 and 7F2 energy sublevels and the splitting of the 7F1 manifold. These calculations were compared with the experimental data reported by[20] and showed good agreement. From the magnitude of the energy sublevels at the 7F1, we can see a difference on the order of 80 cm-1. This behavior is due to the imaginary part of parameter being non-null, although this parameter is not expected for the combination of C4 and C4h symmetries.

Diagrama

Descrição gerada automaticamente

**Figure 4 –** Local structure of the Eu3+ in MgGa2O4

**Table 6 –** Spherical coordinates of the Eu3+ in the in the MgGa2O4 crystal.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| gJ | FJ | R(Å) | θ (º) | φ (º) |
| g1 | O1 | 2.196 | 0 | 0 |
| g2 | O2 | 2.219 | 93.37 | 49.02 |
| g2 | O3 | 2.219 | 93.37 | 130.97 |
| g2 | O4 | 2.219 | 86.62 | -130.98 |
| g2 | O5 | 2.219 | 86.62 | -49.03 |
| g1 | O6 | 2.195 | 180 | 90.38 |

**Table 7 –** CFP (in cm-1) non-null of the MgGa2O4:Eu3+ .

|  |
| --- |
| MgGa2O4: Eu3+ |
| 922  - 120i  -189  1585  90i  65  -57i  -431  917  -120i  -57  82i  442  119i  264 |

**Table 8 –** Experimental and calculated energy sublevels (cm-1) of the MgGa2O4:Eu3+.

|  |  |  |
| --- | --- | --- |
| Manifold | MgGa2O4:Eu3+ | |
|  | Exp. | Cal. |
| 7F1 | 288 | 208 |
| - | 378 |
| 574 | 564 |
| 7F2 | 1048 | 907 |
| - | 983 |
| - | 1021 |
| 1226 | 1302 |
| ∆E (7F1) | 286 | 286 |

1. **Conclusion**

The study of MgGa2O4 was carried out by operating a new interatomic potential and the role of Eu in the host site was methodically examined using atomistic simulation techniques and spectroscopic methods. The results indicate that the antisite defects are the most energetically favorable intrinsic defect, in which the Mg2+ and Ga3+ ions exchange positions, the calculation was performed both in the tetrahedral and in the octahedral position, and those in the octahedral position are slightly more favorable. It was found that trivalent Eu ions are more easily incorporated into the Ga site without charge compensation. From spectroscopic studies, the Eu3+ is incorporated into the Ga3+ site occupying a combination of C4 and C4h symmetries. With two phenomenological charge factors g1 = 0.769 and g2 = 0.455 it was possible to reproduce the energy sublevels 7F1, 7F2 and the 7F1 manifold splitting. This study shows the importance of the computational simulation together with crystal field models applied to lanthanides to indicate the behavior of the Eu3+ in the host lattice luminescence processes.

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