DEFECT STRUCTURES AND MIGRATION MECHANISMS IN OXIDE PYROCHLORES

M.P. van DIJK, A.J. BURGGRAAF

*Twente University of Technology, Department of Chemical Engineering,
Laboratory for Inorganic Materials Science and Catalysis,
P.O. Box 217, 7500 AE Enschede, The Netherlands*

and

A.N. CORMACK, C.R.A. CATLOW

*University College London, Department of Chemistry,
20 Gordon Street, London WC1H 0AJ, UK*

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Using computer simulation techniques the defect structure and oxygen ion migration mechanism of oxide pyrochlores (eg. $\text{Gd}_2\text{Zr}_2\text{O}_7$) was investigated in order to explain the decreased activation enthalpy for oxygen ion conductivity as a function of order. Shell model potentials were found to be necessary in order to obtain sufficiently accurate physical properties for the pyrochlore compound. The oxygen Frenkel defect consisting of 'a split 48f vacancy' and 8b interstitial appeared to be the most stable intrinsic defect, but vacancies related to extended defect structures may play an important role in the diffusion mechanism too. The migration mechanism of oxygen ions is mainly based on 48f-48f jumps and involve 0.9 eV barrier energy, comparable with the experimental activation enthalpies of 70-85 kJ/mol.

1. INTRODUCTION

During the past decades, oxides exhibiting high oxygen ion conductivity have been the subject of many experimental and theoretical studies. Suitable materials have been successfully utilized for a variety of technological applications, like oxygen sensors, pumps and electrochemical reactors (e.g. (1,2)). Nowadays, many studies involve the electrochemical process at the electrode interface, because this process turns out to involve larger resistances than the electrolyte at temperatures below ~ 1000 K. However, from a materials science point of view as well as for theoretical consideration, it is interesting to get a more detailed knowledge of the fundamental mechanisms governing the migration of oxygen ions in the crystal structure and transport of oxygen across the solid-gas interface. There is still a demand for alternative oxygen ion conductors with larger values of specific conductivity and higher oxygen exchange rates at the interface at lower temperatures.

Most materials studied are oxides with fluorite or fluorite-related structures based on

ZrO_2 , CeO_2 , Bi_2O_3 etc. These oxides show a wide variation in stoichiometry by doping with aliovalent (i.e. lower valent) cations. Several mechanisms for oxygen ion migration might be considered, from the dilute range, where classical point defect theory can be applied, to highly defective oxides, where complex defect interactions take place (3,4), to explain the oxygen ion conductivity in terms of mobility and defect concentrations.

Most attention is paid to the role of dopant-vacancy interactions, determining the conductivity parameters. To interpret experimental results, theoretical considerations and computer simulation techniques have established that the dopant ion radius is an important parameter in determining the interaction energies (3,5,6). These computer simulation techniques have been found to provide reliable information on defect formation, association and migration enthalpies for several classes of oxides, fluorides etc. (4). For the determination of structures with long-range ordered defects, using lattice energy minimization techniques, these computer programs have also proved successful (7).

Studies to date on the fluorite oxides have not elucidated the role of ordering, in extended defect aggregates or clusters that occur outside the dilute range, in these systems. For this reason our interest in the current study concerns ZrO_2 , heavily doped with rare earth oxides (especially Gd_2O_3). In this system the degree of pyrochlore order can be manipulated in a rather controlled way. Moreover, the occurrence of oxygen atoms with different binding energies in the pyrochlore structure is interesting from the point of view of oxygen exchange kinetics at the gas-solid interface.

The pyrochlore structure is found for $Ln=La-Gd$ (Ln = rare earth element) around the composition $Ln_2Zr_2O_7$ and is often considered as an ordered, defective fluorite structure with doubled unit cell axes and spacegroup $Fd3m$ ($Z=8$) (see Fig.1). The pyrochlore structure can be deduced from the fluorite structure by ordering both cations and anion vacancies on their respective sublattices.

The crystal chemistry of these zirconates has been investigated by several groups (8,10,11). In general three parameters appear to determine the degree of pyrochlore order in the basic fluorite lattice:

i) Type of rare earth element: only the larger rare earth ions (Ln^{3+}) are found to form the pyrochlore structure. From X-ray diffraction results, Gd^{3+} is the smallest rare earth ion accommodated in the ordered structure. Electron microscopy has shown clearly that the actual structure consists of microdomains, that become smaller in going from La to Gd (9,12). For well ordered $Gd_2Zr_2O_7$ microdomains of about 50-100 nm have been observed. Diffuse scattering in electron diffraction images for $Tb_2Zr_2O_7$ indicates

Fig. 1. Projection of part of the pyrochlore structure along one of the cubic axes.

that even for rare earth ions smaller than Gd^{3+} some ordering is present (12).

ii) The temperature treatment of the material: for $Ln_2Zr_2O_7$ ($Ln=La-Pr$) the pyrochlore structure exists over the whole temperature range up to the melting point, but for smaller rare earth elements the pyrochlore zirconates disorder at a temperature below the melting point. For $Gd_2Zr_2O_7$ a disorder temperature of about 1550°C was found (9), which is reflected in the conductivity parameters (see section 3).

iii) The deviation from pyrochlore stoichiometry ($Ln_2Zr_2O_7$): in the solid solution series $Ln_xZr_{1-x}O_{2-0.5x}$ the domain of pyrochlore structured material around $x = 0.5$, narrows from La to Gd. A hybrid phase model, that permits the coherent intergrowth of domains with pyrochlore structure and defect-fluorite structure, has been suggested to explain the gradual transition from the fluorite to the pyrochlore structure in these solid solution series (11,12).

The oxygen ion conductivity changes markedly as a function of pyrochlore order in a disordered matrix. A synopsis of conductivity measurement results can be found in (12). In general ordering causes both a lower activation enthalpy (ΔH) and pre-exponential factor (σ_0). This fact is best illustrated for $Gd_2Zr_2O_7$. A sample quenched from 1700°C with the defect fluorite structure has $\Delta H \approx 110-115$ kJ/mol ($\approx 1.14-1.19$ eV) and $\sigma_0 \approx 1 \times 10^8 \Omega^{-1} m^{-1} K$ and a sample of same composition annealed at $T < 1500^\circ C$ has $\Delta H \approx 80-85$ kJ/mol ($\approx 0.83-0.88$ eV) and $\sigma_0 \approx 2 \times 10^7 \Omega^{-1} m^{-1} K$. Overall this results in the better conductivity for the ordered sample, which is competitive with values for oxygen ion conductors like $ZrO_2(Y_2O_3, CaO)$. $Nd_2Zr_2O_7$, which is even better ordered than $Gd_2Zr_2O_7$, has $\Delta H \approx 70-75$ kJ/mol ($\approx 0.73-0.78$ eV), but due to a very low value of σ_0 ($\approx 10^4-10^5 \Omega^{-1} m^{-1} K$), the net conductivity is worse. The dependence of the conductivity parameters on the degree of pyrochlore order was explained as follows (12): due to the existence of an ordered cation sublattice, a preferential diffusion path can be found in the pyrochlore structure. This path consists of successive oxygen jumps which involve a relatively low amount of strain energy, because of lesser steric hindrance compared to the disordered fluorite phase. It is supposed that this strain energy is the dominant part of the total activation enthalpy for migration. Meanwhile, the number of free vacancies is reduced on ordering.

It is our aim now to calculate (using computer simulation techniques) migration enthalpies for oxygen ions in the pyrochlore structure, and to elucidate the mechanism of conductivity. It will be assumed that the measured activation enthalpy for well ordered compounds (70-80 kJ/mol or 0.73-0.83 eV) almost reflects the

free ion migration enthalpy. Kilner and Steele suppose a value of ≈ 0.6 eV for the free ion oxygen migration enthalpy in fluorite oxides, obtained from work of Nowick et al. (1,13). It is not expected that in the stoichiometric compound $\text{Ln}_2\text{Zr}_2\text{O}_7$ associates exist and moreover in Arrhenius plots of the conductivity no bends have been found in the temperature interval $300^\circ\text{C} < T < 800^\circ\text{C}$, which otherwise may indicate the existence of associates.

Considering an ideally ordered pyrochlore structure, a problem arises, as to where the free oxygen vacancies are situated. In the defect fluorite structure for $\text{Ln}_2\text{Zr}_2\text{O}_7$, Ln and Zr ions are completely disordered over the cation sublattice and one out of eight indistinguishable anion sites is empty. The pyrochlore structure on the other hand, consists of alternative arrays of same cations (16c and 16d sites in Fd3m), which results in three different possible anion sites. Six oxygen atoms occupy the 48f site, the seventh atom occupies the 8a site, the 8b site being nominally empty. Since jumps to and from 8b sites cannot form a continuous path of their own in the structure, any mechanism for ion motion should include jumps between 48f sites. Previously, it was suggested that some oxygen ions will be trapped on 8b sites, thus creating vacancies at the 48f sublattice (12). Now, we will discuss this defect structure in a greater detail. We will consider both point defects and more complex defect structures. The mechanism for conductivity will then be discussed in relation to these defect structures.

2. TECHNIQUES.

2.1. Computer codes.

The static lattice simulation of the perfect structure, and of the defect structure involved in the transport mechanism for oxygen ions, presented in this paper, makes use of the computer programs METAPOCS and CASCADE (14). Experience in the use of these methods has shown that the reliability of the calculations arises largely from the limitations of the interatomic potential models employed (15). We elaborate on this in section 3.1. The perfect lattice code METAPOCS was used to calculate the coordinates of the ions in an equilibrium structure, together with some crystal properties (e.g. elastic constants, dielectric constants and phonon dispersion curves), to test the validity of the potential model, by comparison with the experimental data, presented in section 2.2. Calculation of the defect energies within the CASCADE program includes complete relaxation of the structure around the defect species. This is a crucial feature of the simulation, as a consi-

derable contribution to the defect energy comes from the response (both elastic and dielectric) of the crystal to the defect. This response can be very long range in the case of charged defect species, such as vacancies. Detailed information about the computational techniques and their applications can be found in a recent review by Catlow and Mackrodt (15).

2.2. Crystal properties.

Several crystal properties including lattice constant, oxygen (48f) position parameter, elastic constant, and dielectric constant have been measured to support the determination of the interatomic potentials. $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Nd}_2\text{Zr}_2\text{O}_7$ were obtained by a wet chemical synthesis process of the powders followed by sintering to dense ceramics (12). The lattice constant was determined from X-ray powder diffraction peak positions. The oxygen (48f) position parameter was determined from integrated peak intensities, using X-ray diffraction ($\text{Gd}_2\text{Zr}_2\text{O}_7$) or neutron diffraction ($\text{Nd}_2\text{Zr}_2\text{O}_7$) results, by means of a least squares refinement program. Young's modulus (E) and Poisson constant (ν) were measured at 10 and 20 MHz by a pulse-echo method. Obtained values were corrected for porosity using an experimental linear relationship between E and the porosity. For materials with cubic symmetry the bulk modulus K can then be obtained from:

$$K = \frac{E}{3(1-2\nu)} \quad (1)$$

The dielectric constant was obtained from frequency dispersion measurements of sample electrical impedances. Bulk and grain boundary contributions to the total impedance can be separated and the static dielectric constant is determined from the bulk polarization semicircle; using:

$$Z^* = \frac{R - j\omega R^2 C}{1 + (\omega RC)^2} \quad (2) \quad \text{and} \quad \epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (3)$$

in which R is the bulk resistance, C is the sample capacity, A and d are sample dimensions, ω is the angular frequency of the AC signal applied and ϵ_0 the permittivity constant of free space. This semicircle was observed in the frequency range $10^3 - 10^6$ Hz for temperatures 250–500°C. Results are presented in table I.

3. RESULTS AND DISCUSSION.

3.1. Potentials.

In the calculation of the perfect lattice structure, rigid ion interatomic potentials of the Born-Mayer-Buckingham form:

Table I. Experimental crystal properties for $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Nd}_2\text{Zr}_2\text{O}_7$.

crystal property	$\text{Gd}_2\text{Zr}_2\text{O}_7$	$\text{Nd}_2\text{Zr}_2\text{O}_7$
pyrochlore lattice constant (Å)	10.532 (± 0.001)	10.674 (± 0.001)
oxygen position parameter O (48f)	0.410 (± 0.005)	0.417 (± 0.002)
elasticity constant K (GPa)	178 (± 5)	204 (± 10)
dielectric constant ϵ_r	60 (± 10)	30 (± 3)

$$V(r) = A \exp(-r/\rho) - Cr^{-6} \quad (4)$$

were tried first. The parameters A, ρ and C were taken from the binary ZrO_2 (cubic) and Ln_2O_3 structures derived by fitting procedures to crystal properties of these oxides (16). Although these potentials describe the structure quite satisfactorily, the rigid ion model predicts too small a value of the dielectric constant, because polarisation effects are neglected ($\epsilon_r \approx 8$). Defect energies depend very largely on the dielectric behaviour of the solid through the response of the crystal structure to the defect charge and thus it is necessary to include ionic polarisation in the description of the simulated crystal structure. This is best done using shell model potentials of the type introduced by Dick and Overhauser (17). Insufficient improvement on the value of ϵ_r was obtained when polarisability was included for the oxygen ions only and it was found necessary to use shell model potentials for the cations too. The choice of parameters for the shell model potentials (the shell charge and spring constant) proved to be crucial in finding an acceptable model. As mentioned earlier, the short-range parameters were taken from a rigid ion potential model fitted to the pertinent crystal structure. However, because of lack of sufficient experimental data, shell model parameters for the binary oxides could not be derived in that particular exercise (16).

Accordingly (although, with hindsight, dangerous) for our pyrochlores these parameters were taken from other trivalent and tetravalent ions, also from ref (16). When included in the model for the pyrochlore structure, these gave reasonable values for the dielectric constant. It was found that including shells (i.e. polarisability) had little effect on the structural properties because the short-range potentials reproduced these very well.

However, it was not possible to obtain any

defect energies using this potential model as the system never converged to an equilibrium configuration, but always diverged. On close examination of these calculations, the reason for this was discovered to be an unrealistic representation of the dielectric properties of the pyrochlore structure at an atomic level. The shell model parameters being used, although giving a reasonable value for the unit cell dielectric constant were not reproducing correctly the local response of the nearest neighbours to the defect. This was confirmed by shell model calculations on the binary compounds (ZrO_2 , Gd_2O_3) for which were obtained negative values of the dielectric constant. When the shell model parameters were refined to give acceptable, physically meaningful, dielectric

Table II. Calculated crystal properties for the equilibrium structure.

calculated crystal properties	$\text{Gd}_2\text{Zr}_2\text{O}_7$	$\text{Nd}_2\text{Zr}_2\text{O}_7$
bulk lattice strains	8×10^{-4}	2.2×10^{-3}
oxygen position parameter O(48f)	core 0.4096 shell 0.4189	0.4130 0.4214
dielectric constant ϵ_r	24.8	22.6
bulk modulus K(GPa)	210	200
lattice energy (eV)	-2846.5	-2825.4

Table III. Interatomic potentials used in the defect energy calculations.

interaction	A(eV)	ρ (Å)	$\frac{6}{C}$ (Å)	ion	shell charge, Y	spring constant
Zr-O	1453.8	0.3500	0.0	O ²⁻	- 2.77739	26.793
Nd-O	1379.9	0.36007	0.0	Nd ³⁺	- 0.25	145.0
Gd-O	1336.76	0.35509	0.0	Gd ³⁺	- 0.25	145.0
O-O	22764.2	0.1491	27.89	Zr ⁴⁺	- 0.611	250.0

constants for the binary compounds these parameters were then used in the pyrochlore potential model and were found to give a good account of the dielectric properties of the pyrochlore. Moreover, defect energy calculations now converged to give the values quoted in section 3.3.

All crystal properties, calculated after complete equilibration of the perfect structure, are presented in Table II. Bulk lattice strains are the differences between the lattice constants used in the calculations (the observed values) and the ones required by the potential model in complete equilibrium. In our opinion the crystal structure is adequately simulated and values for the dielectric constant and bulk modulus seem reasonably good. A relatively high value for the dielectric constant in $\text{Gd}_2\text{Zr}_2\text{O}_7$, observed experimentally, may be due to the greater existence of domain boundaries in this compound, caused by imperfect short range ordering. The calculated value for $\text{Nd}_2\text{Zr}_2\text{O}_7$, being almost completely ordered, comes quite close to the measured value (≈ 30). The final set of potentials used in the defect energy calculations is given in Table III.

3.2. Migration mechanisms.

Before discussing the results of the defect energy calculations, it will first be shown what kind of oxygen ion jump possibilities are taken into account. Fig.2 shows a small part of the pyrochlore structure; in this way the local environments of the three different anion sites are visualized in a representative way. The fluorite anion sites are tetrahedrally surrounded by four cation sites. These tetrahedra are linked to each other by edgesharing in $\langle 100 \rangle$ directions and, in this way, build up the structure. Because of the ordering of cations over the cation sublattice, which implies alternating rows of same cations in $\langle 110 \rangle$ directions, or, equivalently a 1:3 honeycomb lattice in $\{111\}$ planes, the cation compositions of the tetrahedra differ from each other: 48f oxygen sites are surrounded by two Zr and two Ln atoms, 8a sites by four Ln atoms and 8b sites (nominally empty) by four Zr atoms. In addition to the

Fig. 2. This part of the pyrochlore structure shows the vicinity of a 48f oxygen atom.

tetrahedra mentioned before, the fcc cation network can be thought to form octahedra too. These (empty) octahedral sites are denoted 32e ($x=0.25$) in $\text{Fd}\bar{3}\text{m}$ and they play an important role in the defect structure for UO_{2+x} and (doped) fluoride fluorites, which are excess anion conductors (15,4).

The oxygen ion transport in these oxides is considered to go via an oxygen vacancy migration mechanism. This mechanism will be thought to consist of consecutive oxygen jumps between adjacent tetrahedral sites, that are nearest neighbours (in $\langle 100 \rangle$ directions) or perhaps next nearest neighbours ($\langle 110 \rangle$ directions). Possible jumps will be denoted by $(8a-48f)\langle 100 \rangle$, $(48f-48f)\langle 110 \rangle$ etcetera. The role of possible jumps involving 32e sites will be discussed further on. For jumps between normally occupied sites (8a and 48f) the formation of an oxygen vacancy is necessary before migration can take place. On the other hand, if for instance the 8b site is involved this is not necessary, but from structural considerations it is clear that these jumps cannot form a continuous path at their own. Jumps that will turn out to be important

jumps in the mechanism are (8a-48f)<100>, (48f-48f)<100>, (8b-48f)<100> and (48f-48f)<110>. For the <110> jumps there are two symmetrically different paths (see Fig.2), one along the empty 8b site and one along the occupied 8a site. For steric reasons this second possibility is improbable and will not be discussed.

3.3. Defect formation energies.

With the final set of interatomic potentials, described in section 3.1., vacancy and interstitial ion defect energies can be calculated for the pyrochlore structure of $\text{Gd}_2\text{Zr}_2\text{O}_7$. In these calculations ions are moved to or from infinity and the defect energy is obtained after complete relaxation of the structure around the defect centre. The results of the calculations of these raw energies are listed in table IV. With these values Frenkel and Schottky defect formation energies can be calculated. It appears that the most stable oxygen Frenkel defect consists of a 48f vacancy and an 8b interstitial ion and requires 1.96 eV per defect. An oxygen Frenkel defect with an 8a vacancy instead of a 48f vacancy requires 2.71 eV per defect and an oxygen Frenkel defect with a 32e interstitial instead of an 8b interstitial requires 3.34 eV per defect, which implies that these defects are less stable and more unlikely to occur. We found that an 8b interstitial sitting next to a vacant 48f site relaxed spontaneously into the 48f site, thereby annihilating the interstitial vacancy pair.

The predominant vacancy formation on the 48f sublattice may not be compared with the situation in pyrochlores that show large oxygen deficiency (e.g. $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ (19,20)). In these compounds the oxygen deficiency appears at the 8a site, but here not only can cations adopt different valencies, which is not considered in our case, but this vacancy may well be stabilised by the presence of lone pair electrons on the cations at the 16c site.

Considering the 48f vacancy more closely it

Table IV. List of raw defect energy values for $\text{Gd}_2\text{Zr}_2\text{O}_7$.

defect	energy (eV)
0 8a vacancy	19.86
0 48f vacancy	18.38
0 8b interstitial	- 14.45
0 32e interstitial	- 11.70
Zr 16d vacancy	85.87
Gd 16c vacancy	46.28

Fig. 3. Defect structure of the 'split vacancy'. The interstitial oxygen ion is in between the two vacancies at 48f sites and close to the empty 8b site.

appeared that a 'split vacancy' structure is more likely. In this case the defect structure can be thought to be formed by a 48f vacancy pair in <110> direction with an interstitial ion in between. The interstitial ion is close to the empty 8b site as can be seen from Fig.3. This configuration is calculated to be more stable by 0.2 eV than a simple 48f vacancy. Any 48f vacancy may be turned over in this split vacancy.

The Schottky defect energy, obtained by removing a complete formula unit from the crystal, requires an average of 3.5 eV per defect. Thus, it can be concluded that the most probable oxygen defect to occur in the perfect pyrochlore structure is the Frenkel oxygen defect, consisting of a 48f vacancy (or rather 'split vacancy') and an 8b interstitial.

Considering the mechanism of oxygen ion conductivity based on oxygen Frenkel defects only, the following problems can be put forward: The concentration of Frenkel defects with formation energies of 1.5-2.0 eV will be quite low. It is not excluded that more stable, but also more complicated defects, play a role in the mechanism. Defect energies for configurations of vacancy structures including local cation exchanges have not been calculated, as models are not available. However, in section 3.5 some attention will be paid to extended defect structures, and it will be shown that antiphase boundaries might lead to interesting arrangements of oxygen vacancies.

3.4. Saddlepoint energies.

Using the computer code CASCADE, it is possible to determine the migration energies for moving ions. A crucial feature of these calculations is the inclusion of complete relaxation of all ions around the defect. By moving the ion

(or vacancy) in steps along its path the potential surface for the migrating ion and hence the saddlepoint or barrier energies are obtained. It was found that the lowest barrier energy between nearest neighbour sites (in $\langle 100 \rangle$ directions) is between 48f sites. A $(48f-48f)_{\langle 100 \rangle}$ jump involves about 0.9 eV. The coordinates of the saddlepoint denote a position more or less half way between the original site and the neighbouring vacant site, indicating that the ion moves straight through the ribbon shared by both cation tetrahedra surrounding the 48f sites. This is in contrast to what was expected from the strain energy concept (11,12), where a curved path, more or less through the empty fluorite octahedron was suggested. An $(8a-48f)_{\langle 100 \rangle}$ jump was found to involve about 2.5 eV of barrier energy and consequently such a jump is unlikely to occur: 8a oxygen ions will not be involved in the conduction mechanism. This is in agreement with the strain energy model. It also shows that these pyrochlore oxides are different from the pyrochlore oxides that show 8a anion deficiency, because from the latter class of pyrochlore oxides one might suppose that the 8a oxygen ions are more mobile than the 48f oxygen ions. Ionic transport numbers for these semiconductive pyrochlore oxides are not known however.

It was mentioned before that simple oxygen 8b interstitials are found to be unstable, if they are situated next to vacant 48f sites. Thus, $(48f-8b)_{\langle 100 \rangle}$ jumps are predicted not to contribute to the conductivity.

In conclusion, the diffusion mechanism in perfect pyrochlores will be built up from $(48f-48f)$ jumps mainly. Both jumps between nearest neighbour sites ($\langle 100 \rangle$ jumps) and jumps along $\langle 110 \rangle$, involving the 'split vacancy' structure, will contribute to the migration of vacancies. The activation enthalpy will be principally determined by the $(48f-48f)_{\langle 100 \rangle}$ jump and the calculated value of 0.9 eV is quite comparable to the experimentally determined values of 70–85 kJ/mol for $Nd_2Zr_2O_7$ and $Gd_2Zr_2O_7$.

3.5. Effects of ordering.

Generally, in heavily doped oxides with the fluorite structure, the activation energy for oxygen ion conduction increases with the amount of dopant ion. In the literature this is explained by the occurrence of associate behaviour in the disordered structure or by a free energy term for long range ordering (1,21). Extrapolating experimental results for $(1-x)ZrO_2-x(GdO_{1.5})$ in the range $0.15 < x < 0.34$ to $x = 0.50$, an activation enthalpy of at least 1.5 eV is found (see Fig.5 in (12)). Due to the low symmetry of

the disordered fluorite structure for $Gd_2Zr_2O_7$, it was not practical to simulate this activation enthalpy by means of the computer techniques.

It was shown in section 3.4 that pyrochlore order evokes a relatively low activation enthalpy (≈ 0.9 eV). Experimentally this is illustrated by the decrease in activation enthalpy for $0.34 < x < 0.50$ in $(1-x)ZrO_2-x(GdO_{1.5})$ and by annealing a disordered specimen of $Gd_2Zr_2O_7$ ($\Delta H \approx 115$ kJ/mol or 1.19 eV). In both cases the amount of pyrochlore order increases and finally results in an activation enthalpy of 80–85 kJ/mol (0.83–0.88 eV) for well ordered $Gd_2Zr_2O_7$ (12). Ordering then means an increase in size of pyrochlore domains and a gradual decrease of activation enthalpy from the fluorite value to the pyrochlore value, in which, finally, only the migration term contributes to the value of the activation enthalpy. This model implies that a quenched specimen of $Gd_2Zr_2O_7$ ($\Delta H \approx 115$ kJ/mol or 1.19 eV) is ordered already to some extent, as a value of at least 1.5 eV would be expected by extrapolation. This ordering was already demonstrated by means of electron diffraction techniques in the electron microscope (12).

3.6. Extended defect structures.

Electron microscopy also revealed that well ordered pyrochlore oxides $Ln_2Zr_2O_7$ with $Ln=Gd-Nd$ have a domain-like structure (10,12). On ordering in the fluorite matrix 8 orientations of microdomains may develop with the same cubic structure, but with different origin of nucleation. On further ordering these domains will show mismatches and using suitable diffracted beams to construct the image antiphase boundaries are visible in the electron microscope. The perfect pyrochlore structure will be disturbed at these antiphase boundaries and it may be interesting to see if these may contribute to the defect structure governing the mechanism of oxygen ion conductivity.

For the present it is not clear from experiment what the orientation of the boundary planes will be. To see what the defect structures are like and to acquire some information about the stability of domains in the pyrochlore structure a large unit cell was constructed with antiphase boundary planes perpendicular to one of the cell axes. As an example, this was realized by doubling the c-axis and by altering part of the structure, i.e. for ions with $3/4\langle z \rangle 7/4$, either by translation over $\pm 1/2[100]$ or $\pm 1/2[010]$, or by rotation by $\frac{\pi}{2}$. This operation preserves continuity of the structure to the adjacent unit cells. Now, using the METAFACS code the lattice energy per formula unit can be calculated. Because a large number of symmetry unrelated atoms are present now in

Table V. Lattice energy for variants of the pyrochlore structure. For explanation, see text.

structure	lattice energy per formula unit (eV)
perfect pyrochlore	- 355.8
antiphase boundary by rotation	- 355.6
antiphase boundary by translation	- 355.0

the unit cell, calculations were performed with rigid ion potentials only and results are presented in table V.

It appears that the introduction of antiphase boundary planes causes only a very slight increase in lattice energy and that interfacial energies for the translational and rotational variants are small (0.8 and 0.2 eV respectively). In particular, the value for the rotational variant is sufficiently small to expect that these domain structures are stable enough to occur in the real crystal structure.

For the rotational variant the structure of the antiphase boundary region is shown in Fig. 4. In the boundary plane tetrahedra consisting of 3 Ln and 1 Zr, as well as consisting of 1 Ln and 3 Zr are present in contrast to the tetrahedra that are present in the ordinary pyrochlore structure (see section 3.2.). With regard to the occupation of tetrahedra by oxygen in the normal pyrochlore structure, it will be probable that

Fig. 4. Part of the rotational variant of the pyrochlore structure with ions between $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Oxygen sites indicated with the cross and empty sites are supposed to form a continuous pathway with low barrier energies.

in this boundary plane tetrahedra formed by 3 Ln and 1 Zr will be occupied by oxygen and tetrahedra formed by 1 Ln and 3 Zr will be empty to one out of four. These tetrahedral sites appear to be located in separated rows in $\langle 110 \rangle$ directions. It is suggested that low barrier energies may be found for oxygen ion jumps within the second type of rows, because all sites within the row are symmetrically equivalent and the jump path goes along the smaller Zr-ions, which is also the case for a $(48f-48f)\langle 110 \rangle$ jump in the perfect pyrochlore structure. The continuity of the migration path is clear from figure 4 and Frenkel defect formation is not necessary in this case (1/4 part of empty sites is present already). Unfortunately, barrier energies could not be calculated with the computer programs, because a too large memory size is needed for the computations, due to the decrease in symmetry for these complicated structures.

The fact, that in $Gd_2Zr_2O_7$ the domains are much smaller than in $Nd_2Zr_2O_7$ (9) and hence that there are many more antiphase boundary planes with a vacancy defect structure as described above, might explain the large difference in pre-exponential factor for conductivity, as observed, for $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$.

4. CONCLUSIONS.

1. By means of computer simulation techniques, using the computer programs METAPOCS and CASCADE it was established that in the perfect pyrochlore structure for $Gd_2Zr_2O_7$ oxygen Frenkel defects of the type 48f vacancy and 8b interstitial are the most probable intrinsic defects. The actual vacancy structure however, is predicted to be a 'split vacancy' between two neighbouring 48f sites in a $\langle 110 \rangle$ direction.

2. The conductivity mechanism based on these Frenkel defects consists mainly of $(48f-48f)\langle 100 \rangle$ and $(48f-48f)\langle 110 \rangle$ jumps and involves about 0.9 eV of barrier energy. This value is comparable with the experimentally found activation enthalpy of 70-85 kJ/mol for $Nd_2Zr_2O_7$ and $Gd_2Zr_2O_7$. Association effects and the generation of simple Frenkel defects seem to play no important role in the perfectly ordered material.

3. It is likely that at least part of the vacancies in the crystal structure are related to extended defect structures, like for example antiphase boundaries connected to the domain-like texture of the pyrochlores investigated. In these planes interesting defect structures turn up and low barrier energies may be expected.

4. The decrease in activation enthalpy for oxygen ion conductivity in the system $(1-x)ZrO_2-xGdO_{1.5}$ for $0.34 < x < 0.50$ and in annealed specimens of $Gd_2Zr_2O_7$ may be contributed to the increase in pyrochlore order, running from

small domains to large domains with antiphase boundaries.

5. Finally, an important general conclusion from this work is that, whilst short range inter-atomic potentials may be transferred to more complex structures, care must be exercised to the choice of shell model parameters. Consistency between binary and more complex potential models must be realised to obviate unphysical representations in the simulations.

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