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OPTIMIZATION THE GEOMETRY STRUCTURE OF $SrIn_2O_4$ SPINEL DOPED WITH Eu^{3+}

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Abstract
In order to obtain the accurate crystal field parameters in different models of crystal field theory is necessary to optimize the geometry of the host matrices before and after doping. The present work is devoted to optimization the geometry of $SrIn_2O_4$ spinel doped with Eu^{3+} in the frame of the shell model and pair approximation. By doping the Eu^{3+} will substitute the In^{3+} ion, in octahedral site symmetry and this new structure has been optimized.
Keywords: zinc aluminate, europium, geometry optimization.

1. Introduction

In recent years, spinel-type zinc aluminate $ZnAl_2O_4$, undoped and doped with rare earth ions, has become technologically important due to its peculiar optical properties. With an optical band gap of 3.8eV, which results in effective transparency at wavelengths above 320 nm, it is a useful component of photoelectronic devices operating in the ultraviolet region [1-3] Also, its high chemical and mechanical stabilities make it suitable for a variety of applications such as flat panel display electrodes, ceramics, and electronic and catalytic materials [4, 5].

The crystal structure of zinc aluminate is related to AB_2O_4 spinel structure and belongs to the cubic space group orthorhombic *Pnam* (D_{2h}^{16}), with eight formula units per cell [5]. The *A* site has tetrahedral coordination, while the *B* site has distorted octahedral coordination. A cationic site in the structure (In^{3+}) is available for Eu^{3+} substitution and the new complex $[EuO_6]^{9-}$ are created. The Eu^{3+} ion may occupy an octahedral site in the $SrIn_2O_4$ spinel (Fig. 1). Lattice constants determined for undoped zinc aluminate are $a \cong 9.82\text{Å}; b \cong 11.48\text{ Å}; c \cong 3.26\text{ Å}$ [7]. In order to model the crystal field parameters in

semiempirical models of crystal field models, is necessary to use an optimized geometry of the physical system, such zinc aluminate, undoped and doped with rare earth ions. This paper is dedicated to optimize the geometric structure of the Eu^{3+} doped in $SrIn_2O_4$ spinel using the shell model and pair approximation.

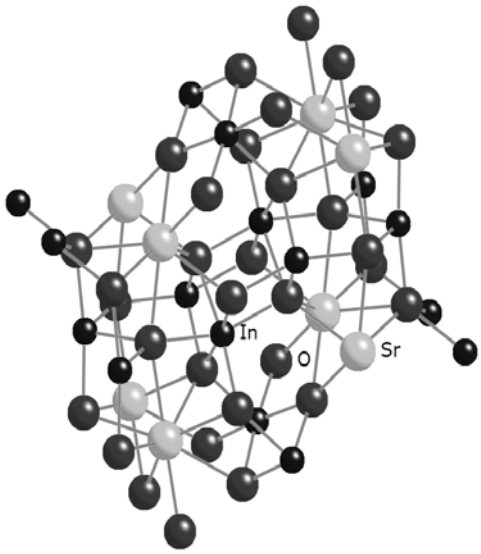

FIGURE 1. The structure of $SrIn_2O_4$ [6].

2. Crystal geometry optimization

By doping the host matrix the cluster formation induces substantially changes in the host structure, both inside the cluster and far from it in the host matrix. We will do the optimization of the geometric structure $SrIn_2O_4$ of the crystal with impurity Eu^{3+}. The calculations were made in the framework of the embedded–cluster method within the shell model, in pair potential approximation [8-10]. We have computed first, the atomic structure of a region of the zinc aluminate host lattice with the embedded europium cluster. For this purpose, computer simulations [10] can be used. The equilibrium positions of the ion cores and shells in the defect region were found by minimizing the crystal energy. In the shell model, in pair-potential approximation, the energy of the crystal lattice with an embedded cluster can be written as:

$$U_{lat} = \frac{1}{2}\sum_i \sum_{k(\neq i)} V_{ik} + \frac{1}{2}\sum_i k_i \vec{\delta}_i^2 \qquad (1)$$

where: $k_i \vec{\delta}_i^2$ - the energy of the core-shell interaction of the *i*-th ion;

V_{ik} - the interaction energy between the *i*-th and *k*-th ions, which can be expressed as:

$$V_{ik} = \frac{X_i X_k}{|\vec{r}_i - \vec{r}_k|} + \frac{Y_i X_k}{|\vec{r}_i - \vec{r}_k + \vec{\delta}_i|} + \frac{X_i Y_k}{|\vec{r}_i - \vec{r}_k - \vec{\delta}_k|} + \frac{Y_i Y_k}{|\vec{r}_i - \vec{r}_k + \vec{\delta}_i - \vec{\delta}_k|} +$$

$$+ f_{ik}(|\vec{r}_i - \vec{r}_k|) + g_{ik}(|\vec{r}_i - \vec{r}_k + \vec{\delta}_i - \vec{\delta}_k|) \quad (2)$$

where: X_i, Y_i - are the core and shell charges of the *i*-th ion;

$\vec{r}_i$ - the vector defining the position of the ion core;

$\vec{\delta}$ is the vector defining the position of the ion shell relative to the ion core.

where functions: $f_{ik}(r) = -B_{ik} \exp(-D_{ik} r)/r$ (3)

- describes the short-range screening of the electrostatic interaction between the ion cores.

$$g_{ik}(r) = A_{ik} \exp(-\rho_{ik} r) - C_{ik}/r^6 \quad (4)$$

- describes the short-range repulsion between the ion shells (which is written in the form of the Born-Mayer potential) and the Van-der-Waals interaction.

The shell charges have been determined from the condition: $Z_i = X_i + Y_i$, where Z_i is the ion charge in the compound. To calculate equations (1) – (4), we will use the cell parameters given in Tables 1, the positions of ions in cell (in Å), given in the Table 2, and the parameters of the potential from equations (3) and (4), given in Table 3.

TABLE 1. Cell parameters [7]

Cell parameters	Exp.
α (degree)	90
β (degree)	90
γ (degree)	90
a (Å)	9.8090
b (Å)	11.4490
c (Å)	3.2650

TABLE 2. Position and charges of ions in the cell of $SrIn_2O_4$ before optimization for undoped crystal [7]

Atom	x	y	z	Xi	Yi
Sr	0.7553	0.6528	0.25	0.169	1.831
In_1	0.4196	0.1064	0.25	0.043	2.957
In_2	0.4292	0.6111	0.25	0.043	2.957
O_1	0.2040	0.1730	0.25	0.513	-2.513
O_2	0.1210	0.4810	0.25	0.513	-2.513
O_3	0.5230	0.7780	0.25	0.513	-2.513
O_4	0.4170	0.4290	0.25	0.513	-2.513

TABLE 3. The short-range interaction potential parameters (a.u) [9]

Pair	A	ρ	C	R_{min}	R_{max}
$O^{2-} – O^{2-}$	25.4	0.694	32.3	0	12
$O^{2-} – Sr^{2+}$	$0.196*10^4$	0.325	0	0	10
$O^{2-} – In^{3+}$	$0.150*10^4$	0.331	4.32	0	10
$O^{2-} – Eu^{3+}$	848	0.379	0	0	10
$k_O = 20.5$	$k_{Sr} = 21.5$	$k_{Eu} = 305$		$k_{In} = 1680$	

Neglecting the short-range screening of the electrostatic interaction between the ion cores, after geometry optimization with Gulp 3.0 computer program [8], we obtained the new parameters of the cell, given in the Table4.

TABLE 4. Cell parameters after optimization.

	Exp.	Optimized
α (degree)	90	90
β (degree)	90	90
γ (degree)	90	90
a (Å)	9.8090	10.1983
b (Å)	11.4490	11.7696
c (Å)	3.2650	3.3413

TABLE 5. The position and charges of ions in the cell of $SrIn_2O_4$ after optimization for crystal undoped.

Atom	x	y	z	Xi	Yi
Sr	0.7551	0.6473	0.25	0.169	1.831
In_1	0.4211	0.1087	0.25	0.043	2.957
In_2	0.4341	0.6139	0.25	0.043	2.957
O_1	0.2044	0.1665	0.25	0.513	-2.513
O_2	0.1178	0.4753	0.25	0.513	-2.513
O_3	0.5289	0.7825	0.25	0.513	-2.513
O_4	0.4211	0.4272	0.25	0.513	-2.513

As can see from Table 4, the values of the cell parameters after optimization are different from that from experimental data, and they correspond to the minimum energy of the cell. Also, from Table 5 it can see that the positions of the ions in the cell of undoped host matrix are slightly different after optimization.

By doping the $SrIn_2O_4$ spinel with Eu^{3+} and optimization the geometry of this new structure we obtained the results given in Table 6. With the results from these tables it is

possible to model the crystal field parameters, which acts on the impurity ions, doped in host matrix.

TABLE 6. The position and charges of ions in the cell of $SrIn_2O_4$ after optimization for doped crystal.

Atom	x	y	z	Xi	Yi
Sr	0.7551	0.6473	0.25	0.169	1.831
Eu	0.4167	0.1083	0.25	0.043	2.957
In_2	0.4341	0.6138	0.25	0.043	2.957
O_1	0.2044	0.1665	0.25	0.513	-2.513
O_2	0.1178	0.4753	0.25	0.513	-2.513
O_3	0.5289	0.7825	0.25	0.513	-2.513
O_4	0.4211	0.4272	0.25	0.513	-2.513

Conclusions

We made the optimization the geometric structure of the Eu^{3+} doped in $SrIn_2O_4$ spinel using the shell model and pair approximation and GULP 3.0 computer program. In the calculations, the internal region around impurity ion consists of about 1300 ions and 40 thousands of ions in the adjoining region to the internal region could relax restrictedly. The lattice parameters of the elementary cell and the positions of the ions in the cell were changed such a way that the energy of the doped crystal is minimum.

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