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Calculation of the crystal field parameters of the $ZnAl_2O_4:Eu^{3+}$

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Zinc aluminate ($ZnAl_2O_4$) doped with rare earth metal ions has been investigated most frequently because of the unique luminescent properties resulting from its stability and high emission quantum yields. The present work is devoted to the calculation of the crystal field parameters and the energy levels of the trivalent europium doped in $ZnAl_2O_4$ spinel, using a theoretical model of the crystal field. The obtained results are compared with the experimental data and discussed.

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1. Introduction

The zinc aluminate spinel ($ZnAl_2O_4$) offers many advantages, such as high thermal and chemical stability, hydrophobic behavior, high mechanical resistance, low sintering temperature, and high quantum yields [1-4].

The structure of the zinc aluminate spinel $ZnAl_2O_4$ is presented in the Fig. 1.

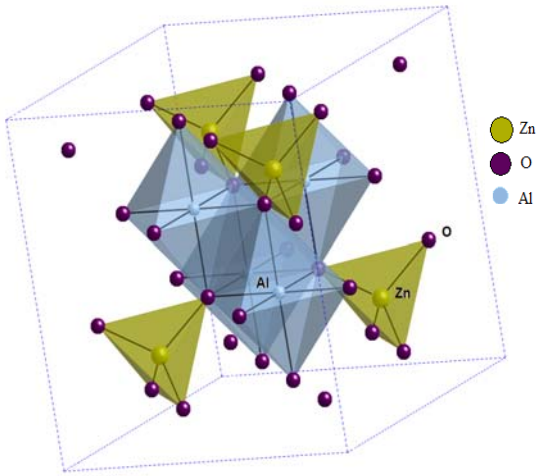

Fig. 1. The structure of $ZnAl_2O_4$.

Zinc aluminate doped with rare earth metal ions has been investigated most frequently because of the unique luminescent properties resulting from its stability and high emission quantum yields. Recently, rare earth metal ions activated $ZnAl_2O_4$ phosphors have been studied thanks to the unique luminescent properties resulting from its stability and high emission quantum yields [1, 2 and 4].

Aluminum-based spinel denotes an interesting sort of oxide ceramics with significant technological applications. Of these, gahnite ($ZnAl_2O_4$) is a useful semiconductor (3.8 eV), and thus it can be used as transparent conductor, dielectric material, and optical material [5].

The normal spinel $ZnAl_2O_4$ belongs to the orthorhombic *Fd3m* space group with the unit cell parameters $a = b = c = 8.0875$ Å [6].

The Eu^{3+} ion will substitute the Al^{3+} ion in an octahedral site in the $ZnAl_2O_4$ spinel, without charge compensation. Despite the existence of the experimental data concerning the Eu^{3+}: $ZnAl_2O_4$ system, the explanation of the theoretical scheme of the energy levels is absent.

The present work is devoted to the modelation the crystal field parameters of the Eu^{3+}: $ZnAl_2O_4$ system in the superposition model of the crystal field and simulation the low-lying energy levels of the trivalent europium doped in $ZnAl_2O_4$ spinel, by diagonalization the Hamiltonian of the system. The obtained results are compared with experimental data and discussed.

2. Modeling of the crystal field parameters

In the normal $ZnAl_2O_4$ spinel structure, the zinc and aluminium cations locate at tetrahedrally and octahedrally coordinated A and B sites with local site symmetry T_d and D_{3d} [6]. Zinc atoms locate on the A- sites are surrounded by four oxygen atoms, whereas aluminium cation at the B-sites, surrounded by six oxygen atoms.

Eu^{3+} ions are expected to occupy Al^{3+} sites in the octahedral symmetry and this substitution does not require charge compensation. These ions have different ionic radii: $r_{Eu^{3+}} = 0.95\text{Å}$ and $r_{Al^{3+}} = 0.54\text{Å}$, and as result the site symmetry of the trivalent europium doped in $ZnAl_2O_4$ will decrees from octahedral to low (close to D_{3d}) symmetry.

In order to describe the energy levels of the ground state of rare-earth ions doped in crystals, we use the Hamiltonian [7]:

$$H = \sum B_k^q O_k^q \quad (1)$$

where:

B_k^q - are the crystal field parameters (CFP) associated with the extended Stevens operators O_k^q.

The crystal field parameters will be calculate using the superposition model. In this model the crystal field parameters may be expressed as [8-10]:

$$B_k^q = \sum_L \overline{B}_k(R_L) K_k^q(\theta_L, \phi_L) \quad (2)$$

where:

K_k^q - are the coordination factors [8-10] defined in terms of the angles θ_L and ϕ_L of the L ligand positions.

The $\overline{B}_k(R_L)$ are the intrinsic parameters and they are given by [8-10]:

$$\overline{B}_k(R_L) = \overline{B}_k(R_0)\left(\frac{R_0}{R_L}\right)^{t_k} \quad (3)$$

Here the $\overline{B}_k(R_0)$ are the intrinsic crystal field parameters corresponding to R_0 reference distance; R_L is the distance from impurity ion to ligand L and R_0 represents the reference distance; t_k are the power law exponents that are adjustable semi-empirical parameters [8-10].

The intrinsic crystal field parameters $\overline{B}_k(R_0)$ can be transferred from similar cluster $[EuO_6]^{9-}$ [7]. R_L can be approximate as [11]:

$$R_L \approx R_h + \frac{1}{2}(r_L - r_h) \quad (4)$$

where:

R_h is the distance between Al^{3+} and ligands, and $r_L(Eu^{3+}) = 0.95\text{Å}; r_h(Al^{3+}) = 0.54\text{Å}$.

Using the geometry of the host matrice [6], the values of the intrinsic parameters $\overline{B}_k(R_0)$ for Eu^{3+}- O^{2-} can be transferred from [12-14]. For the adjustable parameters t_k we taken the values $t_2 = 5, t_4 = 9$ and $t_6 = 13$, given by the point charge model of crystal field theory. Thus, the crystal field parameters B_k^q from (1) are calculated, using the Eqs. ((2), (3)).

3. Results and discussion

In the Table 1 are given the reference distance (R_0) and crystal field intrinsic parameters at reference distance.

Table 1. The intrinsic parameters.

R(Å)	R_0(Å) [12]	$\overline{B}_2(cm^{-1})$ [12-14]	$\overline{B}_4(cm^{-1})$ [12-14]	$\overline{B}_6(cm^{-1})$ [12-14]
2.50	2.98	370	35	21

In the Table 2 are given the crystal field parameters of Eu^{3+} doped in $ZnAl_2O_4$ calculated in the superposition model.

Table 2. The crystal field parameters.

Parameter	Superposition Model
B_2^0	743
B_4^0	-221
B_4^3	-4
B_6^0	-171
B_6^3	1
B_6^6	-1309

With these parameters and the parameters of free Eu^{3+} ions [15] we have diagonalized the Hamiltonian of the title system with SPECTRA, a computer program. The low-lying energy levels are presented in the Table 3.

Tabel 3. The energy levels of the Eu^{3+} doped in $ZnAl_2O_4$ spinel.

Energy levels	Experimental [17]	Calculate (this work)
$^7F_0$	0	0
$^7F_1$	381	372
$^7F_2$	988	1090
$^7F_3$	1987	1944
$^7F_4$	3076	3098
$^7F_5$	-	3920
$^7F_6$	-	5465
$^5D_0$	17301	19015
$^5D_1$	18868	20128
$^5D_2$	21598	22065
$^5D_3$	24038	24478
$^5L_6$	25253	25839

It can see from this table that the calculated values are close with experimental one [16], which confirm the validity of the superposition model of crystal field for this case. Also, we have given the position of two energy levels $^7F_5$ and $^7F_6$ which had not yet observed experimentally.

4. Conclusions

In the present paper has been performed the crystal field calculation parameters and the low-lying energy levels for Eu^{3+} doped in $ZnAl_2O_4$ spinel.

The crystal field parameters of Eu^{3+} doped in $ZnAl_2O_4$ have been calculated in the frame of the superposition model of the crystal field. The low-lying energy level schemes of the europium ions in the studied host, has been calculated by diagonalizing the Hamiltonian of the system.

Reasonable agreement between the calculated and measured crystal field splittings confirms validity of the results obtained in this paper.

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