Computer modelling of intrinsic defects and rare earth doping in KYF_4, K_2YF_5 and KY_3F_{10}

E. M. Maddock[1], R. A. Jackson[1] and M. E. G. Valerio[2]

[1] Lennard-Jones Laboratories, School of Physical and Geographical Sciences, Keele University, Keele, Staffordshire, ST5 5BG, UK.

[2] Physics Department, Federal University of Sergipe, Campus Universitario, 49100-000 São Cristovão, SE, Brazil.

r.a.jackson@chem.keele.ac.uk

Abstract. A computational study of KYF_4, KY_3F_{10} and K_2YF_5 is presented. Energy minimisation techniques have been used to obtain structural models of the materials and intrinsic defect calculations have been performed. Rare earth doping has been considered at all cation sites and solution energies are presented which show the preference of isovalent doping at the Y^{3+} site.

1. Introduction

Mixed metal fluorides of the KYF family have raised interest for the development of solid state lasers since they are able to accommodate rare earth ions at the non-centrosymmetric Y^{3+} sites. This paper presents computational studies of KYF_4, K_2YF_5 and KY_3F_{10}, each of which belongs to a different space group [1-3], however shows similar responses to both intrinsic defect formation and rare earth doping processes.

This work follows studies of other fluoride materials such as BaY_2F_8 [4] and LaF_3 [5] where interesting trends have been obtained which have rendered these materials as possible candidates for optical applications. Rare earth doping can be used to enhance optical properties of materials and therefore calculations can be performed to obtain the solution energies which represent the energy of the whole doping process including any charge compensatory mechanisms that may be required.

2. Methodology

Energy minimisation calculations were carried out using energy minimisation techniques within the GULP code [6]. Buckingham potentials with an additional electrostatic term were used to model the structures (1). The K-F potential was fitted to give good representations of the KYF materials, the Y-F and F-F potentials were obtained from previous work [4]. The Mott-Littleton approximation [7] was used to model defects with region I and region II having cut-off radii of 10 and 15Å respectively.

$$V(r) = Aexp\left(\frac{-r_{ij}}{\rho}\right) - Cr^{-6} + \frac{q_1 q_2}{r_{ij}} \qquad (1)$$

Table 1. Potentials used for KYF material calculations

Interaction	A (eV)	ρ (Å)	C (eV Å^6)	k (eV Å^{-2})
$K_{core} – F_{shell}$	5500.0000	0.2635	11.00	-
$Y_{core} – F_{shell}$	1547.6209	0.3023	0.00	-
$F_{shell} – F_{shell}$	1127.7000	0.2753	15.83	-
F_{core} - F_{shell}	-	-	-	20.77

2.1. Solution Energies

Energies for the substitution of cations by trivalent rare earth ions were calculated and converted into solution energies using the expressions given below. Unbound solution energies were calculated using average vacancy energies while bound solution energies have been calculated by specifying the identity and position of charge compensatory vacancies.

i. Substitution at Y^+ site (expression common to all materials)

$$E_{sol} = M_Y - E_{latt}(MF_3) + E_{latt}(YF_3)$$

ii. Substitution at K^+ site

a. $2K^+$ vacancies as charge compensation (expression common to all materials)

$$E_{sol} = M_K^{\cdot\cdot} + 2V_K^{/} - E_{latt}(MF_3) + 3E_{latt}(KF)$$

b. Alternative charge compensation

i. KYF_4

$$E_{sol} = M_K^{\cdot\cdot} + V_Y^{////} + V_F^{\cdot} + E_{latt}(KYF_4) - E_{latt}(MF_3)$$

ii. KY_3F_{10}

$$E_{sol} = M_K^{\cdot\cdot} + 3V_Y^{////} + 7V_F^{\cdot} + E_{latt}(KY_3F_{10}) - E_{latt}(MF_3)$$

iii. K_2YF_5

$$E_{sol} = M_K^{\cdot\cdot} + V_Y^{////} + V_K^{/} + V_F^{\cdot} + E_{latt}(K_2YF_5) - E_{latt}(MF_3)$$

3. Results and Discussion

Comparison of the generated models for the KYF materials with experimental data shows a good correlation of parameters, with all modelled parameters within 4.5% of the experimental values.

Table 2. Comparison of calculated and experimental structural parameters of (a) KYF_4, (b) KY_3F_{10} and (c) K_2YF_5.

Parameter	Exp.	Calc.	Difference	Units	%
(a) KYF_4 [1]					
Volume	1729.623694	1717.199642	-12.424052	Å^3	-0.72
a/b	14.060000	13.952835	-0.107165	Å	-0.76
c	10.103000	10.185098	0.082098	Å	0.81
(b) KY_3F_{10} [2]					
Volume	1538.059079	1472.215745	-65.843334	Å^3	-4.28
a/b/c	11.543150	11.376024	-0.167126	Å	-1.45
(c) K_2YF_5 [3]					
Volume	517.823843	540.049545	22.225701	Å^3	4.29
a	10.791000	11.067484	0.276484	Å	2.56
b	6.607000	7.753236	0.146236	Å	2.21
c	7.263000	7.225580	-0.037420	Å	-0.52

Intrinsic defect calculations show that the formation of anion vacancies is more favourable than the formation of cation vacancies and in particular yttrium vacancies. For all the materials the energy required for the formation of a fluorine vacancy is between 4.5 - 5.5 eV, with inequivalent fluorine species showing slightly differing vacancy formation energies.

Table 3. Solution energies of rare earth doping in KYF_4

Site RE^{3+}	Y1 Charge compensation not required	Y2 Charge compensation not required	K1 2K vacancy charge compensation	K1 Y and F vacancy charge compensation
La	0.9997	0.5097	6.4401	10.0247
Ce	0.8660	0.4324	6.4556	10.0403
Pr	0.7311	0.3552	6.4638	10.0484
Nd	0.6462	0.3119	6.4825	10.0672
Sm	0.3009	0.0800	6.3484	9.9331
Eu	0.3501	0.1814	6.5200	10.1047
Gd	0.2267	0.1168	6.4800	10.0647
Tb	0.1008	0.0208	6.3972	9.9819
Dy	0.1119	0.0914	6.5051	10.0897
Ho	0.2183	0.1269	6.5453	10.1299
Er	0.0408	0.0408	6.3504	9.9350
Tm	-0.0072	0.0873	6.3583	9.9430
Yb	0.0915	0.0856	6.5449	10.1295
Lu	0.0126	0.1562	6.4065	9.9912

Potassium vacancy formation energies are in the region of 6.0 – 7.5 eV for all materials. In contrast, the energy required for the formation of a yttrium vacancy for the KYF materials is in the region of 47.5 – 51.0 eV. The significantly greater energy required to form a yttrium vacancy can be attributed to the greater structural destabilisation induced by the removal of a trivalent ion.

Anion Frenkel defect energies have been calculated for each of the materials and energies in the region of 0.5 – 2.0 eV have been obtained for all materials. When compared to the calculated Schottky energies of 10.6971 eV for K_2YF_5, 12.2911 eV for KYF_4 and 14.7897 eV for KY_3F_{10}, it can be seen that Frenkel defect formation is much more energetically favourable in these materials.

Table 4. Solution energies of rare earth doping in KY_3F_{10}

Site RE^{3+}	Y Charge compensation not required	K 2K vacancy charge compensation	K 3Y + 7F vacancy charge compensation
La	0.6759	6.9777	34.5358
Ce	0.5557	7.0701	34.6282
Pr	0.4412	7.1562	34.7143
Nd	0.3626	7.2388	34.7969
Sm	0.1293	7.2064	34.7645
Eu	0.1736	7.4791	35.0372
Gd	0.1290	7.4623	35.0204
Tb	0.0383	7.3959	34.9540
Dy	0.0955	7.5647	35.1228
Ho	0.0623	7.6625	35.2206
Er	0.0111	7.6207	35.1788
Tm	0.0992	7.6806	35.2387
Yb	0.0245	7.7445	35.3026
Lu	0.1664	7.8176	35.3757

The solution energy results for unbound defects in all materials show that rare earth doping is significantly more favourable at the yttrium site than the potassium site. This can be attributed to the greater similarity of ionic radii of the rare earth ions to the yttrium ion coupled with no charge compensatory measures being required leading to reduced structural destabilisation. Calculations involving rare earth doping at the potassium site revealed that charge compensation through two potassium vacancies was far more favourable than using the alternative charge compensatory mechanism for each material which involved the formation of yttrium vacancies.

Table 5. Solution energies of rare earth doping in K_2YF_5

Site RE^{3+}	Y Charge compensation not required	K1 2K vacancy charge compensation	K1 Y, K and 2F vacancy charge compensation
La	0.9685	5.9279	12.6677
Ce	0.8364	5.9331	12.6730
Pr	0.7029	5.9343	12.6741
Nd	0.6163	5.9438	12.6837
Sm	0.2871	5.8437	12.5836
Eu	0.3275	6.0012	12.7410
Gd	0.2180	5.9866	12.7265
Tb	0.0978	5.9061	12.6460
Dy	0.1114	6.0047	12.7445
Ho	0.1853	6.0215	12.7613
Er	0.0285	5.9678	12.7076
Tm	0.0047	6.0206	12.7604
Yb	0.0650	6.0168	12.7566
Lu	0.0238	6.0808	12.8207

Bound defect calculations have been carried out to determine whether, when doping at the potassium site, the specific position and identity of the charge compensatory vacancies influences the energetics of the doping process.

Results show that where two potassium vacancies are used as charge compensation the position and therefore identity of the vacancies influences the favourability of the doping process. Figure 5 shows that in K_2YF_5 there are clear energetic differences in response to the specific substitution and vacancy site combination. Despite this, it can be seen that Sm^{3+} and Tb^{3+} dopants are the most favourable irrespective of the particular combination of substitution and vacancy sites. A similar conclusion can be drawn from doping rare earth ions into KYF_4 as shown by Figure 4.

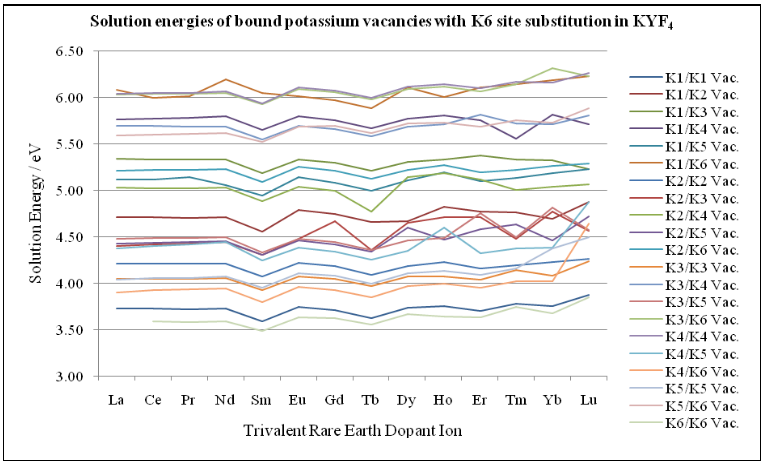

Figure 1. Bound solution energies of rare earth doping at a potassium site in KYF_4.

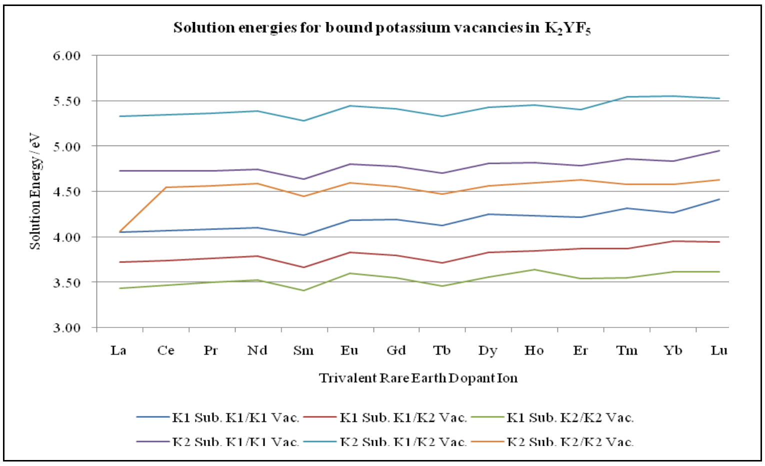

Figure 2. Bound solution energies of rare earth doping at the potassium sites in K_2YF_5.

4. Conclusion

Structural models for KYF_4, K_2YF_5 and KY_3F_{10} have been generated which show reasonable agreement with experimental data. It has been shown that for all materials the formation of anion Frenkel defects is significantly more favourable than the formation of Schottky defects which follows since, the formation of a Y^{3+} vacancy in these materials is particularly unfavourable.

Calculations involving the substitution of trivalent rare earth ions into the materials have shown that substitution at the Y^{3+} site is significantly more favourable. The similarity in ionic radii of the rare earth ions and the Y^{3+} ion allow isovalent substitution with minimal structural distortion. The energetic expense of substitution at the K^+ site can be attributed to the charge compensatory mechanism employed as shown by the bound defect calculations. In general however it can be noted that Sm^{3+} and Tb^{3+} dopants show particular interest as they exhibit lower solution energies.

5. Acknowledgements

The authors would like to thank iEPSAM at Keele University for financial support.

References

[1] Le Fur Y, Khaidukov NM, Aleonard S, Acta Crystallographica C**48** 978-982 (1992)
[2] Kharitonov YA, Gorbunov YA, Maximov BA, Kristallografiya **28** (5) 1031-1032 (1983)
[3] Grzechnik A, Crichton WA, Gesland J-Y, Solid State Sciences **5** 757-764 (2003)
[4] Amaral JB, Couto dos Santos MA, Valerio MEG, Jackson RA, Applied Physics B **81** (6) 841-846 (2005)
[5] Jackson RA, Valerio MEG, Amaral JB, Couto dos Santos MA, Maddock EM, Physica Status Solidi (c) **4** (3) 1185-1188 (2007)
[6] Gale JD, Journal of the Chemical Society Faraday Transactions **93** 629-637 (1997)
[7] Mott NF & Littleton MJ, Transactions of the Faraday Society **34** 485-499 (1938)