Computer modelling of the reduction of rare earth dopants in barium aluminate

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ABSTRACT

Long lasting phosphorescence in barium aluminates can be achieved by doping with rare earth ions in divalent charge states. The rare earth ions are initially in a trivalent charge state, but are reduced to a divalent charge state before being doped into the material. In this paper, the reduction of trivalent rare earth ions in the $BaAl_2O_4$ lattice is studied by computer simulation, with the energetics of the whole reduction and doping process being modelled by two methods, one based on single ion doping and one which allows dopant concentrations to be taken into account. A range of different reduction schemes are considered and the most energetically favourable schemes identified.

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1. Introduction

Rare earth doped aluminates have important applications as phosphor materials. In the case of barium aluminate, $BaAl_2O_4$, long lasting phosphorescence has been achieved by doping with Eu^{2+}, Dy^{3+} [1]; Ce^{3+}, Dy^{3+} [2]; and Ce^{2+}, Mn^{2+} [3]. It has been found that, at least for doping with europium and manganese, ions in the 2+ charge state are needed, while these elements are found in the 3+ charge state in their parent oxides. If the trivalent rare earth oxide material is used as a starting material, it is necessary to reduce the ions before the doping process can take place. The most common method is the use of reducing agents such as N_2/H_2 (95%:5%), H_2, CO_2, or CO when the rare earth containing sample is calcined. Sometimes, NH_3 and metal vapour are also used as reducing agents. Another possibility is to irradiate the rare earth containing sample with high-energy radiation, e.g. UV light, or γ- or X-rays [4]. In a few particular aluminates, rare earth reduction upon calcination can be carried out in air at high temperature, for example, $BaAl_2O_4$:Eu [4].

In this paper, the process of (i) reduction of the rare earth ions and (ii) doping the $BaAl_2O_4$ structure is modelled, for the case of 9 different reducing schemes, enabling the most favourable schemes to be identified for successful sample preparation. The modelling is carried out using two methods, one based on single ion doping and one which allows dopant concentrations to be taken into account.

2. Methodology

In this paper, computer modelling methods are employed that are based on well established approaches that use interatomic potentials to represent the interactions between ions, coupled with energy minimisation to model structures, and Mott–Littleton methods [5] to model defects. All calculations employed the GULP code [6]. The derivation of potentials to describe the barium aluminate framework has been described elsewhere [7]. The potentials for the trivalent rare earth ion–oxygen interactions were taken from Ref. [8] and the divalent rare earth ion–oxygen potentials were obtained using the trivalent values as starting points, and then fitting to the divalent oxide structures. The potential parameters employed are given in Table 1.

The procedure for calculating the energetics of divalent ion doping is as follows:

(i) Calculation of the substitution energies of dopant ions in the $BaAl_2O_4$ lattice.
(ii) Using these substitution energies, solution energies are calculated for each reduction scheme. Solution energies describe the total energy involved in, firstly, reducing the rare earth ions from a 3+ to a 2+ state, and secondly substituting them into the $BaAl_2O_4$ lattice. Two methods are available to calculate these energies, both of which have been described in more detail elsewhere (see e.g. [7,8]), but which are considered briefly below.

The first method effectively models the substitution of a single ion into the $BaAl_2O_4$ lattice. For example, if the ion M^{2+} substitutes at the Ba site, the following process is assumed to take place:

$$MO + Ba_{Ba} \rightarrow M_{Ba} + BaO$$
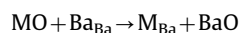
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Table 1

Potential parameters used for the BaAl$_2$O$_4$ and MO calculations (note that the rare earth ions are in the +2 charge state).

Compound	A (eV)	ρ (Å)	C (eVÅ^6)
Ba–O	1316.70	0.3658	0.00
Al–O	1398.40	0.3006	0.00
O–O	22764.0	0.1490	27.88
Ce–O	2157.18	0.3289	27.55
Pr–O	1595.55	0.3399	20.34
Sm–O	1492.85	0.3414	21.49
Eu–O	1772.32	0.3403	20.59
Gd–O	1536.65	0.3399	20.34
Yb–O	1211.35	0.3386	16.57

The solution energy, E_{sol}, corresponding to this process is given by

$$E_{\text{sol}} = -E_{\text{latt}}(\text{MO}) + E(\text{M}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO})$$

where the E_{latt} terms are lattice energies and $E(\text{M}_{\text{Ba}})$ is the substitution energy of the ion M^{2+} at the Ba site.

The second method mimics the growth of the crystal with the dopant incorporated at a particular concentration. The following reaction represents the doping of mole fraction x of M at the Ba site in BaAl$_2$O$_4$

$$x\text{MO} + (1-x)\text{BaO} + \text{Al}_2\text{O}_3 \rightarrow \text{Ba}_{1-x}\text{M}_x\text{Al}_2\text{O}_4$$
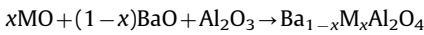
The solution energy, E_{sol}, for this process, is given by the following expression, the basis for which is explained in Ref. [7]:

$$E_{\text{sol}} = [(1-x)E_{\text{latt}}(\text{BaAl}_2\text{O}_4) + xE(\text{M}_{\text{Ba}})] - [xE_{\text{latt}}(\text{MO}) + (1-x)E_{\text{latt}}(\text{BaO}) + E_{\text{latt}}(\text{Al}_2\text{O}_3)]$$

3. Reduction schemes

The following schemes were considered for the reduction of the rare earth ions:

  (i) Reduction in open atmosphere
  (ii) Reduction using H$_2$
 (iii) Reduction using CO
 (iv) Reduction using N$_2$
  (v) Reduction using HF
 (vi) Reduction using CF$_4$
 (vii) Reduction using CH$_4$
(viii) Reduction using CO$_2$
 (ix) Reduction using H$_2$/N$_2$

For each reducing scheme, the equations for the combined reduction-doping process are given in Section 4, for each solution energy method, and solution energies are calculated for each dopant ion.
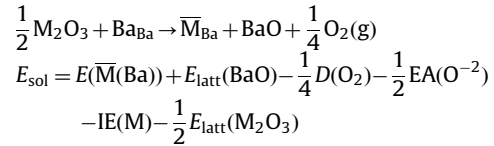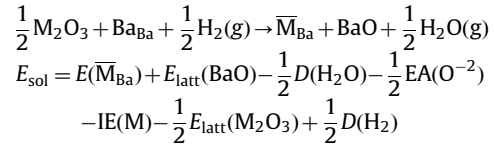
4. Results

4.1. Infinite dilution method

Solution energies were calculated for each of the reduction schemes given in Section 3; the schemes and equations for the solution energies are given below. In the equations, $\overline{\text{M}}_{\text{Ba}}$ denotes the reduced ion substituted at the Ba site. $E_{\text{latt}}(\text{BaO})$ and $E_{\text{latt}}(\text{M}_2\text{O}_3)$ are lattice energies, $E(\overline{\text{M}}_{\text{Ba}})$ is the substitution energy for the dopant, IE(M) is the ionisation energy involved in the reduction process of the rare earth ion, $D(\text{O}_2)$ is the dissociation energy of oxygen, and EA(O^{2-}) is the sum of the first two electron affinities of oxygen.
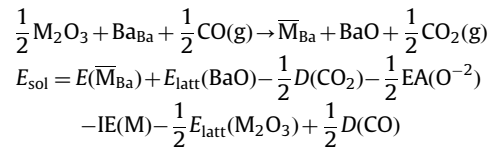
  (i) Open atmosphere

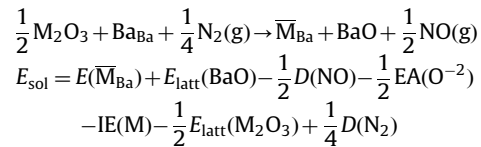$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \tfrac{1}{4}\text{O}_2(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}(\text{Ba})) + E_{\text{latt}}(\text{BaO}) - \tfrac{1}{4}D(\text{O}_2) - \tfrac{1}{2}\text{EA}(\text{O}^{-2})$$
$$- \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3)$$

 (ii) Reducing atmosphere (H$_2$)

$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} + \tfrac{1}{2}\text{H}_2(g) \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \tfrac{1}{2}\text{H}_2\text{O}(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO}) - \tfrac{1}{2}D(\text{H}_2\text{O}) - \tfrac{1}{2}\text{EA}(\text{O}^{-2})$$
$$- \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3) + \tfrac{1}{2}D(\text{H}_2)$$

(iii) Reducing atmosphere (CO)

$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} + \tfrac{1}{2}\text{CO}(g) \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \tfrac{1}{2}\text{CO}_2(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO}) - \tfrac{1}{2}D(\text{CO}_2) - \tfrac{1}{2}\text{EA}(\text{O}^{-2})$$
$$- \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3) + \tfrac{1}{2}D(\text{CO})$$

(iv) Reducing atmosphere (N$_2$)

$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} + \tfrac{1}{4}\text{N}_2(g) \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \tfrac{1}{2}\text{NO}(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO}) - \tfrac{1}{2}D(\text{NO}) - \tfrac{1}{2}\text{EA}(\text{O}^{-2})$$
$$- \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3) + \tfrac{1}{4}D(\text{N}_2)$$

 (v) Reducing atmosphere (HF)

$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} + \text{HF}(g) \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \tfrac{1}{2}\text{H}_2\text{O}(g) + \tfrac{1}{2}\text{F}_2(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO}) - \tfrac{1}{2}D(\text{H}_2\text{O}) - \tfrac{1}{2}\text{EA}(\text{O}^{-2})$$
$$- \tfrac{1}{2}D(\text{F}_2) - \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3) + D(\text{HF})$$

(vi) Reducing atmosphere (CF$_4$)

$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} + \tfrac{1}{2}\text{CF}_4(g) \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \tfrac{1}{2}\text{CO}(g) + \text{F}_2(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO}) - \tfrac{1}{2}D(\text{CO}) - \tfrac{1}{2}\text{EA}(\text{O}^{-2})$$
$$- D(\text{F}_2) - \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3) + \tfrac{1}{2}D(\text{CF}_4)$$

(vii) Reducing atmosphere (CH$_4$)

$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} + \tfrac{1}{2}\text{CH}_4(g) \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \tfrac{1}{2}\text{CO}(g) + \text{H}_2(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO}) - \tfrac{1}{2}D(\text{CO}) - \tfrac{1}{2}\text{EA}(\text{O}^{-2}) - D(\text{H}_2)$$
$$- \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3) + \tfrac{1}{2}D(\text{CH}_4)$$

(viii) Reducing atmosphere (CO$_2$)

$$\tfrac{1}{2}\text{M}_2\text{O}_3 + \text{Ba}_{\text{Ba}} + \text{CO}_2(g) \rightarrow \overline{\text{M}}_{\text{Ba}} + \text{BaO} + \text{CO}(g) + \tfrac{3}{4}\text{O}_2(g)$$
$$E_{\text{sol}} = E(\overline{\text{M}}_{\text{Ba}}) + E_{\text{latt}}(\text{BaO}) - D(\text{CO}) - \tfrac{1}{2}\text{EA}(\text{O}^{-2}) - \tfrac{3}{4}D(\text{O}_2)$$
$$- \text{IE}(\text{M}) - \tfrac{1}{2}E_{\text{latt}}(\text{M}_2\text{O}_3) + D(\text{CO}_2)$$

(ix) Reducing atmosphere (H_2/N_2)

$$\frac{1}{2}M_2O_3 + Ba_{Ba} + \frac{1}{8}N_2(g) + \frac{1}{4}H_2(g) \rightarrow \overline{M}_{Ba} + BaO + \frac{1}{4}NO(g) + \frac{1}{4}H_2O(g)$$

$$E_{sol} = E(\overline{M}_{Ba}) + E_{latt}(BaO) - \frac{1}{4}D(NO) - \frac{1}{4}D(H_2O) - \frac{1}{2}EA(O^{-2})$$
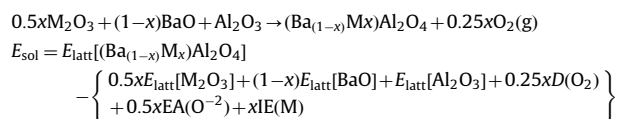$$- IE(M) - \frac{1}{2}E_{latt}(M_2O_3) + \frac{1}{8}D(N_2) + \frac{1}{4}D(H_2)$$

Solution energies are given in Table 5, for the two Ba sites in $BaAl_2O_4$ with all 9 reduction schemes. Tables 2 and 3 contain, respectively, the lattice energies and substitution energies of rare earth ions at the Ba sites, and Table 4 lists the dissociation energies, electron affinities and ionisation energies needed in the calculations.

From Table 5 it can be seen that the most favourable reducing atmosphere at both temperatures is CO using this method. The results will be considered in more detail along with those from the concentration-dependent method.

4.2. Concentration-dependent method

As with Section 4.1, solution energies were calculated for each of the reduction schemes listed in Section 3. The equations for the reactions and solution energies are given below, assuming a dopant mole fraction of x.

(i) Open atmosphere

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 \rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.25xO_2(g)$$

$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4]$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] + 0.25xD(O_2) \\ + 0.5xEA(O^{-2}) + xIE(M) \end{array} \right\}$$

Table 2
Lattice energies calculated at 0 and 293 K used in the calculations.

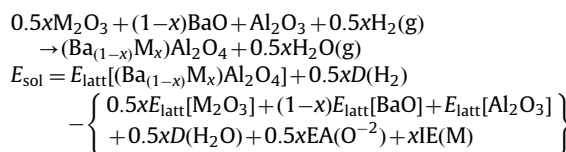| Compound	Lattice energy (eV)	
	0 K	293 K
$BaAl_2O_4(P63)$	−193.58	−193.22
BaO	−32.60	−32.60
Al_2O_3	−158.23	−157.83
Ce_2O_3	−129.30	−129.27
Pr_2O_3	−130.04	−129.85
Sm_2O_3	−131.79	−131.62
Eu_2O_3	−132.58	−132.49
Gd_2O_3	−133.31	−133.14
Tb_2O_3	−133.51	−133.35
Dy_2O_3	−134.67	−134.50
Ho_2O_3	−135.21	−135.05
Er_2O_3	−136.02	−135.85
Tm_2O_3	−136.89	−136.73
Yb_2O_3	−137.15	−136.98
Lu_2O_3	−137.60	−137.44

Table 3
Defect formation energy of divalent ions at barium sites 1 and 2 at 0 K and 293 K, $\overline{M}_{Ba}$.

Ba site	0 K	293 K	0 K	293 K	0 K	293 K
	Ce		Pr		Sm	
Ba1	−1.85	−3.32	−1.77	−3.24	−1.89	−3.36
Ba2	−1.86	−3.22	−1.80	−3.16	−1.92	−3.28
	Eu		Gd		Yb	
Ba1	−1.42	−2.89	−1.89	−3.36	−2.74	−3.84
Ba2	−1.43	−2.80	−1.93	−3.28	−2.66	−3.98

Table 4
Dissociation energies, electron affinities and ionisation energies.

Reaction		Energy in eV
$O_2(g) \rightarrow 2O(g)$	$D(O_2)$	5.17
$F_2(g) \rightarrow 2F(g)$	$D(F_2)$	1.65
$H_2(g) \rightarrow 2H(g)$	$D(H_2)$	4.50
$N_2(g) \rightarrow 2N(g)$	$D(N_2)$	9.79
$H_2O(g) \rightarrow 2H(g) + O(g)$	$D(H_2O)$	9.62
$HF(g) \rightarrow H(g) + F(g)$	$D(HF)$	6.41
$CO_2(g) \rightarrow C(g) + 2O(g)$	$D(CO_2)$	16.67
$CF_4(g) \rightarrow C(g) + 4F(g)$	$D(CF_4)$	9.67
$CO(g) \rightarrow C(g) + O(g)$	$D(CO)$	11.16
$CO(g) \rightarrow C(g) + O(g)$	$D(NO)$	6.55
$CH_4(g) \rightarrow C(g) + 4H(g)$	$D(CH_4)$	17.24
$O(g) + 2e^- \rightarrow O^{2-}(g)$	$EA(O^{2-})$	6.74
$F(g) + e^- \rightarrow F^-(g)$	$EA(F^-)$	−3.40
$Ce^{2+} \rightarrow Ce^{3+} + e^-$	$IE(Ce)$	20.20
$Pr^{2+} \rightarrow Pr^{3+} + e^-$	$IE(Pr)$	21.62
$Sm^{2+} \rightarrow Sm^{3+} + e^-$	$IE(Sm)$	23.42
$Eu^{2+} \rightarrow Eu^{3+} + e^-$	$IE(Eu)$	24.91
$Gd^{2+} \rightarrow Gd^{3+} + e^-$	$IE(Gd)$	20.62
$Yb^{2+} \rightarrow Yb^{3+} + e^-$	$IE(Yb)$	25.03

(ii) Reducing atmosphere (H_2)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + 0.5xH_2(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.5xH_2O(g)$$
$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + 0.5xD(H_2)$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] \\ + 0.5xD(H_2O) + 0.5xEA(O^{-2}) + xIE(M) \end{array} \right\}$$

(iii) Reducing atmosphere (CO)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + 0.5xCO(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.5xCO_2(g)$$
$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + 0.5xD(CO) + 0.5xEA(O^{-2})$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] \\ + 0.5xD(CO_2) + xEA(O^{-2}) + xIE(M) \end{array} \right\}$$

(iv) Reducing atmosphere (N_2)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + 0.125xN_2(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.25xNO_2(g)$$
$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + 0.125D(N_2)$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] \\ + 0.25xD(NO_2) + 0.5xEA(O^{-2}) + xIE(M) \end{array} \right\}$$

(v) Reducing atmosphere (HF)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + xHF(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.5xH_2O(g) + 0.5xF_2(g)$$
$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + xD(HF)$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] \\ + 0.5xD(H_2O) + 0.5xEA(O^{-2}) + xIE(M) + + 0.5xD(F_2) \end{array} \right\}$$

(vi) Reducing atmosphere (CF_4)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + 0.25xCF_4(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.25xCO_2(g) + 0.5xF_2(g)$$
$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + 0.25xD(CF_4)$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] \\ + 0.25xD(CO_2) + 0.5xEA(O^{-2}) + xIE(M) + 0.5xD(F_2) \end{array} \right\}$$

(vii) reducing atmosphere (CH_4)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + 0.5xCH_4(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.5xCO(g) + xH_2(g)$$

Table 5
Solution energies of divalent rare earth ions (infinite dilution method) (eV).

	(i) (Air)	(ii) (H_2)	(iii) (CO)	(iv) (N_2)	(v) (HF)	(vi) (CF_4)	(vii) (CH_4)	(viii) (CO_2)	(ix) (MIX)
0 K									
Ce									
Ba1	5.34	4.07	**3.88**	5.76	7.41	4.24	5.17	8.26	4.91
Ba2	5.33	4.06	**3.87**	5.75	7.40	4.23	5.16	8.25	4.90
Pr									
Ba1	4.37	3.10	**2.90**	4.79	6.43	3.26	4.20	7.29	3.94
Ba2	4.34	3.07	**2.88**	4.76	6.40	3.24	4.17	7.26	3.91
Sm									
Ba1	3.32	2.05	**1.86**	3.74	5.39	2.22	3.16	6.25	2.90
Ba2	3.29	2.02	**1.83**	3.71	5.36	2.19	3.12	6.22	2.87
Eu									
Ba1	2.70	1.43	**1.24**	3.12	4.77	1.60	2.53	5.62	2.27
Ba2	2.69	1.42	**1.23**	3.11	4.76	1.59	2.52	5.61	2.26
Gd									
Ba1	6.88	5.61	**5.42**	7.31	8.95	5.78	6.72	9.81	6.46
Ba2	6.84	5.58	**5.38**	7.27	8.91	5.74	6.68	9.77	6.42
Yb									
Ba1	3.77	2.50	**2.30**	4.19	5.84	2.67	3.60	6.69	3.34
Ba2	3.85	2.58	**2.38**	4.27	5.91	2.75	3.68	6.77	3.42
293 K									
Ce									
Ba1	3.85	2.59	**2.39**	4.28	5.92	2.75	3.69	6.78	3.43
Ba2	3.95	2.69	**2.49**	4.38	6.02	2.85	3.79	6.88	3.53
Pr									
Ba1	2.80	1.54	**1.34**	3.22	4.87	1.70	2.64	5.73	2.38
Ba2	2.88	1.61	**1.42**	3.30	4.95	1.78	2.72	5.81	2.46
Sm									
Ba1	1.77	0.50	**0.30**	2.19	3.84	0.67	1.60	4.69	1.34
Ba2	1.85	0.58	**0.39**	2.27	3.92	0.74	1.68	4.77	1.42
Eu									
Ba1	1.18	− 0.08	**− 0.28**	1.61	3.25	0.08	1.02	4.11	0.76
Ba2	1.27	0.01	**− 0.19**	1.70	3.34	0.17	1.11	4.20	0.85
Gd									
Ba1	5.33	4.06	**3.87**	5.75	7.39	4.23	5.16	8.25	4.90
Ba2	5.41	4.14	**3.94**	5.83	7.47	4.31	5.24	8.33	4.98
Yb									
Ba1	2.36	1.09	**0.89**	2.78	4.43	1.26	2.19	5.28	1.93
Ba2	2.22	0.95	**0.75**	2.64	4.28	1.12	2.05	5.14	1.79

$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + 0.5xD(CH_4)$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] \\ + 0.5xD(CO) + 0.5xEA(O^{-2}) + xIE(M) + xD(H_2) \end{array} \right\}$$

(viii) Reducing atmosphere (CO_2)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + 0.5xCO_2(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.5xCO(g) + 0.5xO_2(g)$$
$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + 0.5xD(CO_2) + xEA(O^{-2})$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] \\ + E_{latt}[Al_2O_3] + 0.5xD(CO) + 0.5xEA(O^{-2}) \\ + xIE(M) + 0.5xD(O_2) + xEA(O^{-2}) \end{array} \right\}$$

(ix) Reducing atmosphere (5%H_2, 95%N_2)

$$0.5xM_2O_3 + (1-x)BaO + Al_2O_3 + 0.025xH_2(g) + 0.11875xN_2(g)$$
$$\rightarrow (Ba_{(1-x)}M_x)Al_2O_4 + 0.025xH_2O(g) + 0.00475xNO_2(g)$$
$$E_{sol} = E_{latt}[(Ba_{(1-x)}M_x)Al_2O_4] + 0.025xD(H_2) + 0.11875D(N_2)$$
$$- \left\{ \begin{array}{l} 0.5xE_{latt}[M_2O_3] + (1-x)E_{latt}[BaO] + E_{latt}[Al_2O_3] \\ + 0.025xD(H_2O) + 0.025xEA(O^{-2}) \\ + 0.2375xD(NO_2) + 0.475xEA(O^{-2}) + xIE(M) \end{array} \right\}$$

Solution energies are given in Table 6, for the two Ba sites in $BaAl_2O_4$ with all 9 reduction schemes, assuming $x = 1$ mol%.
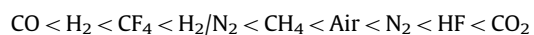
4.3. Comparison of results from both methods

From Tables 5 and 6 it can be seen that the two methods show the same trends for the incorporation of the divalent rare earth ion. Both methods show that incorporation scheme (iv) involving a CO reducing atmosphere, is the lowest energy scheme at both 0 K and at 293 K. Scheme (ii), involving H_2, is the second preferred mechanism. Although H_2 is a good reducing agent, it is very difficult to use due to combustion problems. To solve this problem H_2 is mixed with N_2, which is still good for the reduction process, although not as good as H_2. The mixture that was considered in the infinite dilute method is H_2/N_2 (50% H_2, 50% N_2). In the concentration-dependent method, a mixture of H_2/N_2 (5% H_2, 95% N_2) was used, which is the mixture more often used in experimental procedures. Schemes (v), involving an HF reduction atmosphere, and (viii), involving CO_2 reduction atmosphere, are not as effective.

From Table 5, the order of reducing agent efficiency is seen to be:

$$CO < H_2 < CF_4 < CH_4 < Air = H_2/N_2 < N_2 < CO_2 < HF$$

and from Table 6 it is

$$CO < H_2 < CF_4 < H_2/N_2 < CH_4 < Air < N_2 < HF < CO_2$$
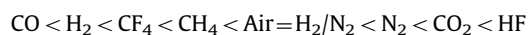
The only difference between the two methods is observed for the mixture of H_2/N_2, due to the different concentrations used in each case, and a change of order between CO_2 and HF.

Table 6
Solution energies of divalent rare earth ions (concentration-dependent method, 1 mol% M_2O_3) (eV).

	(i) (Air)	(ii) (H_2)	(iii) (CO)	(iv) (N_2)	(v) (HF)	(vi) (CF_4)	(vii) (CH_4)	(viii) (CO_2)	(ix) MIX
0 K									
Ce									
Ba1	−0.761	−0.773	**−0.809**	−0.743	−0.740	−0.774	−0.763	−0.746	−0.761
Ba2	−0.761	−0.796	**−0.865**	−0.756	−0.740	−0.774	−0.763	−0.746	−0.761
Pr									
Ba1	−0.771	−0.806	**−0.875**	−0.765	−0.750	−0.783	−0.772	−0.756	−0.770
Ba2	−0.771	−0.806	**−0.875**	−0.765	−0.750	−0.784	−0.773	−0.756	−0.771
Sm									
Ba1	−0.781	−0.816	**−0.885**	−0.776	−0.760	−0.794	−0.783	−0.766	−0.781
Ba2	−0.781	−0.817	**−0.885**	−0.776	−0.761	−0.794	−0.783	−0.767	−0.781
Eu									
Ba1	−0.787	−0.822	**−0.891**	−0.782	−0.767	−0.800	−0.789	−0.773	−0.787
Ba2	−0.787	−0.823	**−0.891**	−0.782	−0.767	−0.800	−0.789	−0.773	−0.787
Gd									
Ba1	−0.745	−0.781	**−0.849**	−0.740	−0.725	−0.758	−0.747	−0.731	−0.745
Ba2	−0.746	−0.781	**−0.850**	−0.740	−0.725	−0.759	−0.747	−0.731	−0.746
Yb									
Ba1	−0.779	−0.814	**−0.883**	−0.773	−0.758	−0.792	−0.780	−0.764	−0.779
Ba2	−0.778	−0.813	**−0.882**	−0.773	−0.757	−0.791	−0.780	−0.763	−0.778
293 K									
Ce									
Ba1	−0.819	−0.832	**−0.868**	−0.802	−0.799	−0.832	−0.821	−0.805	−0.819
Ba2	−0.818	−0.853	**−0.922**	−0.813	−0.798	−0.831	−0.820	−0.804	−0.818
Pr									
Ba1	−0.830	−0.865	**−0.934**	−0.824	−0.809	−0.843	−0.831	−0.815	−0.830
Ba2	−0.829	−0.864	**−0.933**	−0.824	−0.808	−0.842	−0.831	−0.814	−0.829
Sm									
Ba1	−0.840	−0.875	**−0.944**	−0.835	−0.820	−0.853	−0.842	−0.825	−0.840
Ba2	−0.839	−0.875	**−0.943**	−0.834	−0.819	−0.852	−0.841	−0.825	−0.839
Eu									
Ba1	−0.850	−0.885	**−0.954**	−0.845	−0.829	−0.863	−0.852	−0.835	−0.850
Ba2	−0.845	−0.880	**−0.949**	−0.840	−0.824	−0.858	−0.847	−0.830	−0.845
Gd									
Ba1	−0.805	−0.840	**−0.909**	−0.799	−0.784	−0.817	−0.806	−0.790	−0.804
Ba2	−0.804	−0.839	**−0.908**	−0.798	−0.783	−0.817	−0.805	−0.789	−0.804
Yb									
Ba1	−0.834	−0.869	**−0.938**	−0.829	−0.814	−0.847	−0.836	−0.820	−0.834
Ba2	−0.836	−0.871	**−0.940**	−0.830	−0.815	−0.849	−0.837	−0.821	−0.835

Comparing all rare earth ions, the lowest solution energies are obtained for the $Eu^{3+} \rightarrow Eu^{2+}$ process. The order of ease of rare earth ion reduction is $Eu < Sm < Yb < Pr < Ce < Gd$; this sequence is the same as the ionisation energy.

In all the schemes the incorporation of the divalent ion can occur at two different sites, Ba1 and Ba2 at 0 K and room temperature (293 K); this is due a similar and small difference between solution energies. Due the high possibility of Eu^{2+} incorporation at both Ba sites, two Eu^{2+} emission centres in $BaAl_2O_4$:Eu^{2+} are expected. These results are in agreement with recently published papers; using photoluminescence (PL) spectra of $BaAl_2O_4$:Eu^{2+} films Lou et al. [9] found two emission bands at 452 and 485 nm. From emission spectra Ju et al. [10] reported that $BaAl_2O_4$:Eu^{2+} exhibited two dominant peaks at 410 and 500 nm, and Peng et al. [4] reported that $BaAl_2O_4$:Eu^{2+} exhibited two dominant peaks at 495 and 530 nm. This is in agreement with the similar average Ba–O distance for 2.85 Å for Ba1 and 2.87 Å for Ba2.

Peng et al. [11] fabricated $BaAl_2O_4$:Eu^{2+} phosphor in a TCRA (thermal carbon reducing atmosphere) and in air. Through emission spectra it was shown that it is possible to reduce $Eu^{3+} \rightarrow Eu^{2+}$ in air, and that the emission spectrum of TCRA fabricated sample had almost the same characteristics as the air fabricated sample except for the intensity difference. The intensity enhancement of the emission spectrum of the TCRA fabricated sample is due to the Eu^{2+} content increase because the reducing properties of a TCRA is favourable for formation and stabilisation of Eu^{2+} ions. These results are confirmed by the calculations reported, where from the solution energy it can be seen that it is more favourable to reduce $Eu^{3+} \rightarrow Eu^{2+}$ if the Eu_2O_3-containing material is calcined in a reducing atmosphere involving CO reducing agents rather than in one involving air.

From the calculations made using the concentration dependent, it is possible to monitor how the solution energy depends on increase in dopant concentration. This is motivated by interest in $BaAl_2O_4$ doped with 1–3% Eu and Dy for long-lasting phosphorescence applications [1]. Fig. 1 shows how the solution energy changes on addition of Eu^{2+} to the $BaAl_2O_4$ lattice at 293 K. From the figure it can be seen that the solution energy increases as Eu^{2+} concentration changes. The same trend is observed for all other rare earth ions and all schemes simulated. It is also possible also to find the limit of solubility for divalent rare earth doping in the lattice. Fig. 1 indicates that above $\sim$1.4–1.5 mol% all solution energies become positive and that is an indication that the incorporation of the divalent is an endothermic process, leading to the conclusion that the solubility limit for, e.g. Eu^{2+} in $BaAl_2O_4$ is around 1.5 mol%, for the case of a CO atmosphere, and that the solubility limit slightly decreases for the other atmospheres used. The same idea also applies to the other rare earth ions.

5. Conclusions

The reduction and doping of rare earth ions into $BaAl_2O_4$ has been modelled for 9 different reducing atmospheres, and making use of two methods for calculating the overall solution energy of
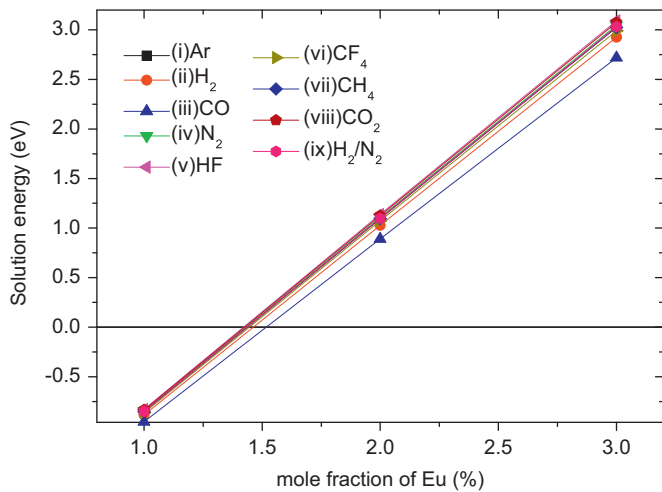
Fig. 1. Solution energies for divalent Eu ions as a function of mole fraction of Eu_2O_3 for all mechanisms at 293 K.

temperatures. The solution energy increases as M^{2+} concentration increases leading to an estimated solubility limit of about 1.5 mol% for the case of Eu^{2+}. These conclusions are in agreement with recent experimental optical measurements.

the process. The scheme involving a CO reducing atmosphere is the most favourable at 0 K and at 293 K, followed by a reducing atmosphere containing H_2. In all situations the incorporation of divalent ions is possible at two different sites, Ba1 and Ba2 at both

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