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Modelling the concentration dependence of doping in optical materials

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Abstract. As well as understanding the location of dopants in optical materials, it is also important to understand how much dopant can be added to a given material. A method for calculating the maximum concentration of dopants has been developed, and applied to dopants in mixed metal fluorides for optical and nuclear clock applications. Applications to rare earth doping in YLiF₄, and Th doping in LiCaAlF₆/LiSrAlF₆ are described, and compared with available experimental data.

1. Introduction

This paper is part of an ongoing modelling study of dopants in optical materials. Previous papers have addressed the question of where dopants are located in the host lattice (see e.g. [1]) and their effect on morphology [2], and an initial study of concentration dependence of dopants has been published [3].

The motivation for this study is to develop a method by which the maximum concentration of a given dopant in a host lattice can be predicted. This is useful information for device development and can potentially save time in crystal growth experiments.

The paper starts with a description of the method to be used, using rare earth doping in YLiF₄ as an example, and it is then applied to the doping of LiCaAlF₆/LiSrAlF₆ and CaF₂ with ²²⁹Th ions, which is relevant to the development of nuclear clocks using these materials discussed previously [4, 5].

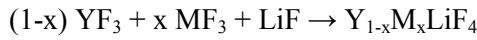
2. Methodology and Results

2.1 The doping process for rare earth ions in YLiF₄

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Doping YLiF₄ with rare earth (M³⁺) ions can be represented as follows (where doping at the Y site is assumed), and x is the mole fraction of dopant:



The energy of this reaction corresponds to the solution energy of the doping process, E_{sol}:

$$E_{\text{sol}} = E(\text{Y}_{1-x}\text{M}_x\text{LiF}_4) - [(1-x) E_{\text{latt}}(\text{YF}_3) + x E_{\text{latt}}(\text{MF}_3) + E_{\text{latt}}(\text{LiF})]$$

The terms in square brackets are calculated lattice energies, E_{latt}, and the only issue is in calculating the first term in the equation. This has been done using the equation below, which effectively splits the defective lattice energy into a perfect lattice component E_p (1) and a defect formation energy term E_D^{ML}:

$$E_{\text{D}}(x) = x E_{\text{D}}^{\text{ML}} + E_{\text{p}}(1)$$

The final solution energy expression then becomes:

$$E_{\text{sol}} = E(x E_{\text{D}}^{\text{ML}} + E_{\text{latt}}(\text{YLiF}_4)) - [(1-x) E_{\text{latt}}(\text{YF}_3) + x E_{\text{latt}}(\text{MF}_3) + E_{\text{latt}}(\text{LiF})]$$

Here the term E_D^{ML} is the substitution energy of an M³⁺ cation at the Y³⁺ site.

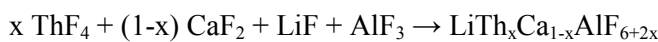
Using this expression, maximum dopant concentrations in mol % have been calculated for rare earth ions in YLiF₄, as given in table 1. These correspond to the value of 'x' when E_{sol} = 0.

Table 1. Calculated maximum dopant concentrations for rare earth ions in YLiF₄ [6]

Ion	Max. mol %	Ion	Max. mol %
La	0.69	Tb	1.41
Ce	0.76	Dy	1.28
Pr	0.85	Ho	1.40
Nd	0.93	Er	1.52
Sm	1.23	Tm	1.33
Eu	1.15	Yb	1.51
Gd	1.22	Lu	1.49

2.2 Th⁴⁺ doping in LiCaAlF₆

In a previous paper [4] the doping of LiCaAlF₆ with Th⁴⁺ has been discussed in the context of developing a 'nuclear clock' material which exploits the unusually low first nuclear excited state energy of the ²²⁹Th isotope. It is necessary to embed the Th in a transparent crystal, and the calculations predict that Th⁴⁺ will substitute at the Ca²⁺ site with charge compensation by the formation of two F⁻ interstitials. The doping process is therefore assumed to follow this reaction:



Using the approach described in 2.1, this leads to a solution energy expression as follows:

$$E_{\text{sol}} = E(\text{LiTh}_x\text{Ca}_{1-x}\text{AlF}_{6+2x}) - [x E_{\text{latt}}(\text{ThF}_4) + (1-x) E_{\text{latt}}(\text{CaF}_2) + E_{\text{latt}}(\text{LiF}) + E_{\text{latt}}(\text{AlF}_3)]$$

Which leads to:

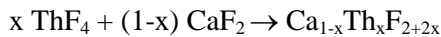
$$E_{\text{sol}} = E (x E_{\text{D}}^{\text{ML}} + E_{\text{latt}} (\text{LiCaAlF}_6)) - [x E_{\text{latt}} (\text{ThF}_4) + (1-x) E_{\text{latt}} (\text{CaF}_2) + E_{\text{latt}} (\text{LiF}) + E_{\text{latt}} (\text{AlF}_3)]$$

Now the term E_{D}^{ML} is the energy of substitution of the Th^{4+} ion at the Ca^{2+} site, plus the energy of formation of two F⁻ interstitials.

Setting $E_{\text{sol}} = 0$ a value of $x = 0.06$ or 6 mol% is obtained for the maximum dopant concentration of Th^{4+} ions in LiCaAlF_6 . Experiments are in progress to test these conclusions.

2.3 Th^{4+} doping in CaF_2

Th^{4+} doping in CaF_2 was considered in [5], where it was again found that the predicted location of the dopant Th^{4+} would be at the Ca^{2+} site, with charge compensation by F⁻ interstitials. The doping scheme is assumed to be:



The corresponding expression for the solution energy is:

$$E_{\text{sol}} = E (\text{Ca}_{1-x}\text{Th}_x\text{F}_{2+2x}) - [x E_{\text{latt}} (\text{ThF}_4) + (1-x) E_{\text{latt}} (\text{CaF}_2)]$$

This can be written as:

$$E_{\text{sol}} = E (x E_{\text{D}}^{\text{ML}} + E_{\text{latt}} (\text{CaF}_2)) - [x E_{\text{latt}} (\text{ThF}_4) + (1-x) E_{\text{latt}} (\text{CaF}_2)]$$

For binary systems like CaF_2 a minimum value of 'x' is not calculated, but it is possible to calculate E_{sol} as a function of x. Preliminary experimental measurements [7] suggest dopant concentrations of between 0.4-0.7 mol%, corresponding to solution energies in the range 2.3 – 3.5 eV. These values are of the same order of magnitude as solution energies calculated for many doping processes in optical materials. However, more detailed measurements are in progress, and a detailed comparison will be reported in a later publication.

3. Conclusions

This paper has presented a method for predicting the maximum concentration of dopants in optical materials, and has been applied to two representative systems. It is expected that the method will be further refined once more experimental data is available, but in its present form reliable predictions have been made.

4. References

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Appendix

Table of lattice energies and defect formation energies used in sections 2.2 and 2.3

Energy term	Energy/eV
$E_{\text{latt}}(\text{CaF}_2)$	-26.99
$E_{\text{latt}}(\text{LiF})$	-10.93
$E_{\text{latt}}(\text{AlF}_3)$	-63.99
$E_{\text{latt}}(\text{ThF}_4)$	-79.98
$E(\text{Th}_{\text{Ca}}^{\bullet\bullet})(\text{CaF}_2)$	-43.4
$E(\text{F}_i^{\prime})(\text{CaF}_2)$	-1.9
$E(\text{Th}_{\text{Ca}}^{\bullet\bullet})(\text{LiCaAlF}_6)$	-41.72
$E(\text{F}_i^{\prime})(\text{LiCaAlF}_6)$	-2.01