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CALCULATION OF THE JUDD - OFELT PARAMETERS OF THE $ZnAl_2O_4$: Eu^{3+}

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Abstract
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 calculate the Judd-Ofelt parameters (Ω_2, Ω_4 and Ω_6) of the trivalent europium doped in $ZnAl_2O_4$ spinel, the quality factor (Q) and the branching ratio (β).

1. Introduction

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 [1-4].

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

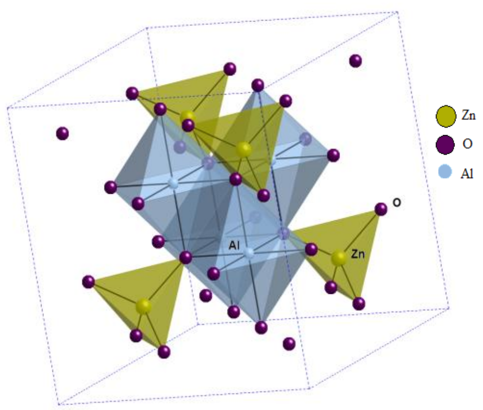

Fig.1. The structure of $ZnAl_2O_4$ [3].

The normal spinel $ZnAl_2O_4$ belongs to the orthorhombic *Fd3m* space group with the unit cell parameters $a = b = c = 8.0875$ Å [3-4]. The Eu^{3+} ion will substitute the Al^{3+} ion in an octahedral site in the $ZnAl_2O_4$ spinel, without charge compensation.

The present work is devoted to calculate the Judd-Ofelt parameters $(\Omega_2, \Omega_4 \text{ and } \Omega_6)$ [5, 6] of the trivalent europium doped in $ZnAl_2O_4$ spinel, the quality factor (Q) and the branching ratio (β).

The experimental support of our calculations is the paper [3].

2. Judd-Ofelt Theory

Judd-Ofelt theory briefly describes the transition intensities for lanthanides and actinides in solids and solutions. Judd-Ofelt utility theory is that it provides a theoretical way of determining the spectral line intensity of a transition [5, 6]:

$$S_{ED} = e^2 \sum_{t=2,4,6} \Omega_t \left| \left\langle f^n [SL] J \left\| U^{(t)} \right\| f^n [S^{'} L^{'}] J^{'} \right\rangle \right|^2 \tag{1}$$

By this expression, Judd-Ofelt theory takes into account the probabilities of transition from a surface to another surface that can cause radiative life times and radiation emission branching reports. Judd-Ofelt analysis is based on more precise measurements of absorption and in particular the integral absorption cross section than the wavelength for a large variety of surfaces. Using the integral absorption cross section can be found so-called line strength, S_m, from the relationship:

$$S_m = \frac{3ch(2J+1)}{8\pi^3 e^2 \bar{\lambda}} n \left(\frac{3}{n^2+2} \right)^2 \int_{\text{sup}rafata} \sigma(\lambda) d(\lambda) \tag{2}$$

where:

- J is total angular momentum of the initial energy state, found the notation $^{2S+1}L_J$.
– $\sigma(\lambda)$ is the absorption cross section as a function of wavelength.

Integral absorption cross section is known as wavelength *bandsum*. Average wavelength, $\bar{\lambda}$ can be found at the beginning of the absorption cross section data:

$$\bar{\lambda} = \frac{\sum \sigma(\lambda)}{\sum \lambda \sigma(\lambda)} \tag{3}$$

Judd-Ofelt analysis minimizes the squared difference between S_m and the S_{ED} with Ω_t adjustable parameters. Basically Judd-Ofelt theory is used to determine a set of phenomenological parameters Ω_λ ($\lambda = 2, 4, 6$), by fitting the experimental data on absorption, eq. (2), or emission measurements, in a minimum amount of square differences, with Judd-Ofelt expression (1).

The Judd-Ofelt parameters for rare-earth ion-host combination are determined by fitting the observed oscillator strength from equation:

$$f[|[S,L]J\rangle,|[S',L']J'\rangle]=\frac{mc}{\pi e^2 N}\int \alpha(\nu)d\nu \qquad (4)$$

where:

- m is the electron mass,
- N the concentration of rare-earth ions in the sample,
- $\alpha(\nu)$ are the absorption coefficient as a function of the frequency ν, and the integral must be taken over the frequency range of the transition.

The quality factor is given by $Q=\frac{\Omega_4}{\Omega_6}$ (5) and the branching ratio (β) for the transition from an initial level, characterized by the quantum numbers $[(S',L')J']$ to a lower level $[(S,L)J]$ is defined by equation:

$$\beta[|[S',L']J'\rangle,|[S,L]J\rangle]=A[|[S',L']J'\rangle,|[S,L]J\rangle]\tau_{rad}=\frac{A[|[S',L']J'\rangle,|[S,L]J\rangle]}{\sum_{S,L,H}A[|[S',L']J'\rangle,|[S,L]J\rangle]} \qquad (6).$$

Once Judd-Ofelt parameters are determined they can be used to calculate transition probabilities, A(J, J ') for all excited states with the equation:

$$A(J';J)=\frac{64\pi^4 e^2}{3h(2J'+1)\overline{\lambda}^3}\left[n\left(\frac{n^2+2}{3}\right)^2 S_{ED}+n^2 S_{MD}\right] \qquad (7)$$

where:

- n is the refractive index of solid
- S_{ED} and S_{MD} is the electric dipole line intensities and magnetic respectively.

In this equation J 'is the total angular momentum of the upper excited state.

Electric dipole line S_{ED} intensity and magnetic dipole line S_{MD} intensity is calculated for each excited state to all lower states of equation (1) and equation (8) using the matrix elements $U^{(\lambda)}$ and Judd-Ofelt parameters and are expressed [7-9]:

$$S_{MD}=\mu_B{}^2\left|\left\langle f^n[SL]J\right|L+2S\left|f^n[S'L']J'\right\rangle\right|^2 \qquad (8)$$

3. Results and discussion

Using the emission spectra represented in the Fig. 2, Judd-Ofelt (J-O) analysis was performed to determine the J-O parameters Ω_2, Ω_4 and Ω_6 are tabulated in the Table 1. The emission peak around 578, 591, 613, 653 and 701 cm^{-1} correspond to the transitions from state of $^5D_0$ to the correspond states of $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ *and* $^7F_4$. The fluorescence branching ratio of transitions is given by equation (6). The total radiative transition probabilities A_{total} for five emission transitions $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ *and* $^7F_4$ are summed up to obtain the τ_{rad} for transitions from $^5D_0$ state to the $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ *and* $^7F_4$ states using equation $\tau_{rad} = 1/A_{total}$.

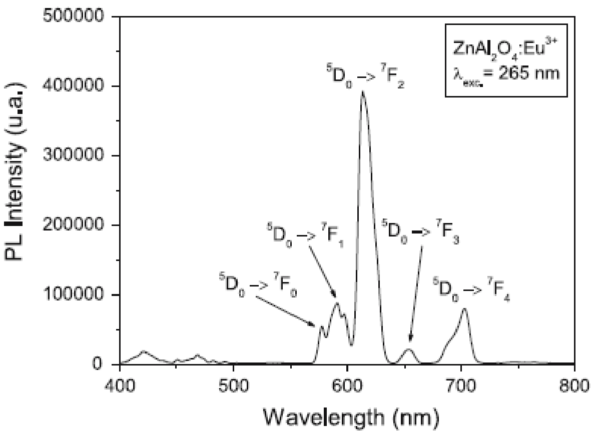

Fig.2. The emission spectra for $ZnAl_2O_4$ doped with Eu^{3+} [3].

Table 1. The Judd-Ofelt parameters

Wavelength $\lambda(nm)$	**Energy** (cm^{-1})	**Transitions**	**Area** $\int E(\gamma)d\gamma$	**Reduced matrix elements**		
				$[U_2]^2$	$[U_4]^2$	$[U_6]^2$
578	17301	$^5D_0 \rightarrow {}^7F_0$	49.744*10^6	0.0000	0.0000	0.0000
591	16920	$^5D_0 \rightarrow {}^7F_1$	1.0849*10^6	0.0000	0.0000	0.0000
613	16313	$^5D_0 \rightarrow {}^7F_2$	6.0134*10^6	0.0032	0.0000	0.0000
653	15314	$^5D_0 \rightarrow {}^7F_3$	17.873*10^6	0.0000	0.0000	0.0000
701	14225	$^5D_0 \rightarrow {}^7F_4$	1.0696*10^6	0.0000	0.0023	0.0000
Judd-Ofelt parameters (cm^2): $\Omega_2 = 1.08*10^{-20}$, $\Omega_4 = 4.82*10^{-20}$, $\Omega_6 = 1.79*10^{-20}$						

The quality factor is calculated using the expression (5) and we have the value 2.69. The electric dipole line intensities and the magnetic dipole line intensities are presented in the Table 2.

Table 2. The branching ratio (β) and the transition probabilities $A(s^{-1})$

Wavelength $\lambda(nm)$	S_{ED}	S_{MD}	$A(s^{-1})$	$B_{mas}(\%)$	$B_{calc}(\%)$
578	0	0	0	0	0
591	0	$5.01*10^{-25}$	$1.40*10^{-17}$	0.112	0.034
613	$2.83*10^{-63}$	$2.50*10^{-24}$	$4.68*10^{-17}$	0.680	0.114
653	0	$7.02*10^{-24}$	$1.13*10^{-16}$	0.020	0.278
701	$6.52*10^{-63}$	$1.50*10^{-23}$	$2.33*10^{-16}$	0.120	0.572

Conclusions

In the present paper has been performed the Judd-Ofelt theory for Eu^{3+} doped in $ZnAl_2O_4$ spinel.

The Judd-Ofelt parameters (Ω_2, Ω_4 and Ω_6) for rare-earth ions are determined by fitting the observed oscillator strength.

The intensity parameters (Ω), the quality ratio (Q), the branching ratio (β) and the transition probabilities (A) were successfully calculated based upon the experimental emission spectrum and the Judd-Ofelt theory.

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