DE GRUYTER OPEN

Analele Universităţii de Vest din Timişoara
Vol. LVI, 2012
Seria Fizică

DOI: 10.1515/awutp -2015-0021

CALCULATION OF THE CRYSTAL FIELD PARAMETERS FOR Eu^{3+} DOPED IN $SrAl_2O_4$ AND $SrIn_2O_4$ SPINELS

M. L. Stanciu

Department of Physics, West University of Timisoara, 3200223 Timisoara, Romania

Article Info
Received: 12December 2011
Accepted: 19 March 2012

Keywords: Energy levels, Crystal field parameters, Normal spinel.

Abstract

Strontium aluminate ($SrAl_2O_4$) and the indium aluminate ($SrIn_2O_4$) spinels have been proven to be efficient host materials, which offer the possibility of generating broadband emission after doping with rare earth trivalent ions. The present work is devoted to the calculation of the crystal field parameters and the energy levels of the trivalent europium doped in $SrAl_2O_4$ and $SrIn_2O_4$ spinels, using the superposition model of the crystal field. Using the intrinsic parameters for Eu^{3+}- O^{2-} bonds, and the geometry structure of the each crystal, we modeled the CFP_s and simulated the low-lying energy levels schemes. The obtained results are compared with the experimental data and discussed.

1. Introduction

Strontium aluminate ($SrAl_2O_4$) has been proven to be efficient host material with a wide band gap, which offers the possibility of generating broadband emission [1]. The spinel $SrAl_2O_4$ has a two phase, where the phase α is monoclinic structure at low temperature, with space group P_{21}, with unit cell parameters $a = 8.447\text{Å}$, $b = 8{,}816\text{Å}$, $c = 5{,}163\text{Å}$, $\beta = 93{,}42^0$ and the β phase, a pseudo-hexagonal structure predominated at higher temperatures [2, 3].

The A site in the Sr^{2+} structure has tetrahedral coordination, with radius equal to 1.12 Å, so their crystallographic positions are too large for Eu^{3+} ions which have the radius equal to 0.95 Å, while the B site in Al^{3+} structure has distorted octahedral coordination. In this case, the Eu^{3+} ions will substitute the Al^{3+} ions which have the radius equal to 0.54 Å, without charge compensation [4], in the octahedral site and a new complex $[EuO_6]^{9-}$ is created.

The structure of the strontium aluminate spinel $SrAl_2O_4$ is presented in the figure 1 [5].

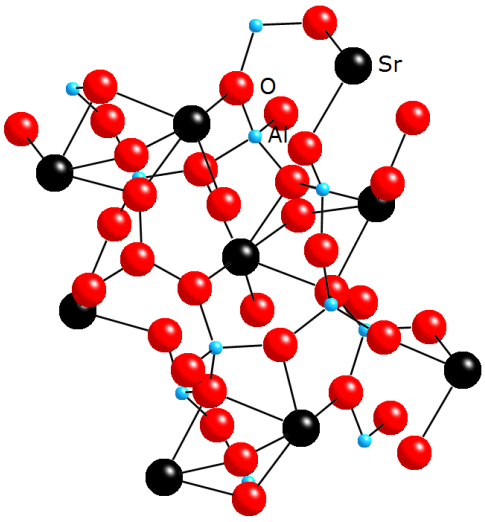

Fig. 1. The structure of $SrAl_2O_4$ [5]. Drawn with VESTA [6]

The structure of the indium aluminate ($SrIn_2O_4$) spinel belongs to the orthorhombic P_{nam} (62) (D_{2h}^{16}), with eight formula units per cell. The constants lattice for $SrIn_2O_4$ spinel undoped is: $a = 9.83\text{Å}, b = 11.5\text{Å}, c = 3.27\text{Å}$ [7] and the local symmetry of the Eu^{3+} in $SrIn_2O_4$ spinel is $C_S = \{E, \sigma_h\}$. The A site in the Sr^{2+} structure has tetrahedral coordination, while the B site in In^{3+} structure has distorted octahedral coordination. In this case, the Eu^{3+} ions will substitute the In^{3+} ions which have the radius equal to 0.79 Å in the octahedral site and a new complex $[EuO_6]^{9-}$ is created.

The structure of the strontium aluminate spinel $SrAl_2O_4$ is presented in the figure 2 [8].

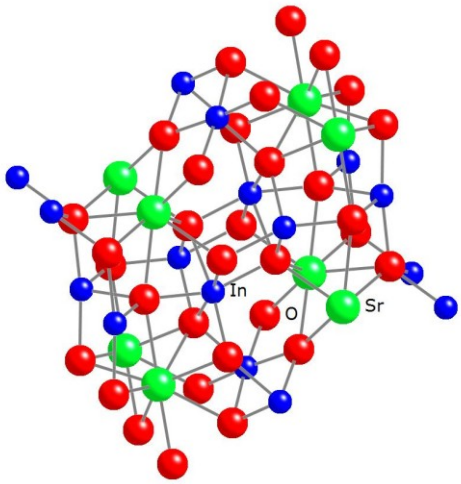

Fig. 2. The structure of $SrIn_2O_4$ spinel [8]. Drawn with VESTA [6]

The present work is devoted to the modelation of the crystal field parameters of the Eu^{3+} doped in the $SrAl_2O_4$ and $SrIn_2O_4$ spinels in the superposition model of the crystal field and simulation the low-lying energy levels of the trivalent europium doped in $SrAl_2O_4$ and

$SrIn_2O_4$ spinels, by diagonalization the Hamiltonian of the systems. The obtained results are compared with experimental data and discussed [9-11].

2. Modeling of the crystal field parameters

The crystal field created by the ligands of the host matrices $SrAl_2O_4$ and $SrIn_2O_4$ spinels type split the energy levels of the impurity ion Eu^{3+} .

In order to describe the energy levels of the ground state of rare-earth ions doped in crystals, we use the Hamiltonian [12]:

$$H = \sum B_k^q O_k^q \tag{1}$$

where:

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

Using the superposition model will be calculated the crystal field parameters. In this model the crystal field parameters may be expressed as [13-15]:

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

where:

K_k^q - are the coordination factors [13-15] defined in terms of the angles θ_L and ϕ_L of the L - ligand positions.

They $\overline{B}_k(R_L)$ are the intrinsic parameters and they are given by [13-15]:

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

Here they $\overline{B}_k(R_0)$ 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 [13-15].

The intrinsic crystal field parameters $\overline{B}_k(R_0)$ can be transferred from similar cluster $[EuO_6]^{9-}$ [13]. R_L can be approximate as [16]:

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

where: R_h - is the distance between Sr^{2+}, Al^{3+}, In^{3+} and ligands.

Using the geometry of the host matrices [2, 3], the values of the intrinsic parameters $\overline{B}_k(R_0)$ for Eu^{3+} - O^{2-} can be transferred from [17-19].

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 Esq. ((2)-(3)).

3. Results and discussion

In the Table 1 are given the reference distance (R_0) and crystal field intrinsic parameters for Eu^{3+}- O^{2-} at reference distance for the Eu^{3+} ion for both spinels.

Table 1. The intrinsic parameters

Eu^{3+} - O^{2-} ($SrIn_2O_4$)				
R(Å)	R_0(Å) [17]	$\overline{B}_2(cm^{-1})$ [17-19]	$\overline{B}_4(cm^{-1})$ [17-19]	$\overline{B}_6(cm^{-1})$ [17-19]
2.17	2.98	370	35	21
Eu^{3+}- O^{2-} ($SrAl_2O_4$)				
R(Å)	R_0(Å) [17]	$\overline{B}_2(cm^{-1})$ [17-19]	$\overline{B}_4(cm^{-1})$ [17-19]	$\overline{B}_6(cm^{-1})$ [17-19]
2.52	2.98	370	35	21

In the Table 2 are given the crystal field parameters of Eu^{3+} doped in $SrAl_2O_4$ and $SrIn_2O_4$ spinels, calculated in the superposition model.

Table 2. The crystal field parameters

Parameter	**Superposition Model (Eu^{3+}: $SrAl_2O_4$)**	**Superposition Model (Eu^{3+}: $SrIn_2O_4$)**
B_2^0	244	1938
B_2^1	764	550
B_2^2	450	-1869
B_4^0	53	-4
B_4^1	116	-73
B_4^2	55	-1173

Parameter	Superposition Model (Eu^{3+}: $SrAl_2O_4$)	Superposition Model (Eu^{3+}: $SrIn_2O_4$)
B_4^3	182	-353
B_4^4	63	-4567
B_6^0	16	-1761
B_6^1	14	-1504
B_6^2	-117	-5270
B_6^3	-70	105
B_6^4	-13	-1054
B_6^5	-300	-223
B_6^6	36	8634

With these parameters and the parameters of the free Eu^{3+} ions [20] we have diagonalized the Hamiltonian of the title system with SPECTRA, a computer program. The low-lying energy levels for this ion are presented in the Table 3.

Table 3. The energy levels of the Eu^{3+} doped in $SrIn_2O_4$ and $SrAl_2O_4$ spinels

Energy levels	Experimental [21-23]	Calculate (this work) (Eu^{3+}: $SrIn_2O_4$)	Calculate (this work) (Eu^{3+}: $SrAl_2O_4$)
$^7F_0$	0	0	0
$^7F_1$	381	408	500
$^7F_2$	988	1729	1085
$^7F_3$	1987	2079	1940
$^7F_4$	3076	3085	3030
$^7F_5$	-	4108	3990
$^7F_6$	-	5162	5345
$^5D_0$	17182	17964	19207
$^5D_1$	-	20217	20163

Energy levels	Experimental [21-23]	Calculate (this work) (Eu^{3+}: $SrIn_2O_4$)	Calculate (this work) (Eu^{3+}: $SrAl_2O_4$)
$^5D_2$	21322	21523	21668
$^5D_3$	-	24482	24585
$^5L_6$	25316	25541	25850

It can see from these tables that the calculated values are close with experimental one [23, 24] which confirm the validity of the superposition model of crystal field for this case.

Also, we have given the position of energy levels $^7F_5$, $^7F_6$, $^5D_1$, $^5D_3$, for systems Eu^{3+}: $SrIn_2O_4$ and Eu^{3+}: $SrAl_2O_4$, 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 the $SrIn_2O_4$ and $SrAl_2O_4$ spinels.

The crystal field parameters of Eu^{3+} doped in $SrAl_2O_4$ and $SrIn_2O_4$ spinels 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.

References

[1] F.C. Palilla, A.K. Levine, M.R. Tomkus, J. Electrochem. Soc. 115 (1968) 642;

[2] B.Y. Geng, J.Z. Ma, F.M. Zhan, J. Phys. Chem. Solid, 36 (1975) 57;

[3] D. Jia, X.-J. Wang, W. Jia, W. M. Yen, Journal of Luminescence, 122–123 (2007) 311;

[4] A. Baszczuk, M. Jasiorski, M. Nyk, J. Hanuza, M. Maczka, W. Strek, Journal of Alloys and Compounds, 394 (2005) 88-92;

[5] M. L. Stanciu, M. G. Ciresan, N. M. Avram, Acta Physica Polonica A, 116 (2009) 544;

[6] K. Momma, F. Izumi, J. Appl. Crystallogr., 41 (2008) 653;

[7] B. S. Girgis, A. M. Youssef, M. N. Alaya, Surf. Technol. 10 (1980) 105;

[8] M. Stanciu, M. G. Ciresan, N. M. Avram, Analele Universităţii de Vest din Timisoara, Vol. LIV (2010) 124;

[9] P. J. R. Montes, M. E. G. Valerio, G. de M. Azevedo, Nucl. Instr. and Meth. in Phys. Res. B 266 (2008) 2923;

[10] C. E. Rodriguez-Garcia, N. Perea-Lopez, G. A. Hirata, S. P. DenBaars, J. Phys. D: Appl. Phys. 41 (2008) 092005;
[11] Z. Yang, J. Tian, S. Wang, G. Yang, X. Li, P. Li, Materials Letters 62 (2008) 1369–1371;
[12] D. J. Newman, B. Ng., Crystal Field Handbook, Cambridge University Press, Cambridge (2000);
[13] D. J. Newman, W. Urban, Adv. Phys., 24 (1975) 793;
[14] D. J. Newman, B. Ng. Rep. Prog. Phys., 52 (1989) 699;
[15] C. Rudowicz, J. Phys. C: Solid State Phys., 20 (1987) 6033;
[16] W. C. Zheng, Physica B, 215 (1995) 255;
[17] J. Newman, Aust. J. Phys., 30 (1977) 315;
[18] S. Vishwamittar, P. Puri, J. Chem. Phys., 61 (1974) 3720;
[19] W. C. Zheng, H. N. Dong, S. Y. Wu, T. Sheng, Physica B, 344 (2004) 103;
[20] W. T. Carnal, G. L. Goldman, K. Rajnak, R. S. Rana, J. Chem. Phys., 90 (1989) 3443;
[21] C. E. Rodriguez-Garcia, N. Perea-Lopez, G. A. Hirata, S. P. DenBaars, J. Phys. D: Appl. Phys., 41 (2008) 092005;
[22] Z. Yang, J. Tian, S. Wang, G. Yang, X. Li, P. Li, Materials Letters, 62 (2008) 1369;
[23] G. Liu, B. Jacquier (Eds.), Spectroscopic Properties of Rare Earths in Optical materials, Springer Verlag, Heidelberg (2005).
[24] P. J. R. Montes, M. E. G. Valerio, G. de M. Azevedo, Nucl. Instr. and Meth. in Phys. Res. B 266 (2008) 2923.