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A COMPUTER SIMULATION STUDY OF OXYGEN DEFECT CENTERS IN BaFBr AND BaFCl

M. S. ISLAM† and R. C. BAETZOLD
Corporate Research Laboratories, Eastman Kodak Company, Rochester, NY 14650, U.S.A.

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Abstract—Atomistic simulation techniques are used to examine several oxygen trapped-hole centers resulting from X-irradiation of BaFBr and BaFCl crystals. The calculations employ recently derived interatomic potentials for the oxide ion–host anion interactions. Particular attention is focused on the sites occupied by the oxide impurity and the energetics of ionization. Our results show the defect model involving O^- substitutional at a Br^-/Cl^- site to be a favorable trapped-hole center, in accord with the assignment proposed from EPR measurements. The defect simulations find a large energy barrier to oxide interstitial formation from the oxide precursor at a substitutional site, which suggests that conversion from O_x^- to O_{int}^- is highly unlikely as has been demonstrated in EPR experiments. Ion displacements following lattice relaxation about the defect are also examined. The position of O^- substituted for Br^- in BaFBr is computed to be displaced from the regular lattice site by 0.53 Å, along the *c* axis towards the Ba^{2+} ion plane, in agreement with models derived later from ENDOR experiments, while O^- substituted for F^- remains on the lattice site in agreement with experiment.

Keywords: Simulation, BaFBr, oxide, sites.

1. INTRODUCTION

A wide range of luminescent and optical properties are obtained by doping BaFBr and BaFCl with various rare-earth elements. These rare-earth activated compounds are of considerable interest owing to the development of new phosphor materials for practical X-ray imaging applications.

The mechanism of the storage phosphor process is known to be highly dependent upon the energetics and mobility of various electron and hole states. Previous work on BaFBr and BaFCl has included a number of studies of such defect states using spin-resonance [1–4] and theoretical [5–7] techniques. The electron states have been characterized as electrons trapped at halide ion vacancies or F-centers [1, 2, 4]. The different hole states that have been identified include the self-trapped hole or V_k center, which has only been detected at low temperatures [3, 8]. Despite the range of studies on BaFBr and BaFCl the exact nature of the storage phosphor mechanism is still not fully understood, and is important in any attempt to optimize the materials' operational properties.

It has been known for some time that the alkali and alkaline-earth halides are readily contaminated with oxygen impurities [9–11]. In addition, the possibility of oxygen impurities has PbFCl, a compound that is isostructural with the barium fluorohalides, has been reported [12, 13]. However, the only evidence as to the structural configurations of oxygen impurity centers specifically in BaFBr and BaFCl has come from a recent EPR study [14] of the nominally pure materials. This work detected oxygen-containing defect centers that serve as hole traps during the exposure to band gap (X-rays) and sub-band gap (deep u.v.) radiation. The trapped-hole centers were tentatively identified as $O^-(2p^5)$ substituting at a Br^-/Cl^- lattice site and O^- at a F^- lattice site in BaFBr [15]; these are referred to as O_x^- (where X = Br or Cl) and O_F^-, respectively. The proposed assignments were based on the analysis of super hyperfine structures, together with a comparison of the observed *g* matrices to those reported for oxygen-containing centers in other materials. These impurity defect centers have been discussed as possible intermediates in the imaging process [14, 15].

The aim of the present study is to use atomistic computer simulation techniques to examine further the defect models for the oxygen impurity centers in undoped BaFBr and BaFCl. For a greater understanding of the role of oxygen impurities in the radiation mechanism, it is apparent that the precise location of the trapped-hole centers in the crystal lattice is important. This problem can be investigated by calculating the relative energetics of substitutional and interstitial formation at different crystal lattice

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†Present address: Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, U.K.

sites. In addition to computing defect energies, the study has been extended to examine ion displacements following lattice relaxation.

2. METHOD

The theoretical methods used to simulate the perfect lattice and calculate defect energies are exactly as in the previous studies of these systems, [6] and other possible phosphor compounds [7], so we will confine ourselves to a brief outline of the model used. The interatomic interactions in the crystal are described by Coulomb and two-body short-range potentials:

$$\phi_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + A \exp(-r_{ij}/\rho) - C/r_{ij}^6. \qquad (1)$$

The Coulombic terms are treated by the shell model [16], which allows for polarization of the lattice ions. The calculations require specification of potentials representing the interaction both between host lattice ions and between host and impurity ions. The parameters for the host materials, BaFBr and BaFCl, are taken from the studies of Baetzold [6], who developed pair-potentials by empirical fitting to the tetragonal PbFCl-type structure adopted by these systems, as illustrated in Fig. 1. The host ion-oxygen impurity ion potentials are also in the form of Buckingham functions. For the O^{2-}–Ba^{2+} interaction the potential was transferred directly from a modelling study of BaO [17]. It was necessary to derive potentials for the O^{2-} anion interactions, which was achieved by semi-empirical procedures based on electron-gas techniques [18] within a computer program developed by Harding and Harker [19].

For the O^- hole state a small polaron model is assumed, in which the hole is localized on a single oxide ion and self-trapped by its own polarization field. We note, however, that for electronic states, such as the F-center, where the electron distribution is considerably delocalized, the appropriate computations would involve quantum mechanical methods. When considering the potentials for the interaction between lattice ions and the O^- hole species, the parameters are treated as identical to the O^{2-} ion, with the shell charge reduced by unity. This approximation has given a satisfactory description of the oxide impurity since substitution energies and equilibrium positions for O^- differed only by minimal amounts when O^- halide ion short-range potentials were employed. All the potentials and shell model parameters employed in the present study are listed in Table 1.

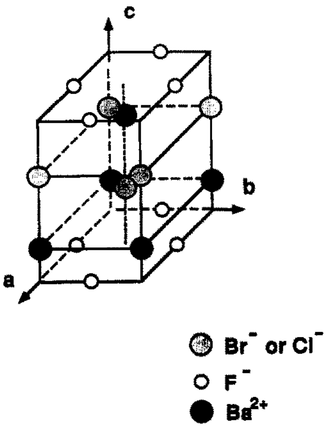

Fig. 1. The tetragonal crystal structure of BaFX (where X = Br or Cl).

The defect calculations were performed using the generalized Mott–Littleton approach [20], which divides the crystal into two regions so that ions in the inner region, close to the defect, are relaxed explicitly,

Table 1. Interatomic potentials

(a) BaFBr and BaFCl

(i) Short-range

Interaction†	Parameter‡	BaFBr	BaFCl
Ba–Ba	A	588,445.0	588,445.0
	ρ	0.2070	0.2070
	C	42.8	0.0
Ba–F	A	5193.3	5193.3
	ρ	0.2795	0.2795
	C	31.5	0.0
F–F	A	1227.7	1127.7
	ρ	0.2753	0.2753
	C	20.9	155.0
Ba–X	A	4431.0	4431.0
	ρ	0.3644	0.3644
	C	477.5	532.0
F–X	A	3588.0	1200.0
	ρ	0.3815	0.3000
	C	829.4	46.3
X–X	A	2745.0	1227.2
	ρ	0.3986	0.3214
	C	387.3	172.0

†X refers to Br or Cl.

‡Units are: A (eV); ρ (Å); C (eV Å^6).

(ii) Shell model

Species	Shell charge (e)	Force constant (eV Å^{-2})
Ba^{2+}	−16.99	1709.1
F^-	−2.38	101.2
Br^-	−2.094	18.30
Cl^-	−2.519	29.38

(b) Oxygen impurity

(i) Short-range

Interaction	A	ρ	C
O–Ba	2027.5	0.34149	0.0
O–F	198.32	0.30102	0.0
O–Br	636.5	0.2877	0.0
O–Cl	342.87	0.28696	0.0

(ii) Shell model

Species	Shell charge (e)	Force constant (eV Å^{-2})
O^{2-}	−2.389	42.0
O^-	−1.389	42.0

Table 2. Formation energies (in eV) of isolated oxygen defect centers

Defect	BaFBr	BaFCl
O^{2-} replace F^- (O_F^{2-})	−12.40	−11.18
O^- replace F^- (O_F^-)	2.52	2.63
O^{2-} replace X^- (O_x^{2-})	−12.06	−11.14
O^- replace X^- (O_x^-)	0.50	0.64
O^{2-} interstitial (O_{int}^{2-})	−14.05	−11.26
O^- interstitial (O_{int}^-)	−0.67	−0.77

while the remainder of the crystal is treated by continuum methods. For detailed reviews of the theoretical techniques used, incorporated into the HADES [21] and CASCADE [22] codes, and their application to other systems we refer to Catlow and Mackrodt [23] and Agullo-Lopez *et al.* [24].

3. RESULTS AND DISCUSSION

We will confine this investigation to the substitutional and possible interstitial species in BaFBr and BaFCl formed after X-ray exposure, namely O_x^- and O_{int}^-. The calculated defect energies for O_x^{2-} and O_x^- substitutionals are reported in Table 2 together with results for O_{int}^{2-} and O_{int}^- interstitials. The energy reference is zero for an ion at infinity. Thus the substitutional energy corresponds to removing the host ion to infinity and replacing it with the foreign ion; likewise the interstitial energy corresponds to introducing an ion from infinity into a nonperfect lattice site. Both calculations allow full ion relaxation of the host ions about the defect species. We note that our defect simulations have confirmed that the most energetically favorable mode of oxygen incorporation is as a doubly-charged substitutional.

The only stable interstitial configuration was found to be in the unit-cell face comprised of Ba^{2+} and X^- ions, but midway between the two adjacent X^- planes; this position is illustrated in Fig. 2. The vector displacements are also shown for the O_{int}^- case, which indicate significant diagonal movement of both the Ba^{2+} ions towards the interstitial, and the X^- ions away from the interstitial ion. The O^- hole center in the interstitial position, therefore, induces a small perturbation in the local structure. We should note that the doubly-charged oxygen interstitial led to instabilities in the defect calculation when allowed to relax. Thus the relevant energies in Table 2 refer to the O^{2-} ion fixed at the interstitial position. These instabilities are probably due to the large Madelung field associated with O^{2-} at the interstitial site. The energies of the O^{2-} interstitials in BaFBr and BaFCl are, therefore, likely to be lower than our calculated values.

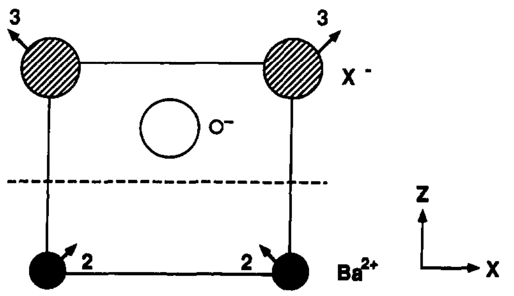

Fig. 2. The stable position for the oxide interstitial ion in the Ba/X face. The dashed line indicates the adjacent X^- ion plane. Approximate displacements are shown in 10^{-1} Å.

Our calculations on hole species enable us to comment on preferential substitution sites within the crystal lattice. For the isovalent substitution of O^- for X^-, charge-compensation is not necessary and hence the energies of O_x^- and O_F^- can be directly compared. Examination of the entries in Table 2 clearly reveals that it is energetically more favorable to form O^- on the X^- rather than the F^- position. By combining the individual defect energies in Table 2 with an electron affinity for O^- of −8.75 eV [25] it is possible to estimate the energies of hole (O^-) formation, with respect to electrons in the vacuum. Alternatively, this reaction may be equated with the appropriate ionization process to give the energy level of the defect. The results are given in Table 3, for both substitutional and interstitial species. We note that there are uncertainties in the absolute magnitude of the hole energies, owing to uncertainties in the free-ion term that must be added to our computed energies. Nevertheless, our concern here is to examine the difference in energetics at various sites, for which the calculation procedures have been shown to have general validity.

Two principal features emerge from examination of the hole energies. First, a hole is found to be trapped endothermically at both substitutional and interstitial O^{2-}, although the values are less than the band gap energy (~8.3 eV). Second, the results show that the formation of O_x^- is energetically preferred to that of O_F^-. This suggests that u.v.-irradiation of the oxygen contaminated material will lead to the formation of the former species in both BaFBr and BaFCl if only the most stable species is formed. The calculations, therefore, support the model in which one of the oxygen hole-trapped centers is

Table 3. Hole formation energies (in eV)†
$O^{2-} \rightarrow O^- + e^-$

Hole	BaFBr	BaFCl
O_F^-	6.17	5.02
$O_{Br,Cl}^-$	3.81	3.06
O_{int}^-	5.97	1.74

†Electron affinity of −8.75 eV was used [25].

characterized as O^- at a Br^- or Cl^- site, in agreement with the structural assignment proposed from EPR measurements [14]. It is important to add that the possibility of O^{2-} positioned at a site on the F^- sublattice should not be ignored, although the entries in Table 3 clearly suggest that photoionization has the smallest threshold energy for O^{2-} on the Br^- or Cl^- sublattice.

Calculations were performed on clusters containing substitutionals and vacancies as well as isolated defects. It is well established that interactions between impurity ions and their charge-compensating defects can lead to distinct impurity–defect pairs, largely due to Coulombic interactions. We have considered electroneutral pair clusters comprised of nearest-neighbor O^{2-} substitutionals and anion vacancies. Since the formation of X^- vacancies has been shown to be far more favorable than F^- vacancies [7], these defects are assumed to be the charge-compensating species.

The results of the calculations are reported in Table 4, which gives the total energies of the defect clusters and the binding energies with respect to the component isolated defects. Our sign convention is such that a negative value for the binding energy indicates the system is bound. Examination of the binding energies reveals that in both BaFBr and BaFCl the clusters are bound and that the O_F^{2-} substitutional has a greater binding energy than the O_x^{2-} substitutional. These results suggest that there will be a greater tendency to clustering and less random distribution at higher oxygen impurity concentrations. Thus the presence of such defect pairs is certainly a possibility in these materials. It is noted, however, that clustering does not necessarily preclude the presence of isolated substitutionals, since clusters will be in equilibrium with single defects.

We now consider the second species possible in BaFBr or BaFCl. The structural models O_F^- and O_{int}^- both have site symmetries that are consistent with the observed g-matrix data in which each oxygen center is surrounded by four equivalent Ba^{2+} ions and four equivalent X^- ions in approximate tetrahedral configurations. Based upon the analysis of the bromine super hyperfine structure this species has been assigned to the substitutional defect model [15].

Table 4. Defect clusters of O^{2-} substitutionals and anion vacancies

Complex	E (eV)	B.E.† (eV)
BaFBr		
$(O_F^{2-}\ X_{vac}^-)$	−8.92	−0.31
$(O_x^{2-}\ X_{vac}^-)$	−8.43	−0.16
BaFCl		
$(O_F^{2-}\ X_{vac}^-)$	−7.40	−0.82
$(O_x^{2-}\ X_{vac}^-)$	−7.27	−0.73

†Binding energy with respect to isolated defects. A negative value indicates the system is bound.

Conclusions on the relative stabilities of O_F^- and O_{int}^- from comparisons of our calculated hole formation energies are handicapped by selection of energy zero, i.e. the two models do not have identical reference points. If we assume that the precursor O^{2-} ion is positioned on either the F sublattice or the interstitial site, then the results in Table 3 indicate that following X-ray exposure the formation of O_{int}^- would be energetically favored. It should be stressed that the precise location of the precursor species has not been unambiguously determined, on account of the O^{2-} ion being diamagnetic and, therefore, not detectable by either EPR or ENDOR techniques.

Here we can estimate the thermodynamics of the formation of the interstitial directly from the substitutional species, by examining the following defect reaction

$$O_x \rightarrow X_{vac}^- + O_{int}, \tag{2}$$

which represents the production of an O_{int} and X^- vacancy pair from the substitutional O_x precursor, for both the O^{2-} and O^- species. The defect pair is assumed to be separated owing to the facile diffusion of the X^- vacancy via an interplanar mechanism [7]. An alternative mechanism involves separation by O^- interstitial diffusion. Our calculations in BaFBr give 0.76 eV as this activation barrier, which is only slightly larger than the vacancy mechanism. The energy changes for this reaction have been derived by combining the energies in Table 2 with vacancy energies from a recent simulation study [6] and are presented in Table 5. The resulting values are found to be strongly endothermic and consequently preclude interstitial formation by this reaction. This finding clearly suggests that no direct conversion occurs from the O_x^- center to the O_{int}^- center, a result that is consistent with the available EPR data and is consistent with greater O_F^- than O_{int}^- stability.

It should be emphasized that the starting materials are commonly nonstoichiometric, and often with an excess of F^- ions. The deviation from stoichiometry is likely to yield anti-site formation [6] or a corresponding concentration of charge compensating anion vacancies, and could, therefore, dominate the site-preference energetics. Furthermore, the presence

Table 5. Energetics† of the reactions $O_x \rightarrow X_{vac} + O_{int}$

Material	O species	ΔE (eV)
BaFBr	O^{2-}	1.80
	O^-	3.62
BaFCl	O^{2-}	4.48
	O^-	4.47

†Vacancy energies from Ref. 6.

Table 6. Displacements of the substitutional O^- ion

	BaFBr		BaFCl	
Undisplaced site†	Displaced site	Δ (Å)	Displaced site	Δ (Å)
O_F^-				
(0.5 0 0)	(0.5 0 0)	0.0	(0.5 0 0)	0.0
O_x^-				
(0 0 0.58)	(0 0 0.46)	0.53	(0 0 0.56)	0.09

†Atomic coordinates in lattice units (a_0).

of oxygen impurities in the nominally pure material suggests that doping with rare-earths is not necessary for oxygen incorporation to occur. It is likely, however, that oxygen incorporation is enhanced by the presence of dopants because of the stabilization from dopant–oxygen complex formation [26]. Further work to investigate such problems would be of considerable interest.

In addition to the calculation of defect energies, the computer simulations generate useful information on the final atomic positions following lattice relaxation. As already remarked, we find significant movement of Ba^{2+} and X^- ions immediately surrounding the O_{int}^- defect center, shown in Fig. 2. For the case of the O^- substitutional centers, the relaxed positions are summarized in Table 6. The results show that there is negligible movement for O^- on the F^- site and only a small O^- ion displacement of 0.09 Å from the Cl^- site. Moreover, there is no significant relaxation of host ions surrounding these two defect species. In contrast, the example of O^- substituting for Br^- is observed to yield a substantial O^- displacement to attain a minimum energy configuration; the O^- ion moves 0.53 Å off the regular lattice position, along the ⟨001⟩ direction towards the F^- plane.

Note that on the basis of ion size factors the various equilibrium displacements are as expected, in view of the large difference in ionic radii of the substitutional O^- and host Br^- ions. Interestingly, from a recent preliminary analysis of ENDOR data for BaFBr using the Lowdin orthogonalization procedure [27] for the calculation of the super hyperfine interactions, Spaeth [28] determined a displacement of 0.5 Å along the c-direction, for the O^- ion on a Br^- site, with the unpaired p orbital perpendicular to the plane. This finding is in excellent agreement with our result. Clearly analogous ENDOR measurements of the O_{Cl}^- center in BaFCl would be of interest towards testing our predicted displacements.

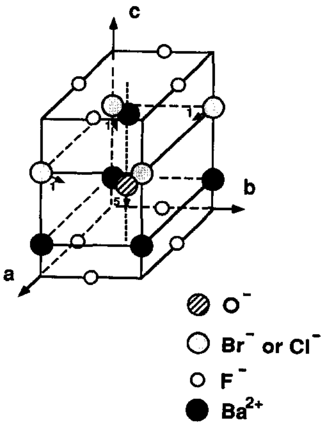

Fig. 3. Relaxation of lattice ions with the formation of the O^- hole center on the Br^- site in BaFBr. Approximate displacements are indicated in 10^{-1} Å.

The vector displacements of ions near the O_{Br}^- center from the defect calculation are shown in Fig. 3. The overall character of the movement of neighboring ions, in response to O^- hole formation, is essentially determined by symmetry requirements. In particular, the O_{Br}^- center preserves four-fold site symmetry even with lattice relaxation, as long as the defect displaces only in the ⟨001⟩ direction. In the case of host ions neighboring the defect there is only small Ba^{2+} displacement of about 0.05 Å and no significant movement of the F^- ions. The largest displacements are associated with the four equivalent Br^- ions moving by about 0.1 Å towards the lattice site of the substituted Br^-.

The cause of the off-center displacement has been discussed in terms of the balance between overlap and polarization terms in the lattice energy [29]. Since the O^- is smaller than Br^- the forces due to overlap of charge clouds are reduced and therefore movement of the substitutional ion off the normal lattice site is possible, with the resulting displacement stabilized by the lattice polarization energy. The energy stabilization gained by moving O^- from the Br^- site to its equilibrium site is 0.08 eV and is in large part due to the balance between O^-–Br^- and O^-–Ba^{2+} short-range forces. This is because the Br^- site is near the center of a cube framed by nearest-neighbor ions comprised by four Br^- ions above and four Ba^{2+} ions below, in the case of BaFBr. In addition, there may be electrostatic fields along the c-axis in this low symmetry crystal structure.

4. CONCLUSIONS

The defect simulations of substitutional species in BaFBr and BaFCl confirm the preferential occupancy of O^- for X^- site and favor the formation of the O_x^-

hole center over that of O_F^-. This supports the O_x^- substitutional as a possible trapped-hole center in the barium fluorohalides, in accord with the structural assignment proposed from EPR measurements. For this model a substantial O^- ion displacement of about 0.5 Å off the regular Br^- position is calculated, in excellent agreement with models derived later from ENDOR experiments. Such a result is particularly encouraging as predictions of off-center behavior provide a strict test of the potentials employed.

Conclusions on the relative stabilities of O_F^- vs O_{int}^- have been hindered by the selection of an appropriate reference point. The calculations have, nonetheless, shown a large thermodynamic barrier to oxide interstitial formation from the oxide substitutional precursor, suggesting that conversion from O_x^- to O_{int}^- is unlikely. ENDOR studies support the O_F^- configuration of this defect center.

The preliminary study has shown that computer simulation techniques provide a useful way of investigating hole state stabilities in BaFBr and BaFCl, and also aid in the interpretation of the available experimental data. The mechanism of oxygen contamination in the barium fluorohalides, however, has not been determined, although previous studies alkaline-earth fluorides [12, 26] have suggested that oxygen is incorporated by a hydrolysis reaction rather than an oxidation process. Further studies will explore this problem.

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