Computer modelling of intrinsic defects and rare earth doping in KYF₄, K₂YF₅ and KY₃F₁₀

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Abstract. A computational study of KYF₄, KY₃F₁₀ and K₂YF₅ 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 Y³⁺ 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 Y³⁺ sites. This paper presents computational studies of KYF₄, K₂YF₅ and KY₃F₁₀, 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 BaY₂F₈ [4] and LaF₃ [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.

\[ V(r) = A \exp\left(-\frac{r_{ij}}{\rho}\right) - C r^{-6} + \frac{e_1 e_2}{r_{ij}} \]  

(1)
Table 1. Potentials used for KYF material calculations

| Interaction          | A (eV)   | \( \rho \) (Å) | C (eV Å\(^6\)) | k (eV Å\(^{-2}\)) |
|----------------------|----------|----------------|-----------------|-------------------|
| \( K_{\text{core}} - F_{\text{shell}} \) | 5500.0000 | 0.2635         | 11.00           | -                 |
| \( Y_{\text{core}} - F_{\text{shell}} \) | 1547.6209 | 0.3023         | 0.00            | -                 |
| \( F_{\text{shell}} - F_{\text{shell}} \) | 1127.7000 | 0.2753         | 15.83           | -                 |
| \( F_{\text{core}} - F_{\text{shell}} \) | -        | -              | -               | 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)

\[
E_{\text{sol}} = M_Y - E_{\text{latt}}(MF_3) + E_{\text{latt}}(YF_3)
\]

ii. Substitution at \( K^+ \) site

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

\[
E_{\text{sol}} = M_{K^+} + 2V_{K^+} - E_{\text{latt}}(MF_3) + 3E_{\text{latt}}(KF)
\]

b. Alternative charge compensation

i. \( KYF_4 \)

\[
E_{\text{sol}} = M_{K^+} + V_{Y^+} + V_{F^-} + E_{\text{latt}}(KYF_4) - E_{\text{latt}}(MF_3)
\]

ii. \( KY_3F_{10} \)

\[
E_{\text{sol}} = M_{K^+} + 3V_{Y^+} + 7V_{F^-} + E_{\text{latt}}(KY_3F_{10}) - E_{\text{latt}}(MF_3)
\]

iii. \( K_2YF_5 \)

\[
E_{\text{sol}} = M_{K^+} + V_{Y^+} + V_{F^-} + E_{\text{latt}}(K_2YF_5) - E_{\text{latt}}(MF_3)
\]

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 (a) \( KYF_4 \) [1] | Exp. | Calc. | Difference | Units | %  |
|-----------------------------|------|-------|------------|-------|----|
| 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 KYF₄

| Site RE³⁺ | 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.

Table 4. Solution energies of rare earth doping in KY₃F₁₀

| Site RE³⁺ | 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$_4$. 
4. Conclusion
Structural models for KYF₄, K₂YF₅ and KY₃F₁₀ 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 Y³⁺ 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 Y³⁺ site is significantly more favourable. The similarity in ionic radii of the rare earth ions and the Y³⁺ 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 Sm³⁺ and Tb³⁺ dopants show particular interest as they exhibit lower solution energies.

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