

An atomistic surface simulation study predicting morphologies and segregation in yttrium lithium fluoride

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ABSTRACT

The aim of this research on the laser material yttrium lithium fluoride (YLiF₄) is to provide the first study of its surface structure, morphology and the properties of rare-earth doped surfaces. The study utilises the METADISE computer code to model the surfaces using interatomic potentials. Equilibrium and growth morphologies are predicted and a detailed profile of segregation of rare-earth dopants to the three dominating surfaces is given. The (001), (011) and (112) surfaces dominate the morphology. Rare-earth dopants La to Sm show segregation to these surfaces, with the (112) surface being of particular interest. As this work demonstrates, it is likely to have dopants clustered towards it.

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1. Introduction

There is continued interest in producing new solid-state laser materials as well as profiling existing ones to improve their quality. Mixed metal fluorides are one group of interest, of which YLiF₄ (YLF) is one such material. YLF has been shown by many authors, for example Okada et al. [1], to be a viable UV laser when doped with Ce³⁺ cations. In addition, Colucelli et al. [2] and Schellhorn [3] describe laser behaviour with Yb³⁺ and Tm³⁺ doping respectively. It is also commercially available doped with Nd³⁺ cations, with wavelengths in the IR or green region [4]. YLF has been subject to a wide range of studies profiling the electronic transitions of the system through spectroscopic methods. However, to date there have been no detailed modelling studies of the surface structure, morphology or properties of defective surfaces.

YLF has the scheelite structure and belongs to the tetragonal crystal system with the centrosymmetric space group of I4₁/a [5]. The presence of the Y³⁺ cation with a similar ionic radius and identical charge state to many rare-earth cations means this material is ideal as a rare-earth doped laser material.

This work builds on the bulk modelling already undertaken [6] to provide the first description of the low index surfaces of YLF and to predict the morphology of the crystal under different conditions. Once the morphologically important surfaces were established, any segregation of the optically active rare-earth dopants was investigated in order to suggest where within the crystal the dopants would

reside. If a rare-earth cation has a strong driving force for surface segregation this is an important consideration for any laser application.

2. Computational method

The code METADISE [7] was used in this study using the interatomic potentials from previous work on the bulk properties of the material [6]. An atomistic simulation approach was employed because it allows defect segregation energies to be calculated with low computational cost compared to other techniques. Also, the natural extension to this work, of considering higher dopant concentrations, can only be achieved through large simulation cells, which this atomistic interatomic potential approach facilitates.

The potentials used were in the form of electrostatic supplemented Buckingham potentials and reproduced the structure to within 2% of the observed lattice parameters. The previous study confirmed that rare-earth cations are most likely to dope at the Y site in the lattice, partially due to the like charge of the cations resulting in no charge compensation being required. This was used as the basis for doped surface calculations in the present study. Also, the bulk defect energy values from the study were used to calculate possible segregation of defects to surfaces.

The approach taken by METADISE is a two region one, where the atoms in region I, which lie close to the surface, are allowed to fully relax through minimisation techniques. The atoms in region II are fixed to represent the bulk. The size of region I was variable due to the different repeat units but was made sufficiently large so that the upper-most atoms relax completely without seeing the presence of region II. This was checked through scaling of region sizes until convergence of the total surface energy was achieved and the lowest

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most ions in region I experienced no displacement during relaxation thereby ensuring there was no disjoint across the region boundary.

Initially all the valid cuts for the low index surfaces were found by systematically slicing through layers of atoms working through the repeat unit of a particular index. It is possible to slice through individual atoms within each layer, but this approach was deemed unnecessary as low surface energy (i.e. highly stable) cuts for all surfaces were found through slicing in layers. A valid cut is one that is non-polar and therefore has a non-infinite surface energy. A type 3 surface, as defined by Tasker [8], has a dipole perpendicular to the surface and can only be studied if the surface is reconstructed to remove the dipole first. As there are no experimental data to suggest such reconstructed polar surfaces appear and only further cuts for indices already calculated were found when allowing polar surfaces, this class of surface was not considered. High index surfaces would be unlikely to appear in the morphology due to their large surface areas and so were also not considered.

The lowest energy cuts were used to draw the morphology of YLF using a Wulff construction. The Wulff theorem states that the height of the normal vector to a surface index is proportional to the surface energy of that index, i.e. low surface energy faces dominate the morphology. This theorem is only true if all surfaces form in equilibrium; thus a morphology plot obtained using this technique is known as the equilibrium morphology. Surface energy is defined as the energy per unit area needed to transform a bulk region into surface region [9] as expressed by Eq. (1).

$$\gamma = (U_{\text{surf}} - U_{\text{bulk}})/A \quad (1)$$

Attachment energies have also been calculated, which provide a method in which growth morphology can be constructed. Attachment energy is defined as the energy released when a new layer is added to the surface [10]. Although attachment energy is a thermodynamic quantity, it can be used as a pseudo-kinetic one [11] because it is a measure of the ease with which a new layer is added. These energies are exothermic and therefore the absolute value is taken when constructing the morphology such that those surfaces with low (absolute) attachment energy are the slow growing faces and therefore dominate the morphology. The limitation with this method is that it is assumed there is bulk termination of the surface and no surface relaxation [10]. Gay and Rohl, with their MARVIN [12] code attempted to include relaxation into the attachment method; however, it is unclear what this represents physically within the model [13]. This work therefore uses the two assumptions of bulk termination and no surface relaxation for the attachment energy morphology.

METADISE incorporates the CHAOS [14] code, which, allows a defect to be added to a lattice site and the defect formation energy calculated. This is done using a two-region approach such that the interactions between ions in regions I and IIa are calculated explicitly while those with the rest of the system are approximated using Mott-Littleton methods. Further approximations have to be made due to the unique properties of surface defect calculation; for example, the energy is calculated as a sum of planar and volume integrals rather than a summation [13,14]. Regions I and IIa were selected as a trade-off between convergence and computation time, at values of 9 Å and 35 Å respectively. Convergence was satisfied when the g_{norm} reached 5×10^{-4} .

Rare earth dopants were added systematically starting at Y site nearest to the surface interface on the most morphologically important surfaces. The dopant was then moved to the next Y site moving down through the system from the surface towards to the bulk. To calculate segregation energies, the defect energies at deep bulk positions in METADISE were compared to the values obtained in the previous study from Mott-Littleton calculations. The surface defect energies were then adjusted by this difference to account for any shift in the defect energies generated by the electrostatic field caused

by the interface. The difference in defect formation energy at the surface and in the bulk was plotted as a function of depth from the surface. Any surface segregation could then be established. The rare-earth fluoride potentials used in this work were taken from Valerio et al. [15].

McLean proposed in 1957 [16] that the main factor in determining surface segregation of isovalent dopants was elastic strain U_{elastic} caused by the difference in cation sizes between the dopant and lattice ions Δr .

$$U_{\text{elastic}} = 6\pi Br^3(\Delta r/r)^2/(1 + 3B/4\mu) \quad (2)$$

Here r is the radius of the lattice cation, and B is the bulk modulus of the dopant and μ is the shear modulus of the host lattice. If B and μ are assumed to be constant for all of the dopants, segregation energy would be proportional to $(\Delta r/r)^2$. A number of studies of oxide materials [13] have shown a good fit to this theory.

3. Results and discussion

3.1. Morphologies

Surface energies and attachment energies have been calculated for all of the valid cuts of the low index surfaces. Table 1 lists the energies for the most stable cut of each of these surfaces. This shows that the most stable surface, in terms of surface energy, is the (112) surface followed by the (011) surface. The slowest growing surface, based on attachment energy, is the (001) surface.

Fig. 1 lists the structure of the first repeat unit for the (112), (001) and (011) surfaces. The cut shown in the bold is the most stable cut and therefore the one used in further calculations. With the exception of the (011) surface the most stable termination is F-F.

The morphologies of YLF were constructed using a Wulff construction. The equilibrium morphology based on surface energy was constructed as well as the growth attachment based morphology, as shown in Fig. 2. These two morphologies show considerable differences. The (001) surface dominates the growth morphology (46.74%), whereas, in the equilibrium morphology it is a much smaller surface (2.28%). Also, the (112) surface, which dominates the equilibrium morphology, does not appear in the growth-based model. The high index surface (211) appears in the equilibrium morphology (1.78%) due to a large reduction in surface energy through relaxation, in which, the anions shift to a different configuration. The percentage coverage for all surfaces is listed in Table 2.

Many other studies have found a similar situation in which the two morphologies are very different from each other [11,17,18].

Table 1
Calculated low index surface energies.

Index	Surface area (Å ²)	Surface energy (J/m ²)	Attachment energy (eV/unit-cell)
(001)	26.972	0.718	−0.101
(010)	54.869	0.657	−0.161
(011)	61.140	0.596	−0.160
(012)	76.946	0.750	−0.367
(021)	113.004	0.645	−0.972
(110)	77.597	0.717	−0.308
(111)	82.151	0.635	−0.401
(112)	94.505	0.560	−0.260
(120)	122.691	0.744	−0.139
(121)	125.621	0.725	−0.584
(122)	134.027	0.766	−1.220
(210)	122.691	0.818	−1.225
(211)	125.621	0.645	−0.853
(221)	157.520	0.838	−1.147

(001)				
Height (Å)		Cut	Height (Å)	Cut
0	F--F--	(a)	5.2	F--F--
0.2			5.4	
0.4			5.6	
0.6			5.8	
0.8	Y--Li--		6	
1			6.2	Y--Li--
1.2			6.4	
1.4			6.6	
1.6	F--F--		6.8	
1.8			7	F--F--
2			7.2	
2.2			7.4	
2.4			7.6	
2.6	F--F--		7.8	
2.8			8	F--F--
3			8.2	
3.2			8.4	
3.4	Y--Li--		8.6	
3.6			8.8	Y--Li--
3.8			9	
4			9.2	
4.2			9.4	
4.4	F--F--		9.6	F--F--
4.6				
4.8				
5				
(011)				
Height (Å)		Cut	Height (Å)	Cut
0.0	F--F--	(a)	0.0	F--F-- (a)
0.2			0.2	
0.4	Li--Li--		0.4	F--F--F--F--
0.6			0.6	
0.8			0.8	
1.0	F--F--	(b)	1.0	F--F--
1.2			1.2	Y--Li--Y--Li--Li--Y--Li--Y--
1.4	F--F--		1.4	F--F--
1.6	F--F--Y--Y--		1.6	
1.8			1.8	
2.0			2.0	F--F--F--F--
2.2			2.2	
2.4			2.4	F--F--
2.6				
2.8	Y--Y--F--F--	(c)		
3.0	F--F--			
3.2				
3.4	F--F--			
3.6				
3.8	Li--Li--	(d)		
4.0				
4.2	F--F--			

Fig. 1. Terminations of valid cuts for the (001), (011) and (112) surfaces. Cuts shown in bold are the most stable ones.

This is to be expected because morphologies depend on a number of factors, including the conditions during growth, and therefore the prediction result depends on which model (and which assumptions) are used. There is currently no experimental data to compare these predictions with, but other studies [11,17,18] have shown that predictions made by these methods are reliable. The reader can therefore have confidence in their reliability.

3.2. Rare-earth doping

YLF is of interest when doped with rare-earth ions. This may affect the energy of some surfaces, particularly where there is strong segregation. Any significant change in surface energies will alter the morphology.

In a previous study the defect energies for substituting 14 rare-earth cations into YLF were calculated [6]. The study confirmed the

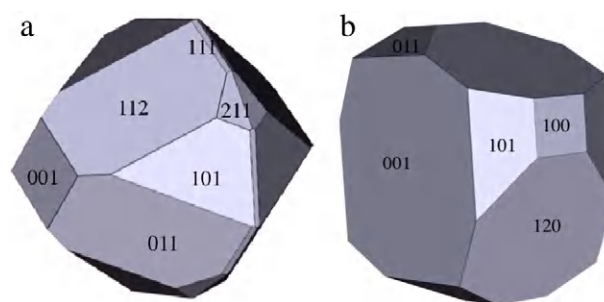


Fig. 2. Predicted morphologies for YLF: (a) equilibrium, (b) growth.

dopants would substitute at the Y site. This present work builds on this to model defective surfaces.

The morphologically dominating surfaces (112), (001) and (011) were doped at Y sites at different depths from the surface working down into the crystal. These three surfaces were chosen because they account for 91% of the total equilibrium morphology. While the (111) surface is more dominant in this mode, the (001) surface was studied, because it also appears strongly in the growth morphology, allowing a comparison to be made. The plots in Fig. 3 show the difference in energy between doping at a particular depth on a surface compared to the bulk. A negative value indicates there is a driving energy for the dopant to lie at the surface rather than in the bulk.

The plots in Fig. 3 show surface segregation for all of the morphologically dominating surfaces; however, it is to a much greater extent with the (112) surface.

At the (001) surface, for the first 7 rare-earth cations the lowest energy position is around 3.8 Å from the surface, with the lowest energy being for La. The amount of segregation decreases moving across the row of rare-earth cations, with ions from Tb onwards having little segregation. The two exceptions are Tm and Lu, where the energy minimum is at the nearest Y site to the surface.

A very similar trend is seen for the (011) surface but with the minimum occurring at around 7 Å. The difference in energy at this depth compared to the bulk is very small, suggesting that surface segregation to this face is unlikely.

The (112) surface segregation plot has a more complicated profile with defect energies not reaching bulk values until 9 Å in depth. Rare-earth cations Tb to Er and Yb and Gd show no segregation to this surface while Tm and Lu show a small segregation tendency. However, the cations La to Sm show a large segregation to this surface. The deep surface depth of strong segregation suggests there are many sites for dopants at this surface, indicating that there may be clustering towards this face. This needs further study with a higher concentration of dopants. Clustering of the dopant ions can cause energy transfer between them due to the small interionic separation. This can result in the degradation of their optical activity [20].

The primary driving force for isovalent dopant segregation is elastic strain induced in the lattice. This results in dopants with ionic radius most different to the lattice ion radius segregating most. The ionic radius of Y is 1.019 Å and the rare-earth cations

have ionic radii starting at 1.16 Å for La (13.8% different) decreasing across the period to 0.977 Å for Lu (−4.1% different) [19]. The ionic radius of Ho is the most similar to Y, being 0.4% different. The segregation profile for the three surfaces studied, showing strong segregation for the first 4 cations in the period, fits this radii mismatch strain perfectly. The large positive values for segregation energy at the surface for Ho ions also agrees with the small elastic strain induced due to the close match in radii of the cations.

To conclude, these plots show for the first 4 rare-earth cations there is likely to be segregation to the (112) surface. The latter rare-earths in all surfaces studied show far less tendency to segregate, with Tm and Lu being the most likely of this group. These results are as expected as they show the driving force for segregation is elastic strain caused by the mismatch of the ions. Most work on YLF as a laser material have used dopants that this study suggests have a strong tendency to segregate to the (112) surface. This therefore should be taken into account in future work on this material.

4. Conclusions

Building on the previous interatomic potentials and bulk properties study on YLiF_4 , this paper has calculated the surface energy and attachment energy for the low index surfaces and used these to predict the equilibrium and growth morphologies. The (001), (011) and (112) indices were found to be the most morphologically important surfaces.

Rare-earth dopant energies were calculated for various sites from the surface down into the bulk. These were compared to bulk defect energies and the segregation profiles were drawn. This showed that for the cations La to Sm there is a large segregation towards the (112) surface. This surface profile also showed a deep depth of 9 Å in which segregation takes place suggesting a doped YLiF_4 crystal may have the dopants clustered towards the (112) surface, but this would need further study.

5. Future work

This study looked at doping a single defect in the surface region. In reality a higher concentration of defects would be present in the system. This can be modelled using METADISE and will form part of a future study. The defective (112) surface, in particular, needs further study as this work suggests it is of importance for rare-earth dopants. The effect of dopants on the surface energy of all surfaces will be calculated and predictions of defective morphology at various defect concentrations made.

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Table 2
Surface coverage, as a percentage of surface area, for all indices studied.

Surface	Percentage Coverage	
	Equilibrium	Growth
(001)	2.28%	46.74%
(010)	0.71%	5.31%
(011)	30.07%	13.17%
(111)	6.30%	–
(112)	58.86%	–
(120)	–	34.78%
(211)	1.78%	–

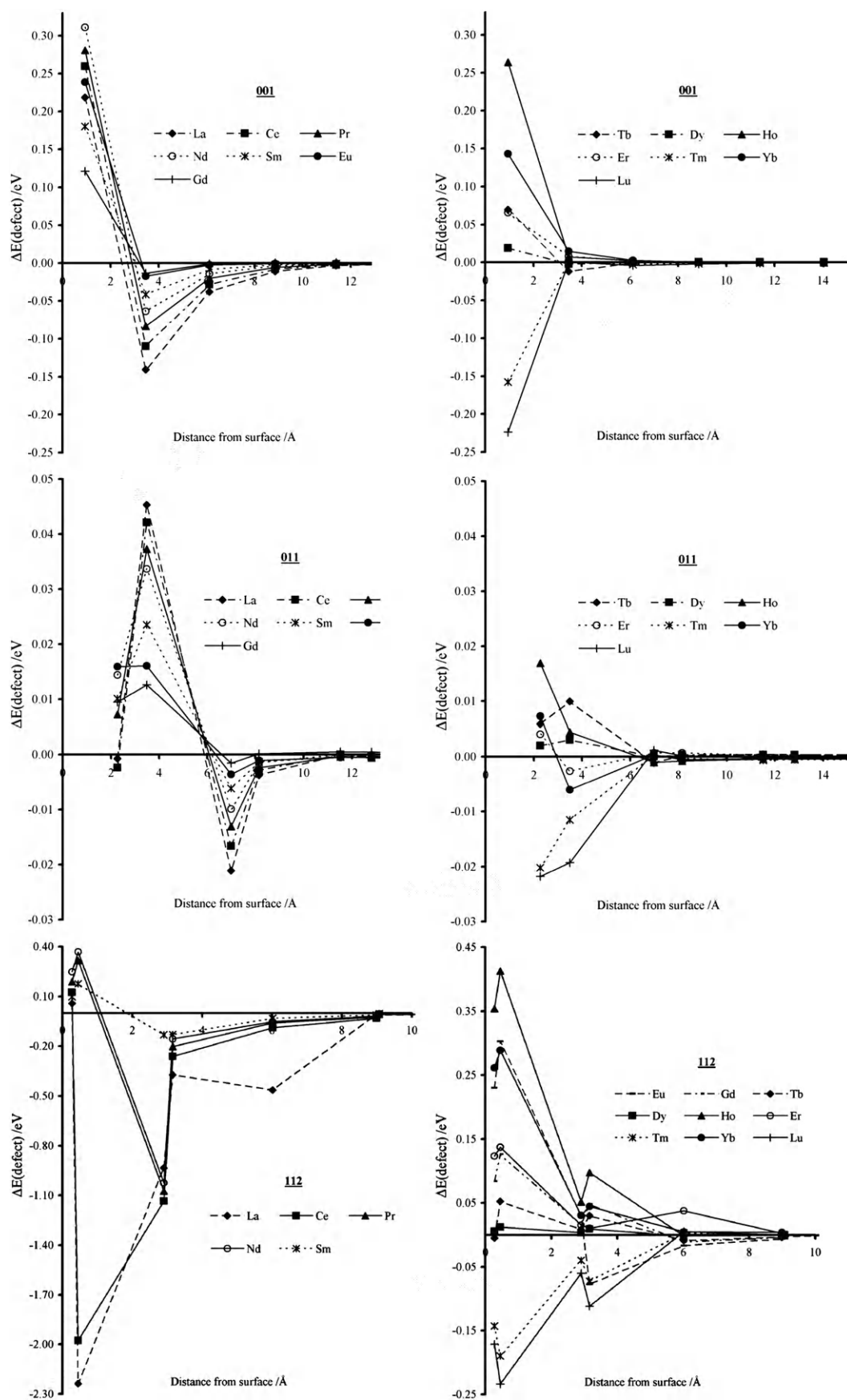


Fig. 3. Plots of the segregation energy for rare-earth ions at various depths from the surfaces studied.

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