OXYGEN ION AND MIXED CONDUCTIVITY IN COMPOUNDS
WITH THE FLUORITE AND PYROCHLORE STRUCTURE

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The effect of pyrochlore order in solid solutions with the defect fluorite structure
was studied. The amount of order was changed by various heat treatments or by
varying the cation composition. Examples of short range order and microdomain-
formation have been observed in $Tb_2Zr_2O_{7+x}$ and $Gd_2Zr_2O_7$. Pyrochlore order results in
a decrease of the activation enthalpy and pre-exponential factor for oxygen ion
conduction. The results are explained by a model based on the occurrence of a
preferential diffusion path with a low strain energy component in ΔH. Optimal
conductivity is achieved in materials which are not completely ordered. Mixed
conductivity in $Ln_2Zr_2O_7$ with P structure can be realized by partial replacement of
Ln by Tb. This results in good ionic as well as electronic conductivities.

1. INTRODUCTION

In the field of oxygen ion conducting materials
there is a special need for compounds with a
low activation enthalpy for migration, a high
mobile vacancy concentration and sufficient ad-
sorption sites for oxygen at the oxide part of
the electrode interface. This is favourable for
low temperature applications and for fast oxygen
transfer reactions at the electrolyte-electrode
interface. Secondly, compounds with mixed conduc-
tivity , having good ionic and electronic con-
ductivity, are of interest for applications like
solid solution electrodes.

Many good oxygen ion and mixed conducting mate-
rials have the well known fluorite (F) structure
or structures that can be derived from it. Com-
pounds $Ln_xZr_{1-x}O_{2-\frac{1}{2}x}$ (Ln = La-Tb x $\approx$ 0.5) can
have the pyrochlore (P) structure, which is an
ordered F structure. The value of the activation
enthalpy (ΔH) for these compounds, is coupled
with a variable degree of order. Therefore these
compounds offer an excellent model system to
study the relationships between the conductivi-
ty parameters and degree of order. Mixed conduc-
tivity can be obtained in P compounds by intro-
ducing cations with variable valency.

In this contribution experimental results of
structural and electrical investigations are
presented. Special attention is paid to the
structural factors that determine the relative-
ly low value of ΔH. The effect of Tb, replacing
for Gd in $Gd_2Zr_2O_7$, will be shown with respect
to the conductivity parameters. A simple model
is proposed that can account for the course of
ΔH as a function of order and composition. This
will be supplemented with preliminary results
of more sophisticated calculations of defect
migration energies.

2. STRUCTURE AND CRYSTAL CHEMISTRY

The P structure can be considered as an ordered

defect fluorite structure and has the gene-
ral composition $A_2B_2O_7$ with spacegroup $Fd3m(Z=8)$.
Several good descriptions of the structure are
available in literature [1-3]. Compared to the
F structure the two types of cations are ordered
into rows in <110> directions. This implies a
1:3 ordering of cations in {111} planes;this type
of cation-order is the same as present in rock-
salt superstructures [4]. For compounds with the
defect F structure the seven oxygen atoms are
distributed over eight equivalent sites. The
anions are surrounded tetrahedrally by four ran-
domly distributed cations. In the P structure
different oxygen sites occur. Six oxygen atoms
occupy 48f sites, surrounded by two A and two B
ions; the seventh oxygen atom occupies a tetra-
hedron formed by four A atoms (8a site); the
tetrahedron formed by four B atoms (8b site) is
nominally empty. The 48f anions are somewhat
shifted from the centre of the tetrahedron to-
wards the smaller B atoms, resulting in a space-
group parameter x(48f), which is 0.375 for ideal
fluorite positions. A projection of the P struc-
ture along one of the cubic axis is shown in
Fig. 1, where cations at z = 0 and z = ¼ and
anions at z $\approx$ $\frac{1}{8}$ have been drawn. It can be seen
that a contraction of the 48f sublattice occurs
around the empty 8b sites.

The crystal chemistry of zirconates, titanates,
stannates etc. with P structure has been exten-
sively reported [3,5,6,7]. Zirconates with rare
earth elements from La to Gd can form a P struc-
ture; smaller rare earth elements form a defect
F structure. The P structure allows a solid
solution series $Ln_xZr_{1-x}O_{2-\frac{1}{2}}$ around x = 0.5.
The region of existence of the P-phase narrows
going from La to Gd. For Nd, Sm, Eu and Gd the
P structure disorders above a certain transition
temperature, which is lowest for Gd; $Gd_2Zr_2O_7$
disorders at about 1530°C [7]. In conclusion
three parameters determine the degree of order
in the P structure: i) the type of rare earth
element, ii) the temperature treatment of the
material and iii) x,determining the deviation from
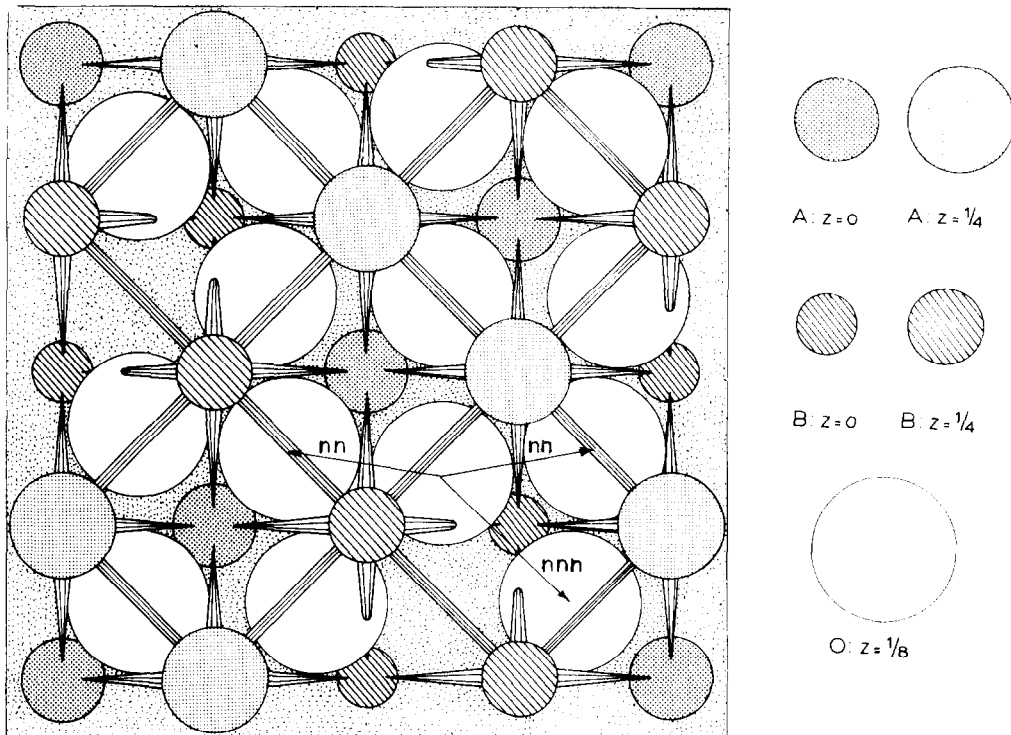
the stoichiometric composition at x = 0.5.

Figure 1: Projection of the P structure along the cubic axis

Michel et al.[7] have shown the existence of a structure with antiphase microdomains in stoichiometric and non-stoichiometric pyrochlores by means of electron microscopy. The domain sizes decrease going from Nd to Gd. T. van Dijk et al. [3,8] proposed a hybrid phase (consisting of a coexisting mixture of P and F phase domains) for compositions $Ln_xZr_{1-x}O_{2-\frac{1}{2}x}$. Titanates $Ln_2Ti_2O_7$ with Ln from Nd to Lu form a cubic P structure [7,9].

An alternative description of the P structure is based on the presence of BO_6 trigonal antiprisms, that form a corner-shared polyhedra network, with interstitial tunnels. A type cations and 8a O ions fill up these tunnels. In this way it is easy to understand that A cation and/or 8a anion deficiency is encountered frequently. This is especially so if the A ion is Pb or Bi [10,11].

3. EXPERIMENTAL

All specimens were obtained via a standard ci-trate synthesis [12], followed by different sintering and annealing procedures. Structure analysis was performed using standard diffrac-tion techniques. For electrical measurements disc-

shaped ceramic specimens were used, covered with Pt-sputtered electrodes. Ionic transference numbers were determined by means of an e.m.f. method, using air and pure oxygen as reference gases. Electrical conductivities were obtained using frequency dispersion analysis methods [13] enabling bulk, grain boundary and interface con-ductivity contributions to be achieved individually ΔH and σ_0 for ionic conductivity were obtained, using the equation

$$\sigma T \sim \sigma_0 \exp(-\Delta H/RT),$$

with T in between 600-1000K. In cases of mixed conductivity the ionic transference number (t_i) was used to separate ionic and electronic con-ductivity contributions.

4. RESULTS AND DISCUSSION

Preliminary transmission electron microscope investigations indicate the existence of small domains in the fluorite matrix. Fig.2a is a dark field image of a well ordered crystallite of $Gd_2Zr_2O_7$, showing domain sizes of about 50-100 nm. This image was constituted with P diffraction beams in the [110] zone only (Fig.2b) using an appropriate diaphragm.
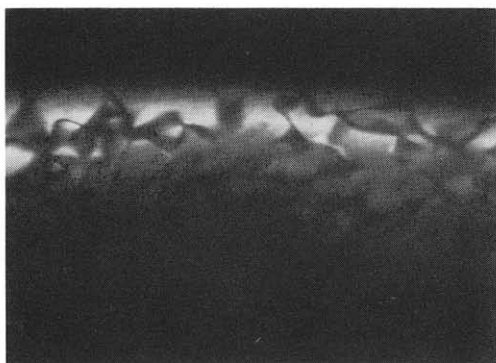
2a
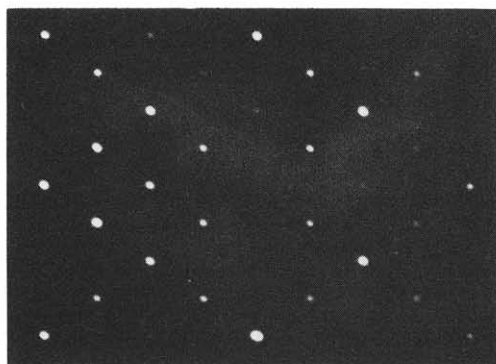
2b
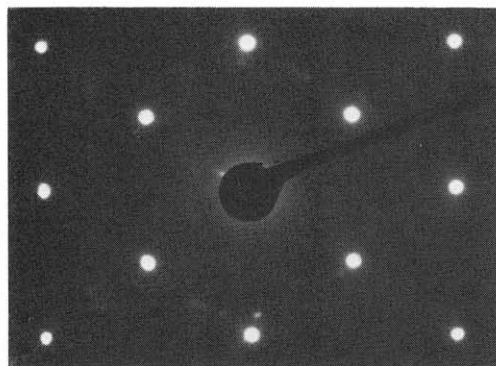
2c

Figures 2a, b and c: Electron microscope dark field image and diffraction patterns. (see text)

Diffuse scattering of intensities is observed for $Tb_2Zr_2O_7$, as can be seen from Fig. 2c, where a [110] diffraction pattern is shown. This result suggests that short range P order occurs in this compound. X-ray diffraction experiments did not show any sign of order. Extensive results will be published elsewhere.

Sharp minima of ΔH and σ_O versus x are observed for solid solutions $Ln_xZr_{1-x}O_{2-\frac{1}{2}x}$ around the stoichiometric P composition (x = 0.5) [14] (Fig. 3)

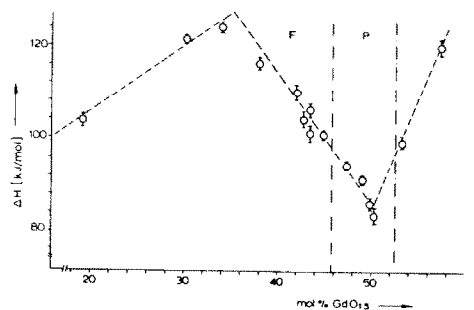Figure 3 : Curve of ΔH as a function of x in $Ln_xZr_{1-x}O_{2-\frac{1}{2}x}$ [14]. Numerical values are for Ln = Gd. The curve of σ_O versus x has a similar shape.

Due to absolute values of ΔH and σ_O, this results in a maximum in the curve of σ versus x in the case of Gd. For Nd a minimum results. Values for ΔH and σ_O for several P-phase oxides are tabulated in Table I. It can be seen that P-compounds have relatively low ΔH and σ_O values compared to most F-compounds [15].

Compound	ΔH (kJ/mole)	σ_O ($\Omega^{-1}m^{-1}K$)
$Nd_2Zr_2O_7$	74–81	4×10^4
$Sm_2Zr_2O_7$	67	3×10^5
$Gd_2Zr_2O_7$ (P)	84	2×10^7
$Gd_2Zr_2O_7$ (F)	112	1×10^8
$Tb_2Zr_2O_{7+x}$	76	1×10^6
$Er_2Ti_2O_7$	116	1×10^6

Table I

Impedances of $La_2Zr_2O_7$ and $Sm_2Ti_2O_7$ turned out to be too high to be measured (at T < 1100K) with normally used electrical circuits. These high impedances are the consequence of low σ_O values. Nevertheless we expect the latter materials have similar low ΔH values. For $Gd_2Zr_2O_7$ different ΔH and σ_O values were obtained for samples with different order, i.e. with F or P structure, depending on the preceding heat treatment.

$Gd_2Zr_2O_7$ samples quenched from 1700°C did not show super structure reflections in X-ray diffraction, whereas specimens annealed at temperatures below 1500°C were P-ordered to a large extent. Differences of ΔH up to 30 kJ/mole have been obtained, suggesting that order-disorder phenomena have an important influence on the values of ΔH and σ_o. For different A cations, the value of ΔH is not only influenced by the different type of ion species in the P structure, but also by a different degree of P-order, which depends on the radii-ratios of the A and B cations.

It appears that $Tb_2Zr_2O_{7+x}$ is a mixed conductor. At lower temperatures and $pO_2 \approx 1$ atm the electronic contribution dominates, but at higher temperatures t_i increases. A sample with 40% Tb and 60% Gd indeed has an intermediate value of t_i as can be seen from Fig. 4. The equilibrium $Tb^{3+} \leftrightarrows Tb^{4+} + e^-$ ions determines the contribution of the electronic conductivity. As a consequence the oxygen content of the material changes from 7 to 7 + x per formula unit. The ionic conductivity for the sample with 40% Tb and 60% Gd at 1000K is about $5 \times 10^{-2} \Omega^{-1} m^{-1}$, the electronic contribution is about $3 \times 10^{-2} \Omega^{-1} m^{-1}$. The ionic conductivity for $Gd_2Zr_2O_7$ at the same temperature is about $8 \times 10^{-1} \Omega^{-1} m^{-1}$.
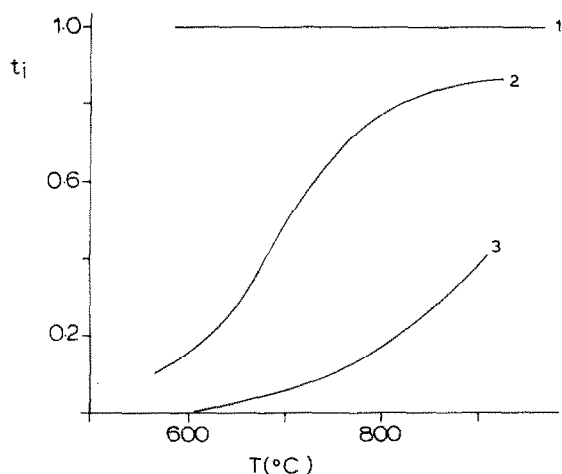

Figure 4: Ionic transference numbers for
1) $Gd_2Zr_2O_7$
2) $0.6Gd_2Zr_2O_7 - 0.4Tb_2Zr_2O_{7+x}$
3) $Tb_2Zr_2O_{7+x}$

Hohnke [16] showed that many solid solutions $ZrO_2(MO, M_2O_3)$ with the F structure give rise to a linear relationship between $\ln\sigma_o$ and ΔH (see Fig. 8 in [16]). An increase in the concentration of M-ions leads to higher values for ΔH and σ_o. Extrapolation for $x \approx 0.5$ in the case of the compounds $Ln_xZr_{1-x}O_{2-\frac{1}{2}x}$ (Ln = Nd-Tb),

however, does not fit into the Fluorite band presented by Hohnke. Instead, it seems that a second band originates for P-zirconates specifically (see Fig. 5). P compounds have relatively low ΔH values (65-85 kJ/mole). σ_o values are low too, but there is a large difference between the lowest and the highest values (10^4-10^7 $\Omega^{-1} m^{-1} K$) obtainable. Both ΔH and σ_o values are lowest for the best ordered compounds, that means compounds with a large ratio r_{A3+}/r_{B4+} and with a high P → F disorder temperature. It is interesting to point out that ΔH and σ_o values of $Tb_2Zr_2O_{7+x}$ (with F-structure according to X-ray investigations) fall within the range of P compounds. This is in accordance with the observation of short range order from electron diffraction experiments. Short range order and/or the formation of small P-domains seems to be sufficient to get a decrease in ΔH, relative to the value expected from the F-band.

For Ln = Gd, the curve of ΔH and σ_o as a function of composition is shown in Fig. 5, indicating a transition from the F to the P band at x = 0.34, in accordance with the onset of hybrid phase [14].

Considering the course of the P-band, it is not expected that P-zirconates with a ΔH lower than 60 kJ/mole will be found. Complete order, even with low ΔH values, is detrimental to the ionic conductivity, because of the strong decrease in free vacancy concentration, resulting in low σ_o values. Optimal conductivity is achieved in some semiordered phase with ΔH relatively low already, but σ_o not yet too low. This is achieved for Gd with x = 0.5 and temperature treatment below 1500°C ($Gd_2Zr_2O_7$-P) and for Nd when x ≈ 0.34 for instance. As expected (see Fig.8) $Er_2Ti_2O_7$ has a much larger value of ΔH.

5.1. SIMPLE MODEL BASED ON STRAIN ENERGY

Van Dijk et al. 3,8 introduced a simple structural model that accounts for the low activation enthalpy in the P-phase. This model is worked out now for the cases of variable stoichiometry, cation composition and degree of order. Finally some preliminary results of more sophisticated migration enthalpy calculations will be presented. Our model considers the steric hindrance for oxygen jumps in structurally comparable compounds. The ionic conductivity can be considered as an ensemble of single jumps with the activation enthalpy reflecting the barrier energy, i.e. the relative energy at the saddlepoint configuration. This barrier energy consists of several contributions, based on electrostatic interactions, repulsive short range interactions and polarization. The repulsive interaction term incorporates the strain energy involved with passage of oxygen ions through cation planes. Geometry and inter-cationic distances therefore play an important role. Kilner [17] proposed a similar model to explain activation enthalpies in oxides with the cubic perovskite structure. We assume that this strain energy is the dominating *variable* term for compounds with similar composition and stoichiometry.
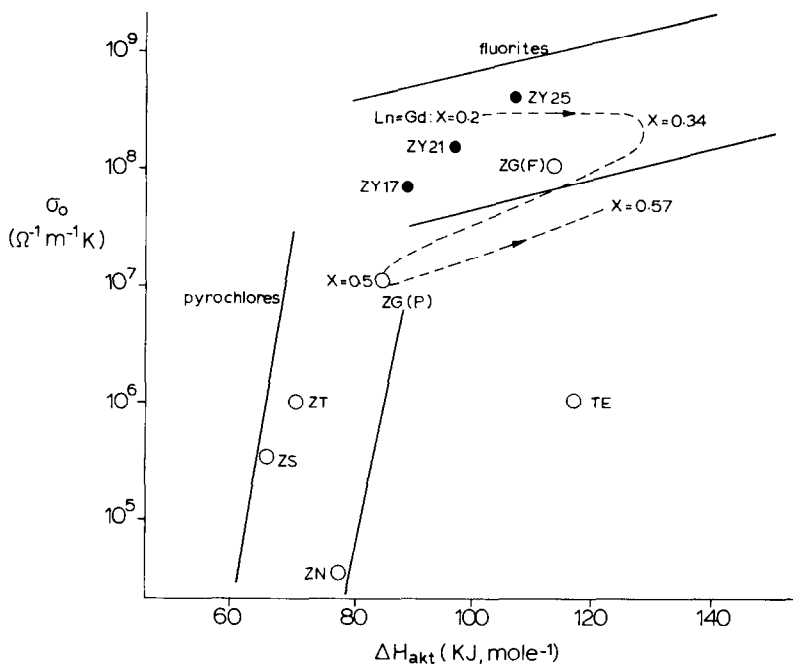
Figure 5: Relation between σ_o and ΔH values for fluorite and pyrochlore
compounds.
explanation of symbols: ZN = $Nd_2Zr_2O_7$; ZS = $Sm_2Zr_2O_7$;
ZG = $Gd_2Zr_2O_7$; ZT = $Tb_2Zr_2O_7$; TE = $Er_2Ti_2O_7$; ZYn = ZrO_2 (Y_2O_3)
with n atom percent of Y (high temperature values).
The line --------- represents $Ln_xZr_{1-x}O_{2-\frac{1}{2}x}$ with varying x.

In order to investigate strain energy as a func-
tion of interatomic space, we consider a cavity
in the material, which is treated as a continuum.
Frenkel [18] showed that the elastic energy,
required to dilate a spherical cavity from
radius r_i to r_o follows from:

$$E_s = 8\pi\, Gr_i(r_o-r_i)^2 \qquad (2)$$

where G is the shear modulus of the material.
Anderson and Stuart [19] used this formula in
silica glasses, but found that a value of 4π
gave better results. Eq. (2) can be derived by
calculating the energy for isotropic elastic
deformation of a continuum. For a cylindrical
cavity, with length b, we derived

$$E_s = AG\,(r_o-r_i)^2 \qquad (3)$$

with A = $2\pi b$.
It is clear that the strain energy is very sen-
sitive to the factor $(r_o-r_i)^2$. The absolute
value of E_s then depends on the factor
A, that varies depending on the geometry of the
saddlepoint. Comparing isostructural compounds,
A will be a constant and E_s depends on G and
$(r_o-r_i)^2$. Values of G, calculated from measured
E and ν values, do not vary much (see Table II).

From Fig. 1 we can see that nearest neighbour
oxygen jumps in F and P structures involve

Compound	E (GPa)	ν	G (GPa)
$Nd_2Zr_2O_7$	219	0.271	86.0
$Sm_2Zr_2O_7$	231	0.277	90.4
$Gd_2Zr_2O_7$ (P)	205	0.276	80.3
$Gd_2Zr_2O_7$ (F)	177	0.243	71.2
$Er_2Ti_2O_7$	214	0.264	84.5

Table II

edge-shared tetrahedra (indicated by nn). Such
a jump is visualized in Figure 6. The jumping
ion can choose for a route through the edge
(route 1 in Figure 6), but within our strain
energy model a calculation shows that a jump
following route 2 requires less strain energy.
Then saddlepoint configurations are on the
tetrahedron faces. Oxygen ions then move through
two cation {111} planes, and through the intersti-
tial octahedral cavity of the structure in be-
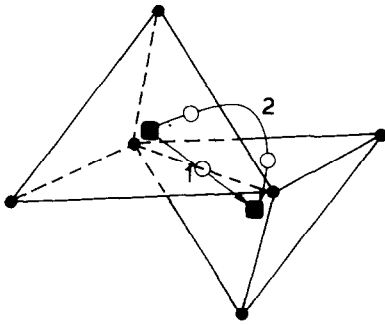tween (imposed by the fcc cation sublattice).

Figure 6: The coordination of two cation
tetrahedra. Two possible jumps
have been indicated.

There are at most two different types of cations
in the structure. The radius of a circle, which
just touches the circles representing the cat-
ions at the corners of the triangular tetrahe-
dron-face determines the dimensions of the
saddlepoint and the strain energy involved.
From geometrical arguments we get:

$$r_i = \frac{a^2 + r_1^2 - r_2^2 - a\sqrt{3}\, r_1}{2(r_2-r_1) + a\sqrt{3}} \qquad (4)$$

The value of a is calculated from the known
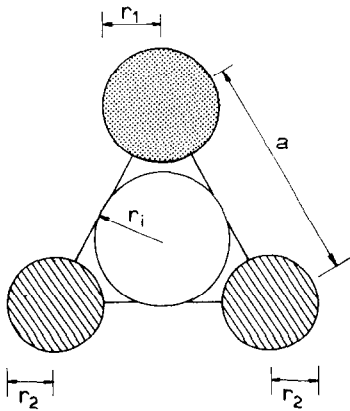unit cell dimension (Fig. 7).

Figure 7: Saddlepoint configuration for
an oxygen jump through the
cation tetrahedron plane.

5.2 IMPLICATIONS OF THE SIMPLE MODEL

In the P structure three types of "nn" jumps
from occupied lattice sites to vacant lattice or
interstitial sites can be distinguished:
8a ↔ 48f, 48f ↔ 48f and 48f ↔ 8b. These
jumps involve the passage of four different
cation planes, with different parameter r_i. The
contributions to the strain energy have been
calculated. For G = 9 x 10^{10} Pa, Ln = Gd and
A = $4\pi r_i$; the results are:

8a ↔ 48f	0.89 eV
48f ↔ 48f	0.27 eV
48f ↔ 8b	nil

A continuous and energetically favourable path-
way can be formed with 48f ↔ 48f jumps, so
that energetically unfavourable 8a ↔ 48f jumps
can be omitted, 48f ↔ 8b jumps do not contri-
bute to the continuous pathway. Because of the
random occupation of cation positions, in the
F structure such an energetically preferential
pathway cannot be formed. A weighted mean value
for jumps in the F structure is 0.42 eV. There-
fore, compounds with a certain degree of P order
always have a lower ΔH value than corresponding
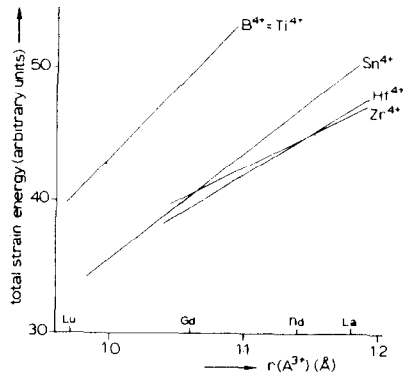F compounds, which was shown already for non-
stoichiometric compounds [8].

Figure 8: Calculated total strain energy for
different pyrochlore type structures
$A_2B_2O_7$.

Considering compounds with the same degree of
order we can calculate the strain energy as a
function of cation radii and unit cell dimensions;
48f ↔ 48f jumps have been taken as representative
jumps. Figure 8 presents the results for some
different A and B cations. The calculations pre-
dict low ΔH values for large B and small A
cations. It must be emphasized, however, that
differences in degree of order between compounds,
might obscure changes due to variation in com-
position. This is certainly the case when we
compare $Gd_2Zr_2O_7$ (P) and $Nd_2Zr_2O_7$. The electron
microscope image of well ordered $Gd_2Zr_2O_7$
(annealed at 1250°C, 10^3hr) (Fig.2a) shows that
complete order has not been achieved. $Nd_2Zr_2O_7$

on the other hand shows only slight disorder [20].

5.3. DEFECT MIGRATION ENERGY CALCULATIONS

Recently we performed some calculations of defect formation and migration energies in co-operation with University College of London [21]. These calculations are more sophisticated than our simple model, because all interatomic interactions are taken into account and atomic relaxations are admitted, while in our simple model the deformation of a continuum is considered. Preliminary results show that indeed 48f ↔ 48f jumps are favourable over 8a ↔ 48f jumps. The jumping ion, however, preferentially follows the route through the edge (route 1 in Fig.6). The barrier energy for route 2 is about 40% higher than for route 1. Like the strain energy model, these calculations show the existence of a preferential diffusion path in the pyrochlore structure too, but the comparison with the disordered structure cannot be made.

It appeared that 'nnn' jumps 48f ↔ 48f (see Fig.1) in the vicinity of empty 8b sites require even less energy. It is not possible, however, to form a continuous path with these jumps only. Other jump possibilities are under investigation. Results of it will be published elsewhere [22].

ACKNOWLEDGEMENT

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