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# Computer Modelling Studies of Defect Structures and Migration Mechanisms in Yttrium Aluminium Garnet

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***Abstract***

*Using computer simulation techniques the defect structure, the ionic migration mechanisms, the solution enthalpies and the oxidation/reduction behaviour of yttrium aluminium garnet was investigated. Based on the saddle point energies a continuous path for a migrating anion was identified. The calculated results for the solution energies of MgO and CaO imply that these oxides have a low solubility in the garnet.*

*Die Defektstruktur, die Mechanismen der Ionenwanderung, die Lösungsenthalpien und das Oxidations-/Reduktions-Verhalten von Ytttrium Aluminium Granat wurden mittels Computer-Simulation untersucht. Durch den Vergleich der Übergangsenergien für verschiedene Ionensprünge in den Untergittern wurden mögliche Diffusionswege der Ionen untersucht. Berechnete Lösungsenthalpien für MgO und CaO weisen auf deren geringe Löslichkeit hin.*

*On a étudié par simulation sur ordinateur la structure des défauts, les mécanismes de migration ionique, les enthalpies de dissolution et le comportement en oxydoréduction d'un grenat yttrium aluminium. En comparant les énergies de transition des différentes migrations ioniques dans les sous-réseaux, on a pu établir les parcours possibles de diffusion des ions. Les valeurs des énergies de dissolution calculées pour MgO et CaO impliquent que ces oxydes aient une faible solubilité dans le grenat.*

## 1 Introduction

The properties of crystalline matter, such as functional or structural ceramics, are, to a large extent, determined by the presence of ionic defects. In recent years there has been a considerable success in the calculation of defect formation energies, ionic migration energies, redox energies, etc., in ionic crystals (e.g. $Al_2O_3$,[1,2] MgO,[3] $Fe_2O_3$,[4] $TiO_2$,[1] $BaTiO_3$,[5] $La_2CuO_4$[6]). The present study reports an application of these methods to the garnet $Y_3Al_5O_{12}$, yttrium aluminium garnet (YAG). Single-crystalline YAG has been well known as a host material for laser-emitting ions since 1964.[7] Later in the 1970s it was found that YAG powders can be sintered to translucency.[8,9] Experiments performed in the 1980s revealed that translucent YAG ceramics have a better corrosion resistance against hot alkali vapour than translucent alumina.[10] This makes YAG a candidate material to produce high-pressure sodium lamp envelopes. Furthermore the optical transmittance and the mechanical properties of YAG are better than those of translucent alumina.

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In this paper studies on the transport properties and defect chemistry of YAG ceramics[11,12] are continued, by performing Mott–Littleton defect calculations available in the CASCADE computer code.[13] Point defect formation energies, the energetics of redox processes, solution enthalpies for CaO and MgO in YAG, the energetics of defect clustering and saddle point energies for elementary diffusion steps in the YAG lattice will be discussed.

## 2 Simulation Methods

The static lattice simulation technique (which refers to methods that do not take into account directly the thermal motion of the crystal lattice) used in this paper makes use of the generalized Mott–Littleton method available in the computer code CASCADE.[14,15] For ionic materials the theory of lattice defects is largely concerned with two main problems:

(1) The derivation of suitable interatomic potentials (in strongly ionic crystals two body potentials are generally adequate).
(2) The treatment of the lattice relaxation around a lattice defect.

For the first of these problems, there are two different approaches. One involves the use of Born–Mayer or Buckingham potentials which are parameterized empirically by fitting the calculated perfect lattice properties, such as lattice energy, dielectric and elastic constants, to experimental values. The Buckingham potential is given by

$$V(r) = A\exp(r/\rho) - Cr^{-6} \qquad (1)$$

where $r$ is the distance between a pair of ions. The parameters $A$, $\rho$ and $C$ must be assigned for each probable ion–ion interaction. By this procedure empirical short-range potentials are obtained; they are used here. Three potentials for the undoped YAG were thought to be necessary to describe fully the system: $Y^{3+}$–$O^{2-}$, $Al^{3+}$–$O^{2-}$ and an $O^{2-}$–$O^{2-}$ potential. Cation–cation interactions were neglected as it was thought that the distance involved meant that this interaction is negligible for this structure. For doped YAG additionally the $Ca^{2+}$–$O^{2-}$ and the $Mg^{2+}$–$O^{2-}$ potentials were used. An alternative approach (not used in the present study) is to calculate the interatomic potentials using the electron-gas method[16] or using ab-initio Hartree–Fock techniques.[17]

An essential feature of the computer simulation of defective ionic solids is the inclusion of ionic polarization. Despite its simplicity the shell model[18] remains the most effective way of doing this.

The second question, dealing with the lattice relaxation around a defect, is treated in terms of a model developed by Mott & Littleton[14] and by Lidiard & Norgett[19] and Norgett.[20] The basic idea behind this model is the equilibration of the total energy of the crystal by independent relaxation of cores and shells of the ions around the lattice defect. A detailed discussion of the simulation procedure is given by Catlow, Dixon & Mackrodt[16] and Catlow.[15]

## 3 The Garnet Lattice

Garnets have a cubic body-centred lattice, space group *Ia3d*. The cations occupy 24 *c*-sites with dodecahedral coordination, 16 *a*-sites with octahedral coordination and 24 *d*-sites with tetrahedral oxygen coordination. There are 8 formula units $\{C_3\}[A_2](D_3)O_{12}$ per unit cell, where O denotes oxygen and the different brackets {}, [] and () symbolize cations in the dodecahedral, octahedral and tetrahedral sites respectively. In YAG the Al ions occupy both the tetrahedral and the octahedral sites, while Y is located on the dodecahedral sites. The formula can therefore be written as $\{Y_3\}[Al_2](Al_3)O_{12}$. The lattice constant is $a = 12{\cdot}000$ Å.

**Table 1.** Input potential parameters and shell constants for YAG

| *Ion* | $A$ ($eV$) | $\rho$ (Å) | $Y^+$ ($\|e\|$) | $K^+$ ($eV$Å$^{-2}$) | $C$ ($eV$Å$^{-6}$) |
|---|---|---|---|---|---|
| $O^{2-}$–$O^{2-}$ | 22 664·0 | 0·149 | 0·848 1 | 74·92 | 27·88 [1] |
| $Y^{3+}$–$O^{2-}$ | 1 345·1 | 0·349 1 | −0·251 | 71·70 | 0·0 [5] |
| $Al^{3+}$–$O^{2-}$ | 1 469·3 | 0·299 1 | 3·00 | — | 0·0 [1] |
| $Ca^{2+}$–$O^{2-}$ | 1 090·1 | 0·343 7 | −1·135 | 110·20 | 0·0 [5] |
| $Mg^{2+}$–$O^{2-}$ | 1 280·1 | 0·317 7 | 2·00 | — | 0·0 [5] |

$A$ and $\rho$ = parameters in the equation for the Buckingham potential; $Y^+$ = charge of the core; $K^+$ = core-shell spring constant, $C$ = attractive contribution.
Note that all short range potentials were cut-off (i.e. set to zero) for distances larger than 0·6$a$ ($a$ = lattice parameter).

**Table 2.** Calculated and experimental values of crystal properties for YAG and $Al_2O_3$ (taken from Ref. 1)

| *Constant* | *YAG* | | *Constant* | *$Al_2O_3$* | |
|---|---|---|---|---|---|
| | *Calculated* | *Experimental* | | *Calculated* | *Experimental* |
| $\varepsilon_0$ | 8·1 | 11·0 | $\varepsilon_0^{11}$ | 9·38 | 9·34 |
| | | | $\varepsilon_0^{33}$ | 11·52 | 11·54 |
| $\varepsilon_\infty$ | 2·9 | 3·5 | $\varepsilon_\infty^{11}$ | 2·08 | 3·1 |
| | | | $\varepsilon_\infty^{33}$ | 2·02 | — |
| $C_{11}$ (GPa) | 395 | 333 | | 429·6 | 496·9 |
| $C_{12}$ (GPa) | 135 | 113 | | 154·8 | 163·6 |
| $C_{44}$ (GPa) | 117 | 115 | | 166 | 147·4 |
| Lattice energy[a] | 1 205 | | | 160·21 | 160·4 |

The experimental data were taken from Refs 22 and 23.
[a] Lattice energy per unit cell in eV (with 8 formula units of YAG).

## 4 Results

### 4.1 Properties of the perfect YAG lattice

Table 1 gives the potential parameters for the perfect lattice simulation and the shell parameters. The small ions Al and Mg are considered to be unpolarizable, while the other ions are treated as polarizable. The polarizability in terms of the core–shell model is introduced by a spring constant $K^+$ which characterizes the coupling between the core and the massless shell. The potential parameters used in this study are reported in Refs 1 and 5.

The calculated dielectric and elastic constants which were derived by the standard procedure available in the PLUTO subroutine[21] are given in Table 2. The values are presented for YAG and for $Al_2O_3$ for the sake of comparison ($Al_2O_3$ is a relatively simply structured material, for which extensive simulation data are available[1,2]).

Calculated perfect lattice data for YAG given in Table 2 are sufficiently close to the experimental values to demonstrate the reliability of the potentials used.

### 4.2 Basic point defect formation energies

The basic defect reactions are the formation of simple point defects. In this section the formation energies of cation and anion vacancies and interstitials are considered; the calculated values are given in Table 3.

From single point defect formation energies a first approximation to the Schottky and Frenkel energies can be derived. Taking the vacancy formation energies for yttrium, aluminium (on the *a*- and *d*-sites) and oxygen leads to a Schottky energy (to form a complete Schottky multiplet) of 106·3 eV (10 257 kJ/mol),† which gives 5·32 eV per defect (513 kJ/mol). The energy per defect to form a Frenkel pair lies between 7 and 10 eV (675 and 965 kJ/mol; see Table 4). Here the energies of isolated defects are taken into account; to consider obtainable physical processes further work is necessary.

However, the calculations indicate that Schottky

† The Schottky energy is the energy necessary to remove a complete formula unit YAG from the crystal interior (the sum of the defect formation energies minus the lattice energy).

**Table 3.** Formation energies for point defects in YAG

| *Defect* | *Symbol* | *Defect formation energy per defect* | |
|---|---|---|---|
| | | *eV* | *kJ/mol* |
| Oxygen vacancy | $V_O^{\cdot\cdot}$ | 22·35 | 2 157 |
| Yttrium vacancy | $V_Y'''$ | 46·5 | 4 487 |
| Yttrium interstitial | $Y_i^{\cdot\cdot\cdot}$ | −25·62 | −2 472 |
| Aluminium vacancy on *d*-site | $V_{Al}'''$ | 58·90 | 5 683 |
| Aluminium vacancy on *a*-site | $V_{Al}'''$ | 60·24 | 5 813 |
| Aluminium interstitial | $Al_i^{\cdot\cdot\cdot}$ | −45·11 | −4 353 |
| Ca-substitutional | $Ca_Y'$ | 23·0 | 2 219 |
| Mg-substitutional | $Mg_Y'$ | 18·3 | 1 766 |

**Table 4.** The formation energies for combined defects in YAG

| | *Defect formation energy* | |
|---|---|---|
| | *eV* | *kJ/mol* |
| Schottky energy | 5·32 | 513 |
| Yttrium Frenkel | 10·44 | 1 007 |
| Aluminium Frenkel | | |
| From an *a*-site | 7·57 | 730 |
| From a *d*-site | 6·88 | 664 |

disorder should be energetically favoured compared with Frenkel disorder. The result is in accordance with the conclusion derived by others on the basis of experimental or theoretical work.[24]

### 4.3 Foreign cations in YAG

The properties of crystalline materials are strongly influenced by the presence of impurities. These ions occupy specific sites depending on their radius. $Ca^{2+}$ and $Mg^{2+}$ both are thought to occupy *c*-sites.

The energies for replacing an Y ion by a $Mg^{2+}$ and a $Ca^{2+}$ ion are 18·3 eV (1766 kJ/mol) and 23·0 eV (2219 kJ/mol) respectively (see Table 3). It is noted that these energies refer to processes with respect to ions at infinity. Thus for Ca-substitution the calculated energy refers to the process

$$Y_Y^x + Ca_{(vacuum)}^{2+} \longrightarrow Ca_Y' + Y_{(vacuum)}^{3+}$$

Using these values it is possible to calculate the solution enthalpies for MgO and CaO in the YAG lattice. The substitutional energy has to be considered together with an appropriate charge compensating defect and a full Born–Haber cycle evaluated for the solution reactions. For low valence ions compensation can be provided by anion vacancies, by cation interstitials and by a self-compensation mechanism. Calculations show that anion vacancy compensation has the lowest energy in YAG. The reaction for the vacancy compensated dissolution of CaO is

$$CaO + Y_Y^x + 1/2O_o^x \longleftrightarrow Ca_Y' + 1/2V_o^{\cdot\cdot} + 1/2Y_2O_3 \quad (2)$$

in which $Y_2O_3$ refers to yttrium oxide on the surface of the crystal. So, to calculate the energetics of the reaction given in eqn (2), the lattice energies for CaO, MgO and $Y_2O_3$ are needed, as well as the point defect formation energies. The lattice energies for CaO and MgO were previously calculated, applying the same potentials as used in the present study, as 36·0 eV (3474 kJ/mol) and 40·74 eV (3931 kJ/mol).[25] For $Y_2O_3$ the lattice energy is calculated to be 135·5 eV (13 074 kJ/mol). The solution enthalpy $E_{Ca}(sol)$ for CaO in YAG was calculated by taking the defect formation energies given in Table 3:

$$E_{Ca}(sol) = E(CaO) + E(Ca_Y') + 1/2E(V_o^{\cdot\cdot}) - 1/2E(Y_2O_3) = 2{\cdot}48\,eV\ (239\,kJ/mol) \quad (3)$$

using the known values of $E(CaO)$ and $E(Y_2O_3)$, the lattice energies of CaO and $Y_2O_3$. From eqn (3) a value of 2·48 eV (239 kJ/mol) per CaO is obtained for the solution enthalpy for CaO in YAG. An analogous reaction can be written for MgO, which leads to a solution enthalpy of 2·52 eV per MgO (or 243 kJ/mol MgO).

### 4.4 Clustering effects

In a crystal lattice which is doped with aliovalent ions clustering of defects may occur, since defects carrying opposite charges attract each other. Thus positively charged oxygen vacancies $V_o^{\cdot\cdot}$ and negatively charged substitutionals $Ca_Y'$ or $Mg_Y'$ can interact by forming stabilized defect clusters:

$$V_o^{\cdot\cdot} + Ca_Y' \longleftrightarrow (V_o^{\cdot\cdot}Ca_Y')^{\cdot} \quad (4)$$

and

$$V_o^{\cdot\cdot} + 2\,Ca_Y' \longleftrightarrow (Ca_Y'V_o^{\cdot\cdot}Ca_Y')^x \quad (5)$$

The defect cluster $(V_o^{\cdot\cdot}\,Ca_Y')^{\cdot}$, carrying a positive charge, has an association energy of 1 eV, while the neutral defect trimer $(Ca_Y'\,V_o^{\cdot\cdot}\,Ca_Y')^x$ is bound by an energy of 1·7 eV. The direct effect of such defect clustering is a reduction of the concentration of free oxygen vacancies; the $V_o^{\cdot\cdot}$ concentration is lowered by the amount which is bound by the $Ca_Y'$ (or $Mg_Y'$). Defect clustering will also result in more negative solution energies.

### 4.5 Energies of oxidation and reduction

Following the discussion of electronic disorder in YAG, which was recently published as a part of a more comprehensive paper on an experimental investigation of the defect chemistry of doped YAG,[12] it is appropriate now to consider calculated energies of oxidation and reduction, as these control the level of non-stoichiometry in the oxides. The processes concerned are

$$O_o^x \longleftrightarrow V_o^{\cdot\cdot} + 1/2O_2 + 2e'\,(E_{red}) \quad (6)$$

which is the equilibration of YAG at low oxygen partial pressure, and

$$1/2O_2 + V_o^{\cdot\cdot} \longleftrightarrow O_o^x + 2\,h^{\cdot}\,(E_{ox}) \quad (7)$$

which represents the hole formation in YAG doped with low valence ions, which was investigated experimentally in a previous study.[12] This reaction is

the most probable one. $E_{red}$ and $E_{ox}$ are oxidation and reduction energies respectively.

Both holes and electrons are treated in terms of the small polaron model. It is assumed that the electron is located on a lattice aluminium ion and the lattice distorts around the centre, i.e. the following reaction is assumed for the electron formation

$$Al^x_{Al} + e' \longleftrightarrow Al'_{Al}\ (E_e) \qquad (8)$$

The polaron formation energy $E_e$ can be derived by combining the energy calculated for replacing $Al^{3+}$ by $Al^{2+}$ (31·6 eV; 3049 kJ/mol) with the third ionization potential of Al (28·53 eV; 2753 kJ/mol).[26] Thus for $E_e$ an energy of 3·07 eV (296 kJ/mol) is obtained. The reduction energy $E_{red}$, which is a combination of eqn (6) and eqn (8), symbolized by eqn (6a)

$$O^x_o + 2Al^x_{Al} \longleftrightarrow V^{\cdot\cdot}_o + 1/2O_2 + 2Al'_{Al} \qquad (6a)$$

is given by

$$E_{red} = E(V^{\cdot\cdot}_o) - 1/2E_{Diss} + E_{12} + 2E_e$$
$$= 18{\cdot}63\ \text{eV}\ (1800\ \text{kJ/mol}) \qquad (9)$$

where $E(V^{\cdot\cdot}_o)$ is the oxygen vacancy formation energy, $E_{Diss}$ the dissociation energy for $O_2$ (5·16 eV; 498 kJ/mol), $E_{12}$ the sum of the first two electron affinities of oxygen (−7·28 eV; −702 kJ/mol)[27] and $E_e$ the polaron formation energy estimated previously. This result, giving a high energy for the reduction, confirms that it is not possible to reduce YAG significantly.

If, however, YAG doped with divalent ions, e.g. $Ca^{2+}$ or $Mg^{2+}$ to create oxygen vacancies (see eqn (7)) is considered, the oxidation energy $E_{ox}$ can be calculated following eqn (11). The released holes are again treated in terms of the formation of small polarons according to the reaction

$$O^x_o + h^{\cdot} \longleftrightarrow O^{\cdot}_o\ (E_h) \qquad (10)$$

with $E_h$ the polaron formation energy.

The energy $E(O'_o)$ for replacing $O^x_o$ by $O'_o$ was calculated to be 18·6 eV (1795 kJ/mol) per defect. This energy has to be combined with the second electron affinity of oxygen (−8·75 eV; −844 kJ/mol) to obtain the polaron formation energy $E_h = 9{\cdot}85$ eV (950 kJ/mol). The energy for the oxidation reaction $E_{ox}$, given by a combination of eqn (7) and eqn (10), is

$$E_{ox} = -E(V^{\cdot\cdot}_o) + 1/2E_{Diss} - E_{12} + 2E_h$$
$$= 7{\cdot}2\ \text{eV}\ (695\ \text{kJ/mol}) \qquad (11)$$

For the doped material a clustering of defects leading to $(Ca'_Y O'_o)^x$ has to be considered. Such an associate is stabilized by 0·31 eV, so the redox energy is altered by this amount. The energy is rather high, suggesting that divalent doped YAG will resist oxidation and be only a poor p-type semiconductor.

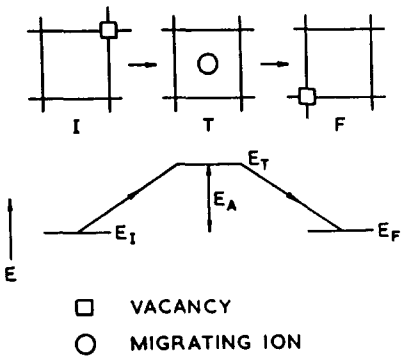


**Fig. 1.** Schematic diagram for ion migration.

## 4.6 Saddle point energies

Saddle point energies were calculated for ions jumping from regular lattice sites to adjacent vacant sites. These represent the activation energy for a single ion diffusion step (as given in Fig. 1). Recent studies on several materials revealed that transition states for jumping ions can have large displacements out of the plane of the adjacent lattice sites.[28]

### *4.6.1 Migrating oxygen ions*

To investigate the saddle point energy and the saddle point displacement for jumping oxygen ions the energy of the transition state for an oxygen ion jumping from an h-site to a vacant h-site on the same tetrahedron following a straight line (see Fig. 2) was calculated. This energy was found to be 2·09 eV (202 kJ/mol).

Considering the position of the regular ions in the region of the lattice surrounding the initial and the final positions of the migrating oxygen ion makes clear that the migration path is influenced by the charged lattice ions. The jump along a straight line, as indicated in Fig. 2, is not the path with the lowest

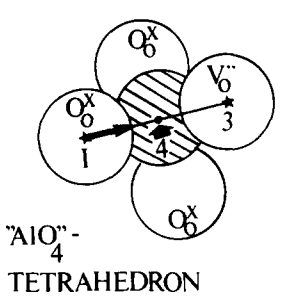


**Fig. 2.** Simple geometry for an oxygen ion jumping from a regular site 1 to vacant site 3 on a tetrahedron. Point 4 marks the saddle point for a straight line jump (for the sake of clarity the ionic radii are not drawn to scale).

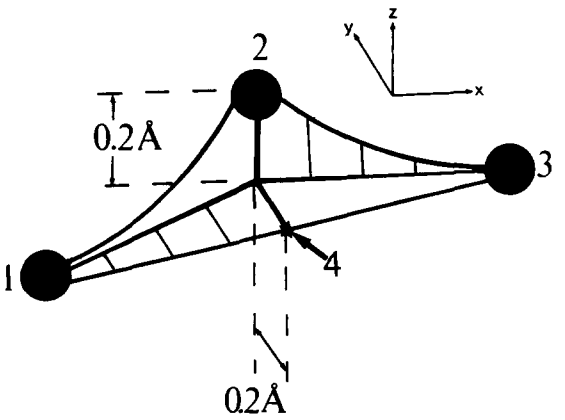


**Fig. 3.** A moving oxygen ion does not move along a straight line from the start to the final position. Due to interactions with adjacent ions the jumping path is displaced as shown here. Point 4 marks the saddle point for an ion moving along a straight line.

transition energy; a somewhat curved jump geometry is expected.

In order to find this path the saddle point energies of about 50 slightly different positions of the transition point located between the initial and the final position were then calculated. This resulted in a curved jump path with a calculated activation energy of 1·5 eV (145 kJ/mol). The saddle point is displaced 0·2 Å in the $y$-direction and 0·2 Å in the $z$-direction, as depicted in Fig. 3. Thus there is a considerable saddle point displacement for jumping oxygen ions in YAG, which is in agreement with simulation results for other crystalline materials.[28]

By considering the polyhedral model of the garnet structure (a network of tetrahedra and octahedra connected with each other) it becomes clear that within the garnet lattice different anion jumps with different saddle point energies are possible; some of these jumps are marked in the projection of a part of the unit cell of the garnet lattice in Fig. 4. The calculated saddle point energies for migration along a straight line are given in Table 5. Again a curved migration path having a somewhat lower transition energy than the straight line jump has to be considered. It seems to be justified to assume a transition energy which is about 10–20% lower for the curved than for the straight jump.

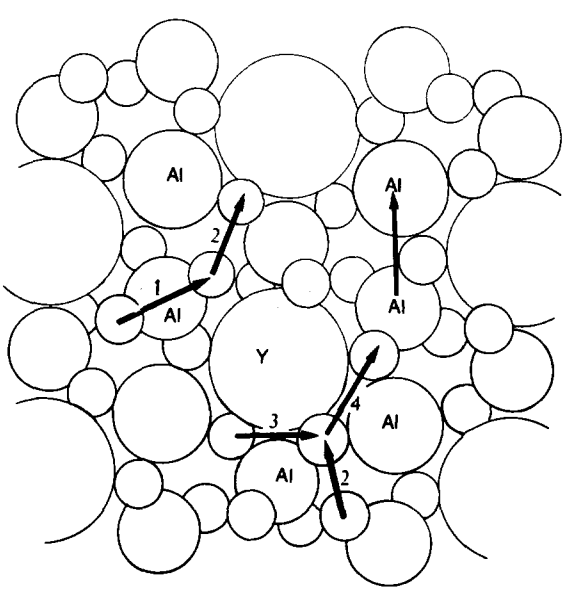


**Fig. 4.** Projection of a part of the garnet unit cell (for the sake of clarity the ionic radii are not drawn to scale). Possible oxygen jumps and the aluminium jump simulated are indicated.

**Table 5.** Saddle point energies for different jump paths

| *Migration path* | *Saddle point energy* | |
|---|---|---|
| | *eV* | *kJ/mol* |
| 1 | 2·09 | 202 |
| 2 | 1·50 | 145 |
| 3 | 3·34 | 322 |
| 4 | 1·84 | 178 |

From a consideration of the crystal structure (a three-dimensional model of the garnet lattice should be used) it can be deduced that a combination of jump 2 and jump 4 is sufficient to find a continuous, low energy path for migrating oxygen ions through the YAG lattice. Jump 2 corresponds to migration between tetrahedra (via empty $b$-sites, within the garnet structure, which have the lowest transition energy found). Jump 4 is the migration along an octahedron. The activation energy for the migrating oxygen ion should be determined by the higher of both saddle point energies. This leads to activation energies for migrating oxygen ions of approximately 1·5 eV (145 kJ/mol), which is somewhat lower than the activation energy of 2·3 eV (222 kJ/mol) and 2·1 eV (203 kJ/mol) for ionic migration reported by Rotman *et al.*[29] and Schuh[30] for YAG derived from electrical conductivity measurements.

*4.6.2 Migrating Al ions*

The possible jumps for Al ions are more difficult to study than those for oxygen. A moving Al ion migrating from a lattice position to an adjacent vacant position has to follow a 'wavy' line; the distance between two Al ions is much longer than the distance between two adjacent O ions. An Al jump from a tetrahedral to an adjacent octahedral site was investigated by checking the energy of an $Al_i$... at 20 different positions in the space between the initial and the final position. The saddle point energy for a migrating Al ion was found to be not lower than 3·5 eV (338 kJ/mol). Röschmann derived, by considering the redistribution energy for iron ions between the tetrahedral and octahedral positions in iron garnets, a saddle point energy of 4·5 eV (405 kJ/mol).[31]

The results on the saddle point energies for aluminium and oxygen jumps indicate that oxygen should exhibit a higher mobility in the YAG lattice than Al ions. The same result followed from diffusion and electrical conductivity experiments performed on pure single crystalline YAG.[24,32] However, it should be noted that in a recent study it has been shown that the transport properties of polycrystalline YAG containing $Al_2O_3$ inclusions are governed by the presence of Al vacancies.[12]

## 5 Conclusion

The authors have applied the technique of computer simulation to derive basic defect properties of YAG. The conclusion of many previous studies that oxygen vacancies are the most probable point defects is supported by our theoretical study; the formation of Al vacancies needs a much higher energy than the formation of O vacancies. With respect to the calculated energies for isolated defects it may be stated to a first approximation that Schottky defects are easier to form than Frenkel defects. Considerations of realistic physical processes should be performed in the future.

By considering saddle point energies the authors have determined a continuous path for a migrating oxygen ion exhibiting an activation energy of approximately 1·5 eV (145 kJ/mol), which is somewhat lower than experimental activation energies for the ionic conductivity due to migrating oxygen ions.

Based on the calculated energy to form $Ca'_Y$ and $Mg'_Y$ substitutionals the authors have derived the solution enthalpy for CaO and MgO in the YAG lattice to be 239 kJ/mol and 243 kJ/mol, respectively, which may explain the low solubility of these oxides in YAG.

Further calculations have shown the association of oppositely charged mobile defect species (clustering) to be energetically favoured. Such effects can reduce the formation energy and enhance the stability of lattice defects.

Finally the authors have calculated the energies of reduction and oxidation reactions in YAG. The redox energies for the processes investigated indicated that YAG will resist both hole and electron creation by redox reactions.

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## References

1. Catlow, C. R. A., James, A., Mackrodt, W. C. & Stewart, R. F., Defect energies in alpha-$Al_2O_3$ and rutile $TiO_2$. *Phys. Rev. B*, **25** (1982) 1006–26.
2. Dienes, G. J., Welsh, D. O., Fisher, C. R., Hatcher, H. D., Lazareth, O. & Shamberg, M., Shell model calculations of some point defect properties in alpha-$Al_2O_3$. *Phys. Rev. B*, **11** (1975) 3060–71.
3. Mackrodt, W. C., Calculated point defect, association and migration energies in MgO and alpha-$Al_2O_3$. In *Advanced Ceramics*, Vol. 10, ed. W. D. Kingery. American Ceramic Society, 1984, pp. 62–78.
4. Catlow, C. R. A., Corish, J., Hennessy, J. & Mackrodt, W. C., Atomistic simulation of defect structures and ion transport in alpha-$Fe_2O_3$ and alpha-$Cr_2O_3$. *J. Am. Ceram. Soc.*, **71** (1988) 42–9.
5. Lewis, G. V., Computer simulation of the defect structure and PTC properties in $BaTiO_3$. PhD Thesis, University College, University of London, 1984.
6. Allan, N. L. & Mackrodt, W. C., The calculated defect properties of $La_2CuO_4$ related to high $T_c$-superconductivity. *Phil. Mag. A*, **58** (1988) 555–69.
7. Hsu, Ta-Lin, *A Nd-YAG Laser Bibliography*. Materials Research Center, Allied Chem. Corp., Morristown, New Jersey, 1973.
8. Gazza, G. E. & Dutta, S. K., US Patent 376 77 45, 27 April 1973.
9. de With, G., Preparation, microstructure, and properties of $Y_3Al_5O_{12}$ ceramics. *Philips J. Res.*, **42** (1987) 119–30.
10. Mulder, C. A. M. & de With, G., Translucent $Y_3Al_5O_{12}$ ceramics: Electron microscopy characterisation. *Solid State Ionics*, **16** (1985) 81–6.
11. Schuh, L., Metselaar, R. & de With, G., Electrical conductivity study of defects in Zr-doped YAG. *Sci. Ceram.*, **14** (1987) 973–8.
12. Schuh, L., Metselaar, R. & de With, G., Electrical transport properties of Ca- and Mg-doped YAG ceramics. *J. Appl. Phys.*, **66** (1989) 2627–32.
13. Leslie, M., Program CASCADE: Description of data sets for use in crystal calculations. SERC Daresbury Report DL/SCI/TM 31 T, 1982.
14. Mott, N. F. & Littleton, M. J., Conduction in polar crystals, electrolytic conduction in solid salts. *Trans. Faraday Soc.*, **34** (1938) 485–99.
15. Catlow, C. R. A., Computer modelling of ionic solids. *J. Phys. Paris, Suppl.*, **41** (1980) C6-53–C6-60.
16. Catlow, C. R. A., Dixon, M. & Mackrodt, W. C., Interionic potentials in ionic solids. In *Lecture Notes in Physics*, Vol. 166, ed. C. R. A. Catlow & W. C. Mackrodt. Springer Verlag, Berlin–Heidelberg–New York, 1982, pp. 130–61.
17. Colbourn, E. A. & Kendrick, J., Ab-initio calculations for defects in the solid state. In *Lecture Notes in Physics*, Vol. 166, ed. C. R. A. Catlow & W. C. Mackrodt. Springer Verlag, Berlin–Heidelberg–New York, 1982, pp. 67–81.
18. Dick, B. G. & Overhauser, A. W., Theory of the dielectric constant of alkali halide crystals. *Phys. Rev.*, **112** (1958) 90–103.
19. Lidiard, A. B. & Norgett, M. J., *Computational Solid State Physics*. Plenum Press, New York, 1972, pp. 1–165.
20. Norgett, M. J., Atomic Energy Research Establishment Report No. AERE R7605, 1972.
21. Catlow, C. R. A. & Mackrodt, W. C., Theory of simulation for lattice and defect energy calculations in crystals. In *Lecture Notes in Physics*, Vol. 166, ed. C. R. A. Catlow & W. C. Mackrodt. Springer Verlag, Berlin–Heidelberg–New York, 1982, pp. 3–20.
22. Kitaeva, V. F., Zharikov, E. V. & Christyi, I. L., The properties of crystals with garnet structure. *Phys. Stat. Sol. (a)*, **92** (1985) 475–88.

23. Wolfmeier, U. H. & Gunßner, W., Landholdt-Börnstein, Bd 12 III, neue Serie, Elastic, thermoelastic and photoelastic properties, ed. K.-H. Hellwege, Berlin, 1978, p. 356–57.
24. Neiman, A. Ya., Tkachenko, E. V. & Zhukovskii, V. M., Nature of defect formation in complex oxides of the composition $Me_3E_5O_{12}$ with a garnet structure. *Dokl. Akad. Nauk SSSR*, **240** (1978) 876–9.
25. Mackrodt, W. C., Defect energetics and their relation to non-stoichiometry in oxides. *Solid State Ionics*, **12** (1984) 175–88.
26. Weast, R. C. (ed.), *Handbook of Chemistry and Physics*. CRC-Press, Florida Boca Raton, 63rd edition, 1982–83, pp. E68.
27. Islam, M. S., Leslie, M., Tomlinson, S. M. & Catlow, C. R. A., Computer modelling studies of defects and valence states in $La_2CuO_4$. *J. Phys. C: Solid State*, **21** (1988) L109–L177.
28. Catlow, C. R. A., Corish, J., Diller, K. M., Jacobs, P. W. M. & Norgett, M. J., Atomic Energy Research Establishment Report AERE TP 713, 1977, pp. 1–145.
29. Rotman, S. R., Tandon, R. P. & Tuller, H. L., Defect property correlations in garnet crystals: The electrical conductivity and defect structure of luminescent cerium-doped YAG. *J. Appl. Phys.*, **57** (1985) 1951–5.
30. Schuh, L., Microstructure and defect chemistry of YAG-ceramics. PhD Thesis, Technical University Eindhoven, The Netherlands, 1989.
31. Röschmann, P., Kinetics of cation site exchange in mixed garnets. *J. Phys. Chem. Solids*, **42** (1981) 337–50.
32. Haneda, H., Miyazawa, Y. & Shirasaki, R., Oxygen diffusion in YAG investigated by $O^{18}$ tracer experiments. *J. Cryst. Growth*, **68** (1984) 581–2.