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Study of the reduction process of rare earth ions in $BaAl_2O_4$ hosts via computer simulations

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Abstract – $BaAl_2O_4$ when doped with rare earth ions presents long lasting phosphorescence [1], which makes it a candidate for emergency signs applications. The first step of the work consists of finding a suitable set of potentials to describe the system and that were done via a empirical approach where the potential parameters were fitted to the structures of all known barium aluminates crystalline phases. In the work we considered seven schemes for the reduction from RE^{3+} to RE^{2+} for different temperature (0 and 300 K), where each schemes is included one room reduction different in $BaAl_2O_4$.

$BaAl_2O_4$ when doped with rare earth ions presents long lasting phosphorescence [1], which makes it a candidate for emergency signs applications. In the present work we employed computer modeling methods that are based on well established approaches using interatomic potentials to represent the interactions between ions, coupled with energy minimization. Defects can be modeled within the Mott–Littleton approach in which point defects are considered to be at the centre of a region where all interactions are treated explicitly, surrounded by a external region where approximate methods are employed. These were all included in the GULP code [2] used in the present work. The first step of the work consists of finding a suitable set of potentials to describe the system and that were done via empirical approach where the potential parameters were fitted to the structures of all known barium aluminates crystalline phases. The potential parameters set were able to reproduce all the crystalline structures within 2%. In the work we considered seven schemes for the reduction from RE^{3+} to RE^{2+} at two different temperatures, 0 and 300 K, and the proposed solid state reactions are shown below. In all cases, the dopant is supposed to be incorporated at the Ba site. The solution energies of all schemes are listed in table 1. From the solution energy it can be seen that the incorporation of the divalent rare earth dopant is preferred to occur in Ba2 site at 0 K and in Ba1 site at 293K, and the preferred mechanism is scheme (ii), with H_2 as the reduction gas. The Ar (scheme (i)) is the second preferred mechanism. Comparing all rare earth, the lowest solution energies are obtained for the $Eu^{3+} \rightarrow Eu^{2+}$ process. Mechanisms (iii), where CO is used as reducing agent, is unlikely to happen since the energies involved in the reaction are quite high. (The authors are grateful to CNPq, FINEP and CAPES program for financial support).

(i)-(Ar) $\frac{1}{2}M_2O_3 + Ba_{Ba} \rightarrow M_{Ba} + BaO + \frac{1}{4}O_2(g)$

(ii)-(H_2) $\frac{1}{2}M_2O_3 + Ba_{Ba} + \frac{1}{2}H_2(g) \rightarrow M_{Ba} + BaO + \frac{1}{2}H_2O(g)$

(iii)-(CO) $\frac{1}{2}M_2O_3 + Ba_{Ba} + \frac{1}{2}CO(g) \rightarrow M_{Ba} + BaO + \frac{1}{2}CO_2(g)$

(iv)-(N_2) $\frac{1}{2}M_2O_3 + Ba_{Ba} + \frac{1}{2}N_2(g) \rightarrow M_{Ba} + BaO + \frac{1}{2}NO(g)$

(v)-(HF) $\frac{1}{2}M_2O_3 + Ba_{Ba} + HF(g) \rightarrow M_{Ba} + BaO + \frac{1}{2}H_2O(g) + \frac{1}{2}F_2$

(vi)-(CF_4) $\frac{1}{2}M_2O_3 + Ba_{Ba} + \frac{1}{2}CF_4(g) \rightarrow M_{Ba} + BaO + \frac{1}{2}CO_2(g) + F_2$

(vii)-(CH_4) $\frac{1}{2}M_2O_3 + Ba_{Ba} + \frac{1}{2}CH_4(g) \rightarrow M_{Ba} + BaO + \frac{1}{2}CO(g) + H_2$

Table 1. Solution energies for rare earth divalent dopant ions in $BaAl_2O_4$ at different temperatures.

		Eu						
		Schemes						
Temperature	Site	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
0K	Ba1	2,70	1,43	7,53	6,24	4,77	1,77	3,31
	Ba2	**2,69**	**1,42**	**7,52**	**6,23**	**4,76**	**1,76**	**3,30**
293K	Ba1	**1,19**	**-0,08**	**6,02**	**4,73**	**3,26**	**0,26**	**1,80**
	Ba2	1,28	0,01	6,11	4,82	3,35	0,35	1,89

References

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