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Computer modelling of thorium doping in LiCaAlF₆ and LiSrAlF₆: application to the development of solid state optical frequency devices

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Abstract

This paper describes computer modelling of thorium doping in crystalline LiCaAlF₆ and LiSrAlF₆. The study has been motivated by the interest in using these materials as hosts for ²²⁹Th nuclei, which are being investigated for use as frequency standards. The dopant sites and form of charge compensation are obtained; this information is essential for the further development and optimization of these devices.

1. Introduction

The mixed metal fluorides LiCaAlF₆ (LiCAF) and LiSrAlF₆ (LiSAF) have previously been investigated for use in photonic devices because they are good hosts for optically active cations and can be easily grown [1]. Examples of applications include the use of Nd³⁺-LiCaAlF₆ in photolithography [2] and Ce³⁺-LiCaAlF₆ in UV chirped-pulse amplification [3]. In addition, both Ce³⁺-doped LiCaAlF₆ and LiSrAlF₆ have been reported as leading candidates for tuneable solid state lasers in the UV region [4, 5]. Computer modelling is a useful technique for determining the location of dopant ions in materials and the energetics of the doping process, and two previous papers from the authors of this study have considered doping of LiCAF and LiSAF by a range of dopants [6, 7].

The interest in doping LiCAF/LiSAF with thorium stems from the recent observation that the ²²⁹Th nucleus has a unique property: unlike most nuclei with excitation energies in the keV range, this particular nucleus has its first excited energy

level only about 8 eV above the ground state [8]. This opens the possibility to excite and manipulate an atomic nucleus with vacuum ultra-violet (VUV) laser radiation. The approach is therefore to dope the thorium atoms into a VUV transparent crystal so that they can be probed by laser spectroscopy. With this system it should be possible to build a novel optical frequency standard, referenced to the VUV transition in the ²²⁹Th nucleus. This ‘nuclear clock’ architecture promises up to six orders of magnitude improvement in precision over next-generation optical atomic clocks, while simultaneously reducing experimental complexity. Because nuclear energy levels are relatively insensitive to their environment, the complicated vacuum apparatus of current atomic clocks could be replaced by a single crystal doped with ²²⁹Th atoms. LiCAF and LiSAF are being considered as candidate crystals for these applications [9].

The present paper will consider the doping of thorium into LiCAF and LiSAF with a view to identifying the preferred doping sites and charge compensation mechanisms. This information is important to help with future development of devices based on these materials.

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Table 1a. Structural agreement obtained for ThF₄ with fitted Th⁴⁺-F⁻ potential and fitted potential parameters.

| | Experimental [11] | Simulated | % difference |
|---|-------------------|-----------|--------------|
| <i>a</i> (Å) | 13.049 | 13.089 | 0.31 |
| <i>b</i> (Å) | 11.120 | 10.993 | -1.15 |
| <i>c</i> (Å) | 8.538 | 8.546 | 0.09 |
| <i>β</i> (deg) | 126.31 | 125.80 | -0.41 |
| Potential parameters: <i>A</i> = 3500.0 eV, <i>ρ</i> = 0.2980 Å | | | |
| <i>(C</i> = 0.0 eV Å ⁶) | | | |

2. Computational method

The methodology adopted in this work is the same as used in the previously published papers on LiCAF/LiSAF [6, 7]. The main additional requirement is a potential to model the interaction of the doped thorium with the lattice. Assuming a charge state of +4 for the thorium, a Th⁴⁺-F⁻ potential is required to supplement the potentials for the host lattice described in [6]. All calculations have been carried out using the GULP code [10], which is a general purpose program well-suited to atomistic calculations on materials, with consistent region I and region IIA radii of 10 Å and 15 Å respectively and a cut-off of 10 Å for the short range potentials.

2.1. Derivation of a potential for the Th⁴⁺-F⁻ interaction

A potential describing the interaction between Th⁴⁺ and F⁻ was obtained by fitting to the ThF₄ structure [11]. As in our previous papers, a Buckingham potential was employed:

$$V(r) = A \exp(-r/\rho) - Cr^{-6}.$$

The structural agreement and the potential parameters are given in table 1a (noting that the fitted value of the ‘*C*’ parameter was 0, in line with similar interactions). The level of agreement obtained is sufficient to give confidence in the use of the potential in the calculations presented later in the paper. In addition, the predicted elastic constant matrix for ThF₄ is given in table 1b.

3. Results

3.1. Possible solution schemes

When Th⁴⁺ is doped into either LiCAF or LiSAF there are three possible dopant sites and a range of possible charge compensation schemes. It is noted that charge compensation will always be needed given the charges of the dopant sites

Table 2. Energies (eV) for substitution of Th⁴⁺ ions onto lattice sites in LiCAF and LiSAF.

| LiCAF | | | LiSAF | | |
|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Th _{Al} ^{••} | Th _{Ca} ^{••} | Th _{Li} ^{••} | Th _{Al} ^{••} | Th _{Sr} ^{••} | Th _{Li} ^{••} |
| -45.94 | -41.68 | -6.93 | -46.89 | -44.34 | -7.41 |

Table 3. Reaction schemes for solution of Th⁴⁺ ions in LiCAF.

| Scheme | Site | Reaction |
|-----------|------------------|---|
| (a) (i) | Li ⁺ | ThF ₄ + Li _{Li} → Th _{Li} ^{••} + V _{Al} ^{•••} + LiF + AlF ₃ |
| (a) (ii) | Li ⁺ | ThF ₄ + 4Li _{Li} → Th _{Li} ^{••} + 3V _{Li} ^{••} + 4LiF |
| (a) (iii) | Li ⁺ | ThF ₄ + 2Li _{Li} → Th _{Li} ^{••} + V _{Ca} ^{••} + V _{Li} ^{••} + 2LiF + CaF ₂ |
| (a) (iv) | Li ⁺ | ThF ₄ + Li _{Li} → Th _{Li} ^{••} + 3F _I ^{••} + LiF |
| (b) (i) | Ca ²⁺ | ThF ₄ + Ca _{Ca} → Th _{Ca} ^{••} + V _{Ca} ^{••} + 2CaF ₂ |
| (b) (ii) | Ca ²⁺ | ThF ₄ + Ca _{Ca} → Th _{Ca} ^{••} + 2V _{Li} ^{••} + CaF ₂ + 2LiF |
| (b) (iii) | Ca ²⁺ | ThF ₄ + Ca _{Ca} → Th _{Ca} ^{••} + V _{Li} ^{••} + F _I ^{••} + CaF ₂ + LiF |
| (b) (iv) | Ca ²⁺ | ThF ₄ + Ca _{Ca} → Th _{Ca} ^{••} + 2F _I ^{••} + CaF ₂ |
| (c) (i) | Al ³⁺ | ThF ₄ + Al _{Al} → Th _{Al} ^{••} + V _{Li} ^{••} + LiF + AlF ₃ |
| (c) (ii) | Al ³⁺ | ThF ₄ + Al _{Al} → Th _{Al} ^{••} + F _I ^{••} + AlF ₃ |

(+1 for Li, +2 for Ca/Sr and +3 for Al). The possible charge compensation schemes are listed below. Four different interstitial sites were considered which will be given in the results tables when they are used.

- (a) Solution at Li⁺
 - (i) 1 Al³⁺ vacancy;
 - (ii) 3 Li⁺ vacancies;
 - (iii) 1 Li⁺ vacancy plus 1 Ca²⁺/Sr²⁺ vacancy;
 - (iv) 3 F⁻ interstitials.
- (b) Solution at Ca²⁺/Sr²⁺
 - (i) 1 Ca²⁺/Sr²⁺ vacancy;
 - (ii) 2 Li⁺ vacancies;
 - (iii) 1 Li⁺ vacancy and 1 F⁻ interstitial;
 - (iv) 2 F⁻ interstitials.
- (c) Solution at Al³⁺
 - (i) 1 Li⁺ vacancy;
 - (ii) 1 F⁻ interstitial.

Table 2 gives the energies needed to substitute a Th⁴⁺ ion at each cation site in LiCAF and LiSAF. It is important to stress that these energies involve removal of a lattice ion from the lattice and substitution by a Th⁴⁺ ion and as such do not have any physical significance until they are combined with the energies of other terms involved in the doping process to obtain solution energies, as discussed in section 3.2.

The reaction schemes corresponding to the solution schemes given above are shown, for LiCAF, in table 3. Corresponding reactions can be obtained for LiSAF.

Table 1b. Calculated elastic constants for ThF₄ (10¹¹ dyne cm⁻² = 10 GPa).

| Indices | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|----------|----------|----------|---------|----------|---------|
| 1 | 20.31186 | 7.68087 | 5.18597 | 0.00000 | -2.06580 | 0.00000 |
| 2 | 7.68087 | 15.43619 | 8.53125 | 0.00000 | 0.34472 | 0.00000 |
| 3 | 5.18597 | 8.53125 | 16.11532 | 0.00000 | -2.12850 | 0.00000 |
| 4 | 0.00000 | 0.00000 | 0.00000 | 6.73454 | 0.00000 | 0.44180 |
| 5 | -2.06580 | 0.34472 | -2.12850 | 0.00000 | 5.15133 | 0.00000 |
| 6 | 0.00000 | 0.00000 | 0.00000 | 0.44180 | 0.00000 | 5.67174 |

Table 4. Solution energies (eV) for Th⁴⁺ doping in LiCAF and LiSAF

| Solution scheme details, including interstitial positions where appropriate (see table 3) | LiCAF | | LiSAF | |
|---|---------|-------|---------|-------|
| | Unbound | Bound | Unbound | Bound |
| (a) (i) | 10.03 | 1.95 | 8.73 | 1.77 |
| (a) (ii) | 3.82 | 1.96 | 3.73 | 1.77 |
| (a) (iii) | 5.57 | 2.84 | 5.41 | 2.70 |
| (a) (iv) $(\frac{1}{2} \frac{1}{2} 0), (\frac{1}{2} 0 0), (\frac{3}{4} \frac{1}{2} 0)$ | 4.18 | 1.92 | 3.99 | 1.66 |
| $(\frac{1}{2} \frac{1}{2} 0), (\frac{1}{2} 0 0), (\frac{1}{4} \frac{1}{4} 0)$ | 4.27 | 1.65 | 3.97 | 1.36 |
| $(\frac{1}{2} \frac{1}{2} 0), (\frac{1}{4} \frac{1}{4} 0), (\frac{3}{4} \frac{1}{2} 0)$ | 4.17 | 1.90 | 3.86 | 1.81 |
| $(\frac{1}{2} 0 0), (\frac{1}{4} \frac{1}{4} 0), (\frac{3}{4} \frac{1}{2} 0)$ | 4.18 | 2.07 | 3.86 | 1.36 |
| (b) (i) | 3.76 | 2.15 | 3.82 | 2.62 |
| (b) (ii) | 2.03 | 1.20 | 2.12 | 1.37 |
| (b) (iii) $(\frac{1}{2} \frac{1}{2} 0)$ | 2.23 | 1.02 | 2.28 | 0.97 |
| $(\frac{1}{2} 0 0)$ | 2.23 | 1.02 | 2.28 | 1.12 |
| $(\frac{1}{4} \frac{1}{4} 0)$ | 2.11 | 1.08 | 2.13 | 0.96 |
| $(\frac{3}{4} \frac{1}{2} 0)$ | 2.23 | 1.02 | 2.10 | 0.97 |
| (b) (iv) $(\frac{1}{2} \frac{1}{2} 0), (\frac{1}{2} 0 0)$ | 2.43 | 0.97 | 2.44 | 0.89 |
| $(\frac{1}{2} \frac{1}{2} 0), (\frac{1}{4} \frac{1}{4} 0)$ | 2.30 | 1.00 | 2.30 | 0.85 |
| $(\frac{1}{2} \frac{1}{2} 0), (\frac{3}{4} \frac{1}{2} 0)$ | 2.42 | 0.83 | 2.26 | 0.68 |
| $(\frac{1}{2} 0 0), (\frac{1}{4} \frac{1}{4} 0)$ | 2.31 | 1.08 | 2.30 | 0.76 |
| $(\frac{1}{2} 0 0), (\frac{3}{4} \frac{1}{2} 0)$ | 2.43 | 0.98 | 2.26 | 0.76 |
| $(\frac{1}{4} \frac{1}{4} 0), (\frac{3}{4} \frac{1}{2} 0)$ | 2.30 | 0.96 | 2.12 | 0.68 |
| (c) (i) | 3.23 | 1.95 | 3.09 | 1.77 |
| (c) (ii) $(\frac{1}{2} \frac{1}{2} 0)$ | 3.52 | 2.36 | 3.33 | 1.92 |
| $(\frac{1}{2} 0 0)$ | 3.53 | 2.43 | 3.33 | 1.92 |
| $(\frac{1}{4} \frac{1}{4} 0)$ | 3.34 | 2.46 | 3.11 | 2.15 |
| $(\frac{3}{4} \frac{1}{2} 0)$ | 3.52 | 2.24 | 3.06 | 1.90 |

3.2. Calculation of solution energies

In modelling the doping of any ion into a lattice, calculation of the solution energy is essential, as this quantity includes all the energy terms involved in the doping process, including lattice energies and defect formation energies (where charge compensation is needed).

Solution energies are calculated for each of the reactions in table 3. The energies have been calculated in two ways: (i) assuming no interaction between defects and (ii) including the defect–defect binding energy.

As an example of a solution energy calculation, consider reaction (b) (i), where the expression for calculation of the solution energy is:

$$E_{\text{sol}} = -E_{\text{latt}}(\text{ThF}_4) + E(\text{Th}_{\text{Ca}}^{\bullet\bullet}) + E(V_{\text{Ca}}^{\prime\prime}) + 2E_{\text{latt}}(\text{CaF}_2).$$

The intrinsic defect formation energies and lattice energies are taken from [6] where their calculation was described in detail.

Solution energies for Th⁴⁺ doping in LiCAF and LiSAF are given in table 4, where the unbound and bound values are given in separate columns. The significant differences between these energies confirm the energetic preference for the Th⁴⁺ dopant to be found in a cluster configuration.

3.3. Discussion of results

The lowest energy solution schemes for Th⁴⁺ in both LiCAF and LiSAF involve solution at the Ca²⁺ site with F⁻ interstitial vacancy compensation. The lower solution energies for LiSAF reflect the larger lattice parameters and resulting additional space for F⁻ interstitials. Thus it is predicted that Th⁴⁺ will substitute at the Ca²⁺ or Sr²⁺ site as applicable, but the existence of F⁻ interstitial ions must be taken into account when considering the effect of the surrounding lattice on the nuclear transitions within the ²²⁹Th nucleus.

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