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Predicting the optical behaviour of eu^3+ doped LiNbO$_3$ by computer modelling

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Abstract:

Computational simulation method is employed to study optical properties LiNbO$_3$ induced by europium dopant. Atomistic modeling is used to predict the doping sites and charge-compensation schemes for LiNbO$_3$: Eu systems. This information is then used to calculate the parameters of the crystal field, which is used to calculate the transitions of energy levels for the Eu^3+. The transition energy for the Eu^3+ doped material is compared to the experimental results.

Palavras chave: Defect. Crystal Field. Energy Minimization. Computer Modelling.

Prevendo o comportamento óptico de eu^3+ LiNbO$_3$ dopado por modelação computacional

Resumo:

O método de simulação computacional é empregada para estudar as propriedades ópticas LiNbO3 induzidas pelo dopante európio. A modelagem atomística é usada para prever os locais de doping e esquemas de carga de indemnização para LiNbO$_3$: sistemas da Eu. Esta informação é então usada para calcular os parâmetros do campo cristalino, que é usado para calcular as transições de níveis de energia para o Eu^3 +. A energia de transição para o material dopado com Eu^3 + é comparada com os resultados experimentais.

Key words: Defeito. O campo de cristal. Minimização de energia . Modelling Computer.

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INTRODUÇÃO

Lithium niobate is a material with many important technological applications due to its diverse physical properties. Much useful information about the material and its defect properties can be obtained by computer modelling, based on the description of interactions between ions by effective potentials. In a previous paper a new interatomic potential was derived for $LiNbO_3$, giving good agreement with the structure and properties of the material [1]. This potential has been subsequently used in a study of the defect chemistry of the material, including doping by rare-earth elements [2]. Here modelling can predict the energetically optimal locations of the dopant ions, and the energy involved in the doping process.

When $LiNbO_3$ is doped with rare-earth ions, the optical properties of the material can be enhanced, and depending on the dopant ion, particular transitions are observed. It would be very useful to be able to predict which dopants cause particular transitions, and this paper presents the application to $LiNbO_3$ of a hybrid modelling method based on a combination of crystal field calculations, and energy minimisation. This method has already been used in studies of other materials[3,4,5,6] and now also applied to the LiNbO doped with Eu^{3+}.

The method uses energy minimisation to predict the location of the dopant ion, and the relaxed positions of the surrounding O^{2-} ions. This information is then input into a crystal field calculation which obtains the crystal field parameters, $B^k{}_q$, which are then used to calculate the energies of the electronic transitions.

Methodology

Crystal field calculation

The crystal field calculations is based on the theory developed by Jud[7] and Ofelt[8] where the interaction between the rare earth ion and the surrounding lattice ions is given by:

$$\boxed{H_{CF} = \sum_{k,q} B_q^k C_q^{(k)}}$$

The B_q^k,s (k=2,4 and 6) are the so-called ligand field parameters of even rank, which describe the angular contribution to H_{LF} from the O^{2-} ligand ions and $C_q^{(k)}$ is a Racah tensor operator, which describe the angular contribution to H_{LF} from the rare earth ion.

The set of non-zero B_q^k components provide an unambiguous indication of the local symmetry of the central optically active ion, and the magnitude of the B_0^2 parameter indicates how far from a center of symmetry site the luminescent ion. This means that the crystal field calculations can give crucial information on the optical behaviour of a particular hostdopant system.

In this case the rare earth ion doping causes lattice distortion not present in the $LiNbO_3$ non-doped lattice. The simulation of that distortion leads to a new set of coordinates of the neigbour ligant ions. Both non-distorted lattice coordinates and the coordinates obtained using the defect simulation technique are used to calculate the B_q^k parameters using the simple overlap model(SOM)[9,10].

According to the SOM, the crystal field effect can be calculated by assuming a potential produced by effective charge distribution over a small region, proportional to the overlap between 4f and ligand wavefunctions, situated aroud the mid point of the metal-ligant distance. The B_q^k parameters are written as $\boxed{B_q^k = \rho\left(\frac{2}{1\pm\rho}\right)^{k+1} A_q^k \left\langle r^k \right\rangle}$ were A_q^k is the lattice sum of neigbours belonging to the first coordination sphere associated with an effective charge, $\boxed{\left\langle r^k \right\rangle}$ are radial integrals, and ρ is the overlap between the 4f orbitals of the central ion and the ligand, the value of which varies as a function of the metal-ligand distance, R, according to the power law $\boxed{\rho = \rho_0\left(\frac{R_0}{R}\right)^{3.5}}$ [11], R_0 being the shortest metal-ligand distance.

The ± sign characterizes the displacement of the charge barycenter from the metal-ligant mid-distance; the minus sign is applied when $r_{metal} < r_{ligand}$[12].

Energy level calculations

The description of an electronic configuration is based on the central field model. This configuration of the ions is evaluated using the following Hamiltonian[13-15]:

$$\boxed{H = H_0 + H_{CR} + H_{SO} + H_{CF}}$$

The first term (H_0) is the spherical symmetric one-electron part of the free-ion Hamiltonian which separates the ground configuration from the excited configurations. The second term (H_{CR}) represents the coulombic repulsion characterized by the Steler integrals F^k (or the Racah parameters B and C); it also includes the two-body interaction (Trees parameter α). The three term is the spin-orbit interaction characterized by the spin-orbity coupling constant $\boxed{\zeta(\lambda = \pm\zeta / 2S)}$[15]. The last term H_{CF} is the crystal field Hamiltonian that has already been described in the previous section.

The energy levels were then computed within this framework, using the SPECTRA code [16]. The code uses the following procedure to diagonalise the matrix leading to the final energy structure of the desired ion. A subset of the $|LS\rangle$ states selected for calculation undergo a filtering process. During this process, the matrix of free-ion $|LS\rangle$ state is diagonalised and the composition of wavefunctions for levels up to the truncation energy level is analysed. If the percentage of a given $|LS\rangle$ state in those wave functions is higher than a specified level, then this $|LS\rangle$ state included for further use in building LSJJM states of the configuration. A complete set of $|LSJJM\rangle$ states is used in diagonalisation. In such way, both free ion and crystal-field interactions are treated simultaneously; there is no separation into a basic Hamiltonian and perturbation.

In this work a set of $|LS\rangle$ states were considered for the calculation of the energy levels.

Results and Discussion

The difference in B_q^k values between tables 2 and 3 show that the inclusion of relaxation is important in the calculations, and this efecct will definitely influence the predicition of the transition energy spectra of the Eu^{3+} dopant. In the paper publicate for Arismendi and Cabrera[17] some evidence that Eu^{3+} actually substitutes for both cations Li^+ and Nb^{5+} was reported. By growing Eu-doped $LiNbO_3$ crystals with different [Li]/[Nb] ratios, we tried to selectively populated either Li^+ and Nb^{5+} sites. All the split bands whose two peaks were attributed to two different sites were observed to change the relative height of their peaks[18]

Table 1. $B^k q$ values for non-distorted lattice for the Li and Nb site at room temperature

Parameter	B_0^2	B_0^4	B_0^6	B_3^4	B_3^6	B_6^6
Li site	-491.68	-327.11	175.67	792.50	-123.60	305.46
Nb site	-792.54	-212.40	-64.64	-836.91	92.56	443.00

Table 2. $B^k q$ values for relaxed lattice for Li and Nb site at room temperature

Parameter	B_0^2	B_0^4	B_0^6	B_3^4	B_3^6	B_6^6
Li site	-224.26	-1730.28	957.87	2312.78	389.21	658.02
Nb site	-846.20	-412.88	170.07	-1392.75	293.52	771.27

In order to apply the SOM, the coordinates of the ligand oxygen atoms were taken from the non-distorted and relaxed lattice and Eu-O distance are in the tables 3 and 4.

Tabela 3. Ligand coordinates (R in units of 10^{-8} cm and angles in degrees) for non-distorted lattice at room temperature.

Li site			Nb site		
R	θ	ϕ	R	θ	ϕ
2.0420	132.2823	175.87	2.2166	42.9639	175.87
2.0421	132.2793	-64.115	2.2167	42.9669	-64.115
2.0423	132.2746	55.8725	2.2169	42.9716	55.8725
1.9779	62.5940	232.05	2.0423	108.917	63.984
1.9782	62.5983	102.0462	2.0425	108.9148	-56.0278
1.9783	62.6001	-7.9428	2.0427	108.9124	3.9851

Tabela 4. Ligand coordinates (R in units of 10^{-8} cm and angles in degrees) for relaxed lattice at room temperature.

Li site			Nb site		
R	θ	ϕ	R	θ	ϕ
2.3596	135.6592	172.744	2.3301	45.0479	-7.2442
2.3596	135.6603	-67.2553	2.3301	45.0487	-67.2434
2.3597	135.6587	52.7445	2.3301	45.0493	52.7542
2.1811	69.2200	233.28	2.2335	104.9364	62.8177
2.1810	69.2189	113.2772	2.2335	104.9359	-57.1817
2.1812	69.2212	-6.7218	2.2335	104.9359	2.8163

In table 5 the diference between the predicted and the experimental[8] transition state of Eu^{3+} in the $LiNbO_3$ lattice are show. The difference is 3% for Li and 2% for Nb^{5+} site.

The agreement with trends from experimental results as reported above, and other recent studies on different material[3] suggest that the method works well. Also, the method presented here is useful as a starting point for experimentalists who wish to fit B_q^k parameters to spectra, since there to assume an ‘a priori C_3 symmetry using the site symmetry of the substituting ion. The method could therefore provide a more reliable and realistic initial B_q^k parameter set to input to fitting routines. The method also proved to be reliable in predicting the energy states transition with out any previous experimental knowledge of the real system, meaning that it can be used as a test benchmark for the experimentalist even prior to actually putting a lot of effort into preparing and growing good optical quality samples. In this sense, it can be viewed as a strategy for realistic materials design, predicting system properties before building it.

Transition	Exp.[14]	Calc.(Li site)	Δ%	Calc.(Nb site)	Δ%
$5D_o - 7F_2$	16192	16498.5	2,5	16407.8	1.33
	15990	16235.3	1,5	16319.4	2.06
$5D_o - 7F_4$	14455	14796.7	2,7	14711.0	1.77
	14397	14793.3	2,7	14604.0	1.43
	14233	14645.8	2,9	14546.5	2.20
	14160	14616.9	3,2	14411.5	1.78
	14148	14570.7	2,9	14491.2	2.43
	14033	14559.9	3,7	14479.9	3.18

Conclusion

This paper has presented a computational study of the defect physics and chemistry of Eu^{3+} in the $LiNbO_3$ as it relates to the potential optical applications of the material. The work combines three different, but complementary, modeling techniques, namely defect calculations, crystal field calculation via the simple overlap model, and energy levels transition calculations, building up methodology that can fulfil the requirements to predict possible optical transitions that arise from the f-levels of Eu^{3+} ions influenced by the crystalline matrix.

Crystal field parameters have been calculated for Eu^{3+} ion-$LiNbO_3$ combination, and the results discussed in terms of optical properties of the doped systems. As a consequence, the energy levels of the Eu^{3+} íon have been calculated. The predicted transitions states to the experimental ones gave good agreement within the range of 2% to 3%.

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