ELSEVIER

Available online at www.sciencedirect.com





Nuclear Instruments and Methods in Physics Research B 218 (2004) 232-235

www.elsevier.com/locate/nimb

Defect simulation and crystal field studies of Ln³⁺:LiCaAlF₆ and LiSrAlF₆

Jomar B. Amaral^a, Mario E.G. Valerio^{a,*}, Marcos A. Couto dos Santos^a, Robert A. Jackson^b

^a Departamento de Física, Universidade Federal de Sergipe, São Cristóvão SE 49100-000, Brazil ^b Lennard–Jones Laboratories, School of Chemistry and Physics, Keele University, Keele, Staffordshire ST5 5BG, UK

Abstract

LiCaAlF₆ (LiCAF) and LiSrAlF₆ (LiSAF) crystal hosts doped with trivalent positive lanthanide ions (Ln³⁺) were studied via defect simulation techniques and crystal field parameter calculations. Depending on the ratio of ionic radius of the dopant to the host divalent cation, the luminescent ions can occupy the Sr^{2+} (or Ca^{2+}) site or the Al^{3+} . When the dopant enters at the divalent cation site, charge compensation is needed that changes drastically the starting symmetry of this site. However, when the Al^{3+} site is preferred, no charge compensation schemes are involved, but nevertheless the lattice is distorted since the sizes of the Ln^{3+} ions are bigger than the Al^{3+} ion. The actual positions of the first neighbours of the Ln^{3+} ion were input in the crystal field parameters equations, through which the conclusions on site symmetry of the optically active ion have been drawn and these results allows the prediction of possible optical activity based on the possibility of the 4f–4f transitions.

© 2003 Elsevier B.V. All rights reserved.

Keywords: LiCaAlF₆; LiSrAlF₆; Ln³⁺ ions; Defect modelling; Crystal field parameter

1. Introduction

Research on laser crystals having tuneable monochromatic activity has received much attention due to the applicability of lasers in human surgery, in laser technology, as well as due to fundamental knowledge [1–3]. The very narrow emission lines of the lanthanide trivalent ions (Ln^{3+}) -doped crystals make such media of special interest [4–7].

^{*}Corresponding author. Tel.: +55-21-79-212-6810; fax: +55-21-79-212-6807.

E-mail address: mvalerio@fisica.ufs.br (M.E.G. Valerio).

In order to predict the reliability of producing this kind of material, structural modelling has been developed in our group [8–12].

Recently, Ce-doped LiCaAlF₆ (LiCAF) and LiSrAlF₆ (LiSAF) appeared as good candidates for tuneable solid-state lasers in the UV-region [2]. Our aim in this work is to study Ln^{3+} (Ce, Nd, Eu, Yb) doping these structures by a combination of the defect simulation technique and crystal field theory.

2. Defect simulation technique

The defect calculations were performed based on empirical potential fitting [13] and lattice

⁰¹⁶⁸⁻⁵⁸³X/\$ - see front matter @ 2003 Elsevier B.V. All rights reserved. doi:10.1016/j.nimb.2003.12.027

Table 1 Interatomic potentials for LiCaAlF₆ and LiSrAlF₆

*		-		
Interaction	A/eV	$ ho/ m \AA$	C/eVÅ ⁶	k/eVÅ ⁻²
Li core F shell	443.83	0.2714	0.0	_
Al core F shell	1400.00	0.2571	0.0	-
Ca core F shell	3400.00	0.2661	0.0	-
Sr core F shell	3400.00	0.2906	0.0	-
F shell F shell	911.69	0.2707	13.80	_
F core F shell	-	_	_	24.36

energy minimisation, embodied in the general utility lattice program (GULP) [14], in which materials are described in terms of ions interacting through effective potentials. The potentials were fitted to the structure of the LiCaAlF₆ and LiSrAlF₆ crystal (atomic positions and lattice parameters). This procedure is described in detail in [12]. In Table 1, the potential parameters used in the present simulations are presented, with the dopant-lattice potentials being taken from [12]. Defects are modelled using the Mott-Littleton approximation [15–17] in which a spherical region of lattice surrounding the defect is treated explicitly, with all interactions being considered (region I) and more distant parts of the lattice are treated as a dielectric continuum (region II).

3. Crystal field parameters

The interaction between the Ln^{3+} ion and the ligand (L) ions in the first sphere of co-ordination is described in the Judd–Ofelt theory by the hamiltonian $H_{\text{CF}} = \sum_{k,q} B_q^k C_q^{(k)}$ [18,19]. The $C_q^{(k)}$ are the so-called Racah spherical tensors, which accounts for the angular part of the interaction related to the Ln^{3+} ion. The B_q^k are the crystal field parameters, which accounts for the radial and angular part of the H_{CF} related to the ligand ions.

$$B_q^k(\mathbf{JO}) = g \mathbf{e}^2 \sqrt{\frac{4\pi}{2k+1}} \sum_j \frac{\langle r_i^k \rangle}{R_j^{k+1}} Y_q^k(j).$$

The simple overlap model (SOM) is an alternative way of describing the $Ln^{3+}-L$ interacting charge (ge) which appears in the J-O theory, g being a charge factor. The SOM assumes that this interacting charge is located in small regions around the mid point of the Ln³⁺–L distance, is modulated by the overlap integral (ρ) between the Ln³⁺ and L wavefunctions, being written as ρge . The standard overlap ρ_0 is that of the nearest ligand ion (R_0) and the overlap of the other ligand ions are assumed to be inversely proportional to the Ln³⁺-L distance (R) as follows: $\rho = \rho_0 (R_0/R)^n$ [20–22]. The values of ρ_0 and *n* are taken from Jørgensen [23]. With those arguments, the connection between the J-O theory and SOM is $B_q^k(SOM) = \rho(2/(1+\rho))^{k+1}$ $B_a^k(J-O).$

This simple overlap model is indeed a description of a mean field potential created by the modulated charge ρge and can be interpreted as an alternative way of taking into account shielding effects, because the spread of the 4f wavefunctions is limited by the 5s and 5p closed shells, then the overlap integral, as well as chemical bond effects, because the ρge is a sharing charge between the Ln³⁺ and L ions.

4. Results and discussions

Table 2 gives the solution energies for the lanthanide dopants in LiCAF and LiSAF, calculated as described in [12]. These show the energetically favoured locations and charge compensation mechanisms for the dopants and this information is then used to calculate the B_q^k values, in that it predicts the site symmetry of the substitution site. It is seen that the different dopants are predicted occupy different sites with different charge compensation mechanisms in LiCAF and LiSAF, and for example, in the case of Eu³⁺ and Nd³⁺ in Li-CAF, there are two possible sites that might be occupied.

Tables 3 and 4 show the values of the B_0^2 parameters calculated for the Ln^{3+} :LiCAF and LiSAF crystals in that order. The choice of showing only q = 0 components is due to fact that a nonvanishing B_0^2 value indicates that the site occupied by the Ln^{3+} ion is not an inversion

Defect	$M_{ m Al}$	$M^{\bullet}_{\mathrm{Ca/Sr}}$ -1/2	V'' _{Ca}	$M^{\bullet}_{\mathrm{Ca/Sr}} - V'_{\mathrm{Li}}$	$M^{\bullet}_{\mathrm{Ca/Sr}}-F'_i$			$M_{\rm Li}^{\bullet \bullet} - V_{\rm Ca/Sr}''$
		Ln^{3+} at (±100)	Ln^{3+} at (00 ± 1)		F'_i at (1/4 1/4 0)	F'_i at (1/2 1/2 0)	F'_i at (3/4 1/2 0)	
$LiCaAlF_6$								
Ce	3.96	2.41	2.35	1.89	1.97	2.11	2.15	1.45
Nd	3.56	2.44	2.35	1.90	1.95	2.08	2.59	1.90
Eu	2.95	2.50	2.40	1.92	2.59	2.09	2.11	1.92
Yb	2.37	2.59	2.46	1.97	2.11	2.12	2.10	5.25
$LiSrAlF_6$								
Ce	3.64	2.81	2.88	2.34	1.99	1.96	1.99	2.36
Nd	3.27	2.92	2.97	2.46	2.28	5.45	2.01	2.48
Eu	2.71	3.10	3.11	2.59	2.39	2.12	2.13	5.29
Yb	2.18	3.31	3.29	2.80	2.89	2.55	2.27	nc

Solution energies	for Ln ³⁺	dopants in	LiCaAlF ₆ and	LiSrAlF6.	taken from	[12]
Solution energies	IOI LII	dopants m	Licui in 6 and	Lion_{6}	taken non	[14]

Lowest energy solution schemes are highlighted. 'nc' means that the calculation did not converge.

Table 3 B_0^2 values of the Ln³⁺:LiCAF

Parameters	Ln ³⁺	$Ln_{Li} + V_{Ca}^{\prime\prime}$	$Ln_{Ca} + V'_{Li}$
B_{0}^{2}	Ce	72.73	_
	Nd	122.06	293.87
	Eu	141.99	269.96
	Yb	_	191.74

Table 4

 B_0^2 values of the Ln³⁺:LiSAF

Parameters	Ln ³⁺	$Ln_{Sr} + F'(2)$	$Ln_{Sr} + F'(3)$	Ln _{Al}
B_{0}^{2}	Ce	352.81	250.70	_
-	Nd	_	-254.83	-
	Eu	163.93	99.99	-
	Yb	_	_	-22.99

centre. Indeed, all values of B_q^k are nonzero, indicating that the Ln³⁺ site symmetry is rather low (see Table 5). This then implies that the 4f–4f transitions are allowed by electric dipole mechanism. As one can readily note, the Ce³⁺:LiCAF and Yb³⁺:LiSAF do not have very high values of B_0^2 , especially in the Yb case. This means that in both cases the site symmetry is close to an inversion centre, indicating that those crystals may not be very effective as laser materials. For the sake of comparison, the experimental value of B_0^2 component of Nd:LiYF₄, which is an important laser material, is 421 cm⁻¹ [24].

Table 5 B_a^k values of the Eu:LiCAF and LiSAF

$ B_a^k $	Eu ³⁺ :LiCAF	Eu ³⁺ :LiSAF
' <i>q</i> '	[(Ca + vLi)]	[Sr + F'(2)]
$ B_{0}^{2} $	270	164
$ B_{1}^{2} $	93	170
$ B_{2}^{2} $	166	168
$ B_0^{\overline{4}} $	1136	756
$ B_{1}^{4} $	40	190
$ B_{2}^{4} $	53	310
$ B_{3}^{4} $	1235	561
$ B_{4}^{4} $	41	229
$ B_{0}^{6} $	445	141
$ B_{1}^{6} $	27	135
$ B_{2}^{6} $	3308	2090
$ B_{3}^{6} $	531	337
$ B_{4}^{6} $	118	245
$ B_{5}^{6} $	131	237
$ B_{6}^{6} $	312	44

In Table 5 the B_q^k values of both Eu-doped systems are given. The high value of B_2^6 is an indication that a site symmetry involving a C₂ element is the most probable one.

5. Conclusions

We have studied the Ln^{3+} (Ce, Nd, Eu and Yb) LiCaAlF₆ and LiSrAlF₆ systems by computer modelling and crystal field theory. By analysing the B_q^k values the spectroscopic behaviour of

Table 2

Ln³⁺:LiCAF and LiSAF could be predicted. A very important prediction has been that doping with Ce³⁺ and Yb³⁺ may not have strong optical activity, because B_0^2 is small (specially Yb³⁺), when compared to the B_0^2 value of the Nd:LiYF4, which is an important laser crystal. All nonzero B_q^k values indicate that the site symmetry is low, which is good for optical purposes, for all cases whose B_0^2 values are not low.

Acknowledgements

The authors would like to thank CNPq and FAPESE (Brazilian agencies) for financial support.

References

- D.T.L. Liu, J.M.S. Lai, D.S.C. Lam, Am. J. Ophtalmol. 134 (2002) 621.
- [2] N.D. Vieira Jr., I.M. Ranieri, L.V.G. Tarelho, N.U. Wetter, S.L. Baldochi, L. Gomes, P.S.F. de Matos, W. de Rossi, G.E.C. Nogueira, L.C. Courrol, E.A. Barbosa, E.P. Maldonado, S.P. Morato, J. Alloys Comp. 344 (2002) 231.
- [3] D. Aberg, S. Edvardsson, J. Alloys Comp. 303–304 (2000) 345.
- [4] A.A. Kaminskii, Phys. Stat. Sol. A 148 (1995) 9.
- [5] B. Bureau, G. Silly, J.Y. Buzaré, J. Phys. Chem. Solids 58 (1997) 951.

- [6] M.A. Couto dos Santos, E. Antic-Fidancev, J.Y. Gesland, J.C. Krupa, M. Lemaître-Blaise, P. Porcher, J. Alloys Comp. 275–277 (1998) 435.
- [7] Z. Xiong, Z.G. Li, N. Moore, W.L. Huang, G.C. Lim, IEEE J. Quantum Elect. 39 (2003) 979.
- [8] R.A. Jackson, M.E.G. Valerio, J.F. Lima, Radiat. Eff. Def. Sol. 151 (1999) 249.
- [9] M.E.G. Valerio, R.A. Jackson, J.F. Lima, J. Phys.: Condens. Matter 12 (2000) 7727.
- [10] R.A. Jackson, M.E.G. Valerio, J.F. Lima, J. Phys.: Condens. Matter 13 (2001) 2147.
- [11] M.A. Couto dos Santos, M.E.G. Valerio, R.A. Jackson, J.F. Lima, Chem. Phys. Lett. 369 (2003) 90.
- [12] J.B. Amaral, D.F. Plant, M.E.G. Valerio, R.A. Jackson, J. Phys.: Condens. Matter 15 (2003) 2523.
- [13] J.D. Gale, Philos. Mag. B 73 (1996) 3.
- [14] J.D. Gale, J. Chem. Soc., Faraday Trans. 93 (1997) 629.
- [15] J. Corish, C.R.A. Catlow, P.W.M. Jacobs, S.H. Ong, Phys. Rev. B 25 (1982) 6425.
- [16] N.F. Mott, M.J. Littleton, Trans. Faraday Soc. 34 (1938) 485.
- [17] C.R.A. Catlow, J. Chem. Soc., Faraday Trans. II 85 (1989) 335.
- [18] B.R. Judd, Phys. Rev. 127 (1962) 750.
- [19] G. Ofelt, J. Chem. Phys. 37 (1962) 511.
- [20] O.L. Malta, Chem. Phys. Lett 88 (1982) 353.
- [21] O.L. Malta, S.J.L. Ribeiro, M. Faucher, P. Porcher, J. Phys. Chem. Solids 52 (1991) 587.
- [22] P. Porcher, M.A. Couto dos Santos, O.L. Malta, Phys. Chem. Chem. Phys. 1 (1999) 397.
- [23] C.K. Jørgensen, Modern Aspects of Ligand Field Theory, North Holland, Amsterdam, 1971.
- [24] M.A. Couto dos Santos, P. Porcher, J.C. Krupa, J.Y. Gesland, J. Phys.: Condens. Matter 8 (1996) 4643.