Computer modelling of rare-earth dopants in BaLiF$_3$

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Abstract
Doping of BaLiF$_3$ by rare-earth ions is considered using computer modelling techniques. Solution energies for a range of possible doping mechanisms are calculated, and predictions made of doping sites and charge-compensation schemes. It is shown that there are definite trends going along the rare-earth series. Comparisons with experimental measurements are made where these are available.

1. Introduction

The incorporation of rare-earth dopants into BaLiF$_3$ is of interest because the presence of these dopants can give rise to potential technological applications in solid-state laser and other optical devices.

Experimental work on rare-earth-doped BaLiF$_3$ has included crystal growth studies of Ce^{3+}-doped and Ce^{3+}–Na$^+$ co-doped samples [1], EPR studies of Nd^{3+}-doped systems [2], and optical and ESR studies of Ce^{3+}-doped systems [3]. An important aspect of this work is the determination of the sites occupied by the dopant ions, which is still a matter of debate. For example, in [2] it is concluded that Nd^{3+} ions substitute at the Li site, while [3] suggests that Ce^{3+} ions substitute at the Ba site, while it might be expected that they would show similar behaviour.

Computer modelling based on lattice energy-minimization techniques can be used to provide useful information on the energetically favoured locations for dopant sites in BaLiF$_3$. Recent work by the authors on divalent-ion-doped BaLiF$_3$ predicted that Pb^{2+} would preferentially substitute at the Ba site, while Co^{2+} and Ni^{2+} substitute at the Li site, with charge compensation by Li/Ba substitution [4, 5]. This prediction was confirmed later by EXAFS measurements [6]. The present paper applies the same strategy to rare-earth-doped systems, with the aim of predicting the preferred location of the dopant ions.

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2. Methodology

The computational method employed in this paper is based on empirical potential fitting, followed by lattice energy minimization, and calculation of defect properties using the methodology of Mott and Littleton [7]. The approach will be summarized below; previous papers contain more detailed accounts [4, 5].

2.1. Empirical potential fitting

The potentials used in this study use the Buckingham form, supplemented by an electrostatic term:

$$V(r_{ij}) = q_i q_j / r_{ij} + A \exp(-r_{ij}/\rho) - C r^{-6}.$$

Here q_i and q_j are charges on ions i and j, and A, ρ, and C are parameters to be fitted. A shell model is used for the fluoride ions, for which ionic polarizability is expected to be significant. The ionic polarizability, α, is related to the shell charge, Y, and spring constant, k, by the expression

$$\alpha = Y^2/k.$$

A potential was fitted to the structure and lattice properties of $BaLiF_3$. A slightly different approach was used from the previous papers [4, 5], in that the F–F interaction was represented using a potential taken from a previous study [8], with the remaining terms in the potential being fitted. Table 1 gives the agreement between experimental and calculated lattice properties, showing that the potential gives a good account of the perfect-lattice properties. Table 2 gives the potential parameters themselves.

Table 1. Comparison of experimental and calculated lattice properties for $BaLiF_3$.

Property	Experimental value	Calculated value
a/Å	3.995	3.995
Elastic constants		
c_{11}	12.98	12.98
c_{12}	4.65	4.65
Dielectric constants		
ε_0	11.71	11.70
ε_∞	2.25	2.24

Table 2. Interionic potential parameters for $BaLiF_3$.

Interaction	Potential type	Parameters
Ba–F	Buckingham	$A = 2190.01$ eV, $\rho = 0.3068$ Å
Li–F	Buckingham	$A = 113.72$ eV, $\rho = 0.3654$ Å
F–F	Buckingham (four regions)	$A = 1127.7$ eV, $\rho = 0.2753$ Å, $C = 15.83$ eV Å^6, $r_1 = 2.0$ Å, $r_{\min} = 2.795$ Å, $r_2 = 3.031$ Å[a]
F_{core}–F_{shell}	Harmonic	$Y = -1.59\, e$, $k = 20.77$ eV Å^{-2}

[a] r_1, $r_{\min}$, and r_2 are the cut-offs for the four-region Buckingham potential.

2.2. Defect calculations

As already mentioned, defects are modelled using the Mott–Littleton approach [7], in which a spherical region immediately surrounding the defect is treated explicitly, and a continuum approach is used for more distant regions of the lattice. In modelling the substitution of dopant ions into the lattice, an important quantity is the solution energy, which is defined as the total energy involved in the substitution of the dopant ion at a given lattice site, including charge compensation where required.

All calculations were performed using the GULP code [9], which is a general-purpose computer code for empirical potential fitting, lattice energy minimization, and defect calculations on solids.

3. Results

When the BaLiF$_3$ lattice is doped with rare-earth ions, there are two possibilities for the location of the dopant ions, and several possibilities for charge compensation. In general terms, substitution might occur at either the Ba or Li site, and in each case charge compensation is needed. The possible schemes are given below:

(i) *Substitution at the Ba site.* Charge compensation can occur by (i) Li vacancies, (ii) F interstitials, (iii) a Li at a Ba site, and (iv) Ba vacancies. In the case of Ba vacancy compensation, it should be noted that one Ba vacancy compensates for two substituted rare-earth dopant ions. In addition, each charge-compensation mechanism may have more than one possible symmetry. The interstitial sites used are given in a previous paper [4]. The reactions describing the solution process are given in table 3.

Table 3. Reaction schemes for solution of rare-earth dopants in BaLiF$_3$.

M^{3+} at a Ba^{2+} site	M^{3+} at a Li$^+$ site
$MF_3 + Ba_{Ba} + Li_{Li} \rightarrow (M^{\bullet}_{Ba}-V'_{Li}) + BaLiF_3$	$MF_3 + 3Li_{Li} \rightarrow (M^{\bullet\bullet}_{Li}-2V'_{Li}) + 3LiF$
$MF_3 + Ba_{Ba} \rightarrow (M^{\bullet}_{Ba}-F'_i) + BaF_2$	$MF_3 + Li_{Li} \rightarrow (M^{\bullet\bullet}_{Li}-2F'_i) + LiF$
$MF_3 + 2Ba_{Ba} + LiF \rightarrow (M^{\bullet}_{Ba}-Li'_{Ba}) + 2BaF_2$	$MF_3 + 2Ba_{Ba} + Li_{Li} + LiF \rightarrow (M^{\bullet\bullet}_{Li}-2Li'_{Ba}) + 2BaF_2$
$2MF_3 + 3Ba_{Ba} \rightarrow (2M^{\bullet}_{Ba}-V''_{Ba}) + 3BaF_2$	$MF_3 + Li_{Li} + Ba_{Ba} \rightarrow (M^{\bullet\bullet}_{Li}-V''_{Ba}) + BaLiF_3$

(ii) *Substitution at the Li site.* Charge compensation occurs by the same four mechanisms as for the Ba site but for the first three possibilities, two compensating defects are required per dopant rare-earth ion. However, in the fourth case there is direct charge compensation. Again, there may be more than one symmetry for a given charge-compensation mechanism. The reactions are also given in table 3.

(iii) *Defect formation and solution energies.* It is important to distinguish between the defect formation energies and solution energies. The former energies only involve the creation of the defect in the lattice. The latter, however, include all the terms in the thermodynamic cycle involved when the formation process occurs. These are the important energies when deciding which site and form of charge compensation occurs, and they are calculated from the reactions given in table 3.

Table 4 contains the defect formation energies, and table 5 contains the solution energies. The notation used in tables 4 and 5 for the different symmetries is explained in the appendix.

Table 4. Defect formation energies (eV).

Defect	La	Ce	Pr	Nd	Sm	Eu	Gd
Basic defects							
$M_{Ba}^{\bullet}$	−20.84	−21.13	−21.40	−21.69	−21.72	−22.31	−22.20
$M_{Li}^{\bullet\bullet}$	−26.47	−27.42	−28.36	−29.13	−30.31	−31.54	−31.95
$M_{Ba}^{\bullet}-V_{Li}'$							
	−13.17	−13.47	−13.75	−14.05	−14.16	−14.81	−14.76
$M_{Ba}^{\bullet}-F_{i}'$							
$(\frac{1}{2}\,0\,0)$	−22.98	−23.50	−24.00	−24.49	−24.85	−25.76	−25.78
$(\frac{1}{2}\,\frac{1}{4}\,\frac{1}{4})$	−22.98	−22.91	−23.40	nc	nc	nc	nc
$(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	−22.30	−22.80	−23.29	−23.75	−24.16	−25.02	−25.10
$M_{Ba}^{\bullet}-Li_{Ba}'$							
(1 0 0)	−9.11	−9.45	−10.20	−10.03	−10.13	−11.73	−11.69
(1 1 0)	−9.27	−9.57	−10.09	−10.14	−10.03	−11.60	−11.84
(1 1 1)	−9.27	−9.56	−9.84	−9.98	−10.16	−10.59	−10.68
$2M_{Ba}^{\bullet}-V_{Ba}'$							
L (1 0 0)	−24.18	−25.14	−25.64	−26.45	−27.73	−28.50	−26.83
L (1 1 0)	−23.96	−24.39	−25.47	−26.19	−25.62	−28.22	−28.14
L (1 1 1)	−23.84	−24.39	−24.91	−25.46	−25.46	−26.62	−26.44
b1	−23.57	−24.76	−25.38	−25.17	−25.37	−28.36	−28.58
b2	−24.11	−25.02	−25.78	−26.64	−25.71	−28.71	−28.64
b3	−24.07	−24.63	−25.60	−26.40	−27.06	−28.65	−28.03
b4	−24.09	−24.64	−25.74	−26.05	−25.66	−28.74	−28.89
b5	−23.93	−24.48	−25.35	−26.30	−26.66	−26.69	−28.65
$M_{Li}^{\bullet\bullet}-2V_{Li}'$							
L (1 0 0)	−11.42	−12.37	−13.31	−14.09	−15.28	−16.51	−16.93
L (1 1 0)	−11.47	−12.42	−13.36	−14.14	−15.32	−16.55	−16.96
L (1 1 1)	−11.82	−12.75	−13.68	−14.45	−15.61	−16.83	−17.23
b1	−11.46	−12.41	−13.34	−14.12	−15.33	−16.55	−16.97
b2	−11.95	−12.60	−13.52	−14.28	−15.46	−16.69	−17.10
b3	−14.24	−13.62	−15.66	−16.29	−16.11	−17.37	−17.18
b4	−12.56	−13.29	−13.94	−14.84	−15.86	−17.10	−17.47
b5	−11.93	−12.85	−13.76	−14.53	−15.69	−16.91	−17.31
$M_{Li}^{\bullet\bullet}-2F_{i}'$							
L $(\frac{1}{2}\,0\,0)$	−32.76	−33.45	−34.13	−34.75	−35.39	−36.46	−36.59
V1 $(\frac{1}{2}\,0\,0)$	−35.23	−35.99	nc	−37.40	−38.08	−39.22	−39.35
V2 $(\frac{1}{2}\,0\,0)$	−32.74	−33.46	−34.13	−34.75	−35.37	−36.46	−36.59
L $(\frac{1}{2}\,\frac{1}{4}\,\frac{1}{4})$	−32.76	−33.45	−34.13	−34.75	−35.38	−36.46	−36.59
V $(\frac{1}{2}\,\frac{1}{4}\,\frac{1}{4})$	−32.74	−33.43	−34.12	−34.73	nc	−27.87	nc
L $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	−32.14	−34.95	−33.72	−34.41	−35.16	−36.31	−36.47
V $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	−33.22	−34.00	nc	−35.45	−36.17	−37.34	−37.52
$M_{Li}^{\bullet\bullet}-2Li_{Ba}'$							
L	−5.45	−6.28	−7.10	−7.80	−8.79	−9.94	−10.27
V1	−6.05	−6.78	−7.52	−8.18	−9.07	−10.18	−10.48
V2	−5.25	−6.08	−6.90	−7.61	−8.62	−9.77	−10.11
$M_{Li}^{\bullet\bullet}-V_{Ba}'$							
	−10.32	−11.12	−11.92	−12.61	−13.61	−14.76	−15.10

Table 4. (Continued)

Defect	Tb	Dy	Ho	Er	Tm	Yb	Lu
Basic defects							
$M_{Ba}^{\bullet}$	−22.20	−22.47	−22.21	−22.91	−22.78	−22.57	−23.05
$M_{Li}^{\bullet\bullet}$	−32.22	−33.11	−30.54	−33.91	−34.53	−34.34	−35.36
$M_{Ba}^{\bullet}$–V_{Li}'							
	−14.80	−15.17	−14.62	−15.68	−15.71	−16.04	−16.12
$M_{Ba}^{\bullet}$–F_i'							
($\frac{1}{2}$ 0 0)	−25.85	−26.37	−25.38	−27.04	−27.10	−24.06	−23.94
($\frac{1}{2}$ $\frac{1}{4}$ $\frac{1}{4}$)	nc	−26.35	nc	−26.18	−25.29	nc	−26.96
($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$)	−25.21	−25.75	−24.60	−26.36	−26.59	−23.47	−27.14
$M_{Ba}^{\bullet}$–Li_{Ba}'							
(1 0 0)	−12.24	−12.78	−10.58	−13.47	−10.95	−13.95	−11.43
(1 1 0)	−11.68	−12.35	−11.24	−12.81	−12.93	−13.16	−12.73
(1 1 1)	−10.69	−11.02	−10.65	−10.65	−11.26	−11.88	−12.46
$2M_{Ba}^{\bullet}$–V_{Ba}'							
L (1 0 0)	−29.71	−30.75	−28.76	−32.12	−27.19	−27.93	−27.56
L (1 1 0)	−28.33	−27.28	−27.59	−30.69	−30.11	−31.06	−31.88
L (1 1 1)	−26.46	−27.11	−26.43	−28.09	−28.04	−28.80	−28.81
b1	−29.15	−30.20	−28.19	−30.32	−31.07	−32.48	−32.25
b2	−28.83	−29.78	−28.00	−31.36	−31.36	−31.50	−33.01
b3	−28.88	−29.27	−28.09	nc	−30.34	nc	−32.50
b4	−26.59	−29.92	−27.96	−31.81	−28.09	−31.41	−28.83
b5	−28.24	−29.04	−27.86	−28.14	−28.08	−32.15	−30.97
$M_{Li}^{\bullet\bullet}$–$2V_{Li}'$							
L (1 0 0)	−17.20	−18.10	−15.50	−18.90	−19.53	−19.33	−20.37
L (1 1 0)	−17.23	−18.12	−15.54	−18.93	−19.55	−19.36	−20.38
L (1 1 1)	−17.50	−18.38	−15.84	−19.18	−19.79	−19.61	−20.62
b1	−17.24	−18.13	−15.57	−18.94	−19.57	−19.37	−20.41
b2	−17.37	−18.26	−15.68	−19.06	−19.68	−19.49	−20.51
b3	−17.44	−18.33	−15.80	−19.13	−19.75	−19.56	−20.58
b4	−17.74	−18.62	−16.09	−19.42	−20.03	−19.85	−20.86
b5	−17.58	−18.46	−15.92	−19.26	−19.87	−19.69	−20.70
$M_{Li}^{\bullet\bullet}$–$2F_i'$							
L ($\frac{1}{2}$ 0 0)	−36.73	−37.40	−35.86	−38.18	−38.51	−38.67	−39.92
V1 ($\frac{1}{2}$ 0 0)	−39.49	−40.18	−38.59	−40.99	−41.19	−41.53	−41.86
V2 ($\frac{1}{2}$ 0 0)	−36.73	−37.34	−35.86	−38.92	−39.18	−39.41	nc
L ($\frac{1}{2}$ $\frac{1}{4}$ $\frac{1}{4}$)	−36.73	−37.40	−35.86	−38.18	−38.40	−38.67	−39.06
V ($\frac{1}{2}$ $\frac{1}{4}$ $\frac{1}{4}$)	nc	−29.21	−35.84	nc	−30.50	−38.64	nc
L ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$)	−36.62	−37.34	−35.63	−38.14	−38.38	−38.66	−39.06
V ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$)	−37.64	−38.38	−36.67	−39.18	−39.43	−39.74	−40.10
$M_{Li}^{\bullet\bullet}$–$2Li_{Ba}'$							
L	−10.49	−11.31	−9.07	−12.08	−12.60	−12.52	−13.38
V1	−10.69	−11.47	−9.37	−12.23	−12.71	−12.66	−13.46
V2	−10.34	−11.17	−8.89	−11.94	−12.60	−12.38	−13.26
$M_{Li}^{\bullet\bullet}$–V_{Ba}'							
	−15.33	−16.15	−13.89	−16.93	−17.47	−17.37	−18.25

Table 5. Solution energies (eV)

Defect	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$M_{Ba}^{\bullet} - V'_{Li}$														
	2.30	2.46	2.62	2.76	2.86	3.11	3.16	3.20	3.36	4.51	3.54	3.59	3.69	3.76
$M_{Ba}^{\bullet} - F'_{i}$														
$(\frac{1}{2}\,0\,0)$	3.10	3.04	2.98	2.93	2.77	2.77	2.76	2.76	2.78	4.36	2.80	2.81	6.28	6.55
$(\frac{1}{2}\,\frac{1}{4}\,\frac{1}{4})$	3.10	3.63	3.58	nc	nc	nc	nc	nc	2.80	nc	3.66	4.63	nc	3.54
$(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	3.79	3.74	3.69	3.67	3.46	3.51	3.43	3.40	3.40	5.15	3.48	3.33	6.87	3.35
$M_{Ba}^{\bullet} - Li'_{Ba}$														
(1 0 0)	3.00	3.12	2.80	3.42	3.52	2.83	2.86	2.38	2.39	5.18	2.39	4.99	2.41	5.09
(1 1 0)	2.84	3.00	2.92	3.31	3.61	2.95	2.71	2.95	2.82	4.53	3.05	3.01	3.21	3.78
(1 1 1)	2.84	3.00	3.16	3.47	3.48	3.96	3.87	3.93	4.14	5.12	5.21	4.68	4.48	4.06
$2M_{Ba}^{\bullet} - V''_{Ba}$														
L (1 0 0)	2.19	2.16	2.35	2.39	1.95	2.47	3.31	1.94	1.96	3.55	1.97	4.51	4.57	4.90
L (1 1 0)	2.30	2.54	2.44	2.52	3.01	2.61	2.65	2.63	3.70	4.14	2.68	3.05	3.00	2.75
L (1 1 1)	2.36	2.54	2.72	2.89	3.08	3.41	3.50	3.57	3.78	4.72	3.99	4.09	4.13	4.28
b1	2.49	2.35	2.48	3.03	3.13	2.54	2.43	2.22	2.24	3.84	2.87	2.57	2.29	2.56
b2	2.22	2.22	2.28	2.30	2.96	2.37	2.40	2.38	2.45	3.93	2.35	2.42	2.78	2.18
b3	2.24	2.42	2.37	2.42	2.29	2.40	2.71	2.35	2.70	3.89	nc	2.94	nc	2.43
b4	2.23	2.41	2.30	2.59	2.99	2.35	2.28	3.50	2.38	3.95	2.12	4.06	2.83	4.27
b5	2.31	2.49	2.50	2.47	2.48	3.38	2.40	2.68	2.82	4.00	3.96	4.06	2.46	3.20
$M_{Li}^{\bullet\bullet} - 2V'_{Li}$														
L (1 0 0)	9.37	8.87	8.37	8.04	7.04	6.72	6.30	6.10	5.75	8.94	5.64	5.08	5.71	4.82
L (1 1 0)	9.31	8.82	8.32	7.99	7.00	6.68	6.26	6.07	5.72	8.90	5.61	5.06	5.68	4.81
L (1 1 1)	8.97	8.48	8.00	7.68	6.71	6.40	6.00	5.81	5.47	8.60	5.36	4.82	5.43	4.57
b1	9.33	8.83	8.33	8.00	6.99	6.68	6.26	6.07	5.71	8.87	5.60	5.04	5.67	4.79
b2	8.83	8.64	8.16	7.84	6.86	6.54	6.13	5.94	5.59	8.76	5.47	4.93	5.55	4.68
b3	6.55	7.62	6.02	5.83	6.21	5.86	6.05	5.86	5.52	8.64	5.40	4.86	5.48	4.61
b4	8.22	7.95	7.74	7.28	6.46	6.13	5.75	5.57	5.23	8.35	5.11	4.58	5.19	4.33
b5	8.85	8.39	7.92	7.60	6.63	6.32	5.91	5.73	5.39	8.52	5.27	4.74	5.35	4.49
$M_{Li}^{\bullet\bullet} - 2F'_{i}$														
L $(\frac{1}{2}\,0\,0)$	7.31	7.07	3.56	6.65	6.22	6.05	5.91	5.85	5.72	7.86	5.63	5.38	5.65	4.55
V1 $(\frac{1}{2}\,0\,0)$	4.84	4.53	nc	4.00	3.52	3.28	3.16	3.10	2.94	5.13	2.82	2.71	2.79	2.61
V2 $(\frac{1}{2}\,0\,0)$	7.33	7.06	6.82	6.66	6.23	6.05	5.92	5.86	5.78	7.86	4.90	4.71	4.91	nc
L $(\frac{1}{2}\,\frac{1}{4}\,\frac{1}{4})$	7.31	7.07	3.56	6.65	6.22	6.05	5.91	5.85	5.72	7.86	5.63	5.49	5.65	5.41
V $(\frac{1}{2}\,\frac{1}{4}\,\frac{1}{4})$	7.33	7.09	6.84	6.67	nc	14.64	nc	nc	nc	7.88	nc	13.39	5.68	nc
L $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	7.93	5.57	3.62	6.99	6.45	6.20	6.04	5.96	5.79	8.09	5.68	5.51	5.66	5.41
V $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	6.84	6.52	nc	5.95	5.43	5.17	4.99	4.95	4.74	7.05	4.63	4.47	4.58	4.38
$M_{Li}^{\bullet\bullet} - 2Li'_{Ba}$														
L	6.66	6.28	5.90	5.65	4.85	4.61	4.28	4.13	3.86	6.69	3.78	3.34	3.84	3.14
V1	6.06	5.78	5.48	5.27	4.57	4.37	4.07	3.94	3.70	6.39	3.63	3.23	3.70	3.05
V2	6.86	6.48	6.10	5.84	5.03	4.78	4.44	4.28	4.00	6.87	3.92	3.34	3.99	3.25
$M_{Li}^{\bullet\bullet} - V'_{Ba}$														
	5.16	4.81	4.45	4.20	3.40	3.15	2.82	2.66	2.38	5.24	2.29	1.84	2.36	1.63

4. Discussion and conclusions

The following conclusions may be made about the results given in table 5:

(i) All the solution energies are positive, indicating that the rare-earth ions are not readily soluble in the BaLiF$_3$ lattice.

(ii) The rare-earth ions can be classified into four groups according to the solution energies:

- *Group I, La–Nd.* The lowest-energy process involves substitution at the Ba site with Ba vacancy compensation, and the second lowest also involves substitution at the Ba site but with Li vacancy compensation.
- *Group II, Sm–Eu.* The lowest-energy process is the same as for group I, but the second-lowest-energy process changes to substitution at the Ba site with F interstitial compensation.
- *Group III, Gd–Tb.* The lowest-energy process is the same as for group I, but the second-lowest-energy process changes to substitution at the Ba site with compensation by Li–Ba exchange.
- *Group IV, Dy–Lu (except Ho).* Substitution at the Li site becomes more favourable, and is the lowest-energy option for Tm and Lu, with barium vacancy compensation.

Ho has high energies for all processes, and is very unlikely to be dissolved in BaLiF$_3$. The lowest energies are as for group II.

(iii) In all cases there are a number of different types of defects with solution energies within 20%. Given this small difference in energy, it should be possible to have more than one kind of charge compensation for a given rare-earth ion.

(iv) Finally, it is useful to make some comments concerning agreement with experimental work on the subject. It is clear from the calculations, for example, that Nd^{3+} prefers energetically to substitute at the Ba site, which is contrary to the results presented in [2]. However, using similar experimental techniques [1, 3], Ce^{3+} is found to substitute at the Ba site, a result confirmed by the calculations. In this regard, the calculations provide a useful complementary source of information to experimental measurements.

Appendix. Explanation of symmetry notation used in tables 4 and 5

In tables 4 and 5, according to the specific charge-compensation mechanism, different symmetries of the defects are possible. These are explained below:

- $M_{Ba}^{\bullet}$–F_i'. Here there are three possibilities depending on the position of the fluorine interstitial.
- $M_{Ba}^{\bullet}$–Li_{Ba}'. The three possibilities are related to the position adopted by the lithium ion, assuming the rare-earth ion to be at (0 0 0).
- $2M_{Ba}^{\bullet}$–V_{Ba}''. Eight possibilities are considered. In all cases the barium vacancy is at (0 0 0). The first three are linear arrangements of the defect, while the remaining five are bent arrangements. The numbers in the first three descriptions refer to the direction along

which the defect is aligned. The bent configurations are defined as follows, where the coordinates are those of the rare-earth cations:

b1	1 0 0	0 1 0
b2	1 1 0	-1 1 0
b3	1 1 0	0 1 1
b4	1 1 1	-1 1 1
b5	1 1 1	-1 -1 1.

- $M_{Li}^{\bullet\bullet}$–$2V_{Li}'$. The rare-earth cation is always at (0 0 0), and the two lithium vacancies are arranged in the same manner as above.
- $M_{Li}^{\bullet\bullet}$–$2F_i'$. Seven different configurations have been considered. In the first three, the fluorine interstitials are located at ($\frac{1}{2}$ 0 0) or symmetrically equivalent sites. Of these three, the first is a linear configuration and the other two are V-shaped, with the rare-earth ion located in the ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) position. In the V-shaped configurations, one has the fluorine interstitials in two different edges of the same face, and for the other one they are on different faces. The next two configurations involve the second interstitial site, which is at ($\frac{1}{2}$ $\frac{1}{4}$ $\frac{1}{4}$). One of these is linear and the other is V-shaped. The last two are similar, involving the third interstitial site at ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$).
- $M_{Li}^{\bullet}$–$2Li_{Ba}'$. There are three configurations, one of which is linear, in the 1 1 1 direction, and two which are V-shaped, V1 having the two lithiums on the same edge, and V2 which has them on the face diagonal.

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