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Neutron Powder Diffraction Studies of Fluorite and Pyrochlore $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ Solid Solutions with $0.25 < x < 0.55$

By

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Dedicated to Prof. Dr. Dr. h. c. Dr. E. h. P. GÖRLICH on the occasion of his 75th birthday

Neutron powder diffraction studies on stoichiometric and non-stoichiometric pyrochlore phases of the $\text{ZrO}_2\text{-Nd}_2\text{O}_3$ system show remarkable differences in the occupation factor of the 8b site of space group $\text{Fd}\bar{3}\text{m}$ to which the pyrochlore phase belongs. Stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ can be described as a perfect pyrochlore phase in which the 8b site is either vacant or at least has a low occupation factor. The occupation factors of the 8b sites of non-stoichiometric $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ pyrochlores reveal that these contain a large degree of disorder in the anion sublattice. Best refinement results on non-stoichiometric materials are achieved when the overall structure of the non-stoichiometric pyrochlore phase is described as a hybrid phase consisting of a major volume fraction of the stoichiometric pyrochlore phase and a minor fraction of the defect fluorite phase.

Neutronenbeugungsuntersuchungen an Pulverproben von stöchiometrischen und nichtstöchiometrischen Pyrochlorphasen des $\text{ZrO-Nd}_2\text{O}_3$ -Systems zeigen deutliche Unterschiede im Besetzungsfaktor des 8b-Platzes der Raumgruppe $\text{Fd}\bar{3}\text{m}$, zu der die Pyrochlorphase gehört. Stöchiometrisches $\text{Nd}_2\text{Zr}_2\text{O}_7$ kann als perfekte Pyrochlorphase beschrieben werden, bei der der 8b-Platz entweder leer ist oder wenigstens einen niedrigen Besetzungsfaktor besitzt. Der Besetzungsfaktor des 8b-Platzes von nichtstöchiometrischen $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ -Pyrochloren zeigt, daß diese einen großen Fehlernungsgrad im Anionengitter enthalten. Verbesserte Ergebnisse an nichtstöchiometrischen Materialien werden erhalten, wenn die Gesamtstruktur der nichtstöchiometrischen Pyrochlorphase als Hybridphase beschrieben wird, die aus einem größeren Volumenanteil der stöchiometrischen Pyrochlorphase und einem kleineren Anteil der fehlgeordneten Fluoritphase besteht.

1. Introduction

The ionic conductivity behaviour of zirconia substituted with relatively large amounts of lanthanide oxide is interesting because the cation ordered pyrochlore phase can have a high ionic conductivity [1].

From this investigation [1] it followed that both in the $\text{ZrO}_2\text{-Gd}_2\text{O}_3$ and in the $\text{ZrO}_2\text{-Nd}_2\text{O}_3$ systems the activation enthalpy (ΔH) and the pre-exponential factor (σ_0) for conductivity are minimum in the stoichiometric pyrochlore phase, while σ_0 is anomalously low for $\text{Nd}_2\text{Zr}_2\text{O}_7$. However, neither ΔH nor σ_0 are simply related to the long-range cation order in the systems investigated.

For this reason we started a neutron diffraction study of the defect structure in the anion sublattice of stoichiometric and non-stoichiometric pyrochlore solid solu-

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tions $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$. Unfortunately comparison of the neutron diffraction results of this system with the results of $\text{Gd}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ is not possible because of the very large absorption cross-section of Gd for neutrons.

Up to now neutron diffraction studies of stabilized zirconias have been performed mainly at compositions at the low substitution side of the cubic phase field where the conductivity is maximum [2 to 4]. Of most concern has been the establishment of the oxygen vacancy model in the defect fluorite structure and the relaxational shifts of the oxygen ions from their ideal fluorite positions [3, 5, 6].

The lanthanides with $r_{\text{Ln}^{3+}} \geq r_{\text{Gd}^{3+}}$ form with zirconia a compound $\text{Ln}_2\text{Zr}_2\text{O}_7$ with pyrochlore structure (space group Fd3m). The pyrochlore structure of stoichiometric $\text{Ln}_2\text{Zr}_2\text{O}_7$ (or more general $\text{A}_2\text{B}_2\text{X}_6\text{X}^{\text{II}}$) can be derived from the fluorite structure by doubling the fluorite cell edge, placing the large Ln^{3+} ions at site 16c, the smaller Zr^{4+} ions at 16d, and the oxygen ions at 8a and 48f of Fd3m. The 8b positions are supposed to be vacant in *completely ordered stoichiometric pyrochlores*. In the pyrochlore structure the 48f anions have shifted towards the vacant 8b sites along $\langle 100 \rangle$ from their ideal fluorite positions for which $x(48f) = 0.375$. The x -parameter of the 48f position is the only variable coordinate in the pyrochlore structure. Values of $0.400 < x(48f) < 0.430$ are commonly found for stoichiometric pyrochlore phase titanates, stannates, and zirconates [7, 8] depending on absolute and relative sizes of $r_{\text{A}^{3+}}$ and $r_{\text{B}^{3+}}$.

Shifts in the $\langle 100 \rangle$ directions are commonly found for defect fluorite-type yttria stabilized zirconia [3, 5, 6]. Actually these shifts are analogous to the shifts of the 48f ions of the pyrochlore structure and may be indicative for pyrochlore-like anion ordering even at the low substitution side of these types of systems. Some X-ray powder refinements have been done on stoichiometric pyrochlores [7, 8] with the major aim to investigate the $x(48f)$ parameter as a function of $r_{\text{A}^{3+}}$ and $r_{\text{B}^{3+}}$ but the standard deviations are relatively large. Deviations from perfect cation order were not reported, although we found [9] that the results of X-ray powder refinements on cation positions are somewhat ambiguous. Because of the small X-ray scattering factor of O^{2-} compared with the one for the cations, X-ray investigation of the defect structure of the anion sublattice is not possible at all.

The result of the $x(48f)$ shift is a distorted octahedral six-coordination of the smaller Zr^{4+} ions and a distorted cubic coordination of the larger lanthanide ions.

The pyrochlore phases of the lanthanide substituted zirconias exist in a certain composition range, mainly determined by the ionic size ratio $r_{\text{Ln}^{3+}}/r_{\text{Zr}^{4+}}$ [10]. Hence defect pyrochlores exist which can be either hypostoichiometric or hyperstoichiometric depending on substitution of less or more than 50 mol% $\text{Ln}_{1.5}$, respectively. Neutron diffraction studies of pyrochlores are known to the present authors only for $\text{Y}_2(\text{Ti}_{0.64}\text{Zr}_{0.36})_2\text{O}_7$ and $\text{Sc}_2\text{Zr}_2\text{O}_7$ [7]. It appeared that for $\text{Y}_2(\text{Ti}_{0.64}\text{Zr}_{0.36})_2\text{O}_7$ none of the refinements were satisfactorily. The neutron diffraction pattern of $\text{Sc}_2\text{Ti}_2\text{O}_7$ was neither that of pyrochlore nor that of fluorite although the X-ray powder photographs of this product could be indexed on the basis of a fluorite cell.

Disagreement exists in literature for the ZrO_2 - Nd_2O_3 phase diagram. According to Perez y Jorba [10] the lower boundary of the cubic phase is at 22 mol% $\text{NdO}_{1.5}$, the pyrochlore single phase being located between 30 and 57 at% Nd^{3+} . However, according to the phase diagram given by Rouanet [11] the pyrochlore single phase is only found in a very narrow region around the stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ composition, the hypo- and hyperstoichiometric compositions actually being two-phase mixtures of the pyrochlore phase with cation disordered defect fluorite and C-type rare-earth (Ti_2O_3) structure, respectively.

2. Experimental Procedures

2.1 Preparation and characterization of specimens

ZrO₂-NdO_{1.5} solid solutions with compositions 25.7, 44.1, 50.2, and 53.4 mol% NdO_{1.5} were prepared by means of the wet-chemical citrate synthesis [1]. After thermolysis of the viscous precursor at 900 to 1000 °C the powder was heated at 1550 °C for at least 70 h and subsequently annealed at 1000 °C for 100 h. This procedure gives excellent homogeneous specimens of which the exact compositions were determined by X-ray fluorescence analysis having a relative accuracy better than 0.4%. The well ground material was investigated by X-ray diffraction. Superstructure reflections due to the presence of the pyrochlore phase are present in the specimens with 44.1, 50.2, and 53.4 mol% NdO_{1.5} while they could not be detected with X-ray diffraction in the composition with 25.7 mol% NdO_{1.5}.

2.2 Neutron diffraction

Neutron diffraction diagrams have been collected at room temperature and at 600 °C on the powder diffractometer at the HFR reactor at Petten. Neutrons of wavelength 2.58 Å were obtained from the (111) planes of a copper crystal. As a second-order filter, a block of pyrolytic graphite with a thickness of 10 cm was employed [12]. Soller slits with a horizontal divergence of 30' were placed between reactor and monochromator and in front of the BF₃ counter. The samples were contained in cylindrical vanadium sample holders at room temperature or stainless steel holders at 600 °C.

As absorption was not negligible the data were corrected for this effect.

3. Models Used for Neutron Refinement

For the refinements of the stoichiometric and non-stoichiometric pyrochlore compositions Nd_xZr_{1-x}O_{2-x/2} three distinct models were evaluated:

- the perfect pyrochlore model (A),
- the imperfect pyrochlore model (B),
- the hybrid phase model (C).

These models will be discussed below.

3.1 The perfect pyrochlore model

In the stoichiometric case, Nd³⁺ is at site 16c of space group Fd3m, Zr⁴⁺ at 16d, while the oxygen ions fully occupy 8a and 48f, leaving position 8b completely vacant.

In the hypostoichiometric case ($x < 0.5$) there is an excess of oxygen ions and both from size and fluorite analogy reasons this excess of oxygen is supposed to fill part of the 8b sites of the structure.

In the hyperstoichiometric case where $x > 0.5$ there is an excess of anion vacancies, situated at either 8a or 48f or both of them, the 8b position leaving completely vacant as in the stoichiometric case. Hence in the perfect pyrochlore model both in the stoichiometric and non-stoichiometric cases the occupancies of the 8b positions can be predicted from composition as follows:

$$n_0(8b) = 1 - 2x \quad \text{for } x < 0.5, \quad (1a)$$

$$n_0(8b) = 0 \quad \text{for } x \geq 0.5, \quad (1b)$$

in which n_0 is the oxygen occupancy at a given site.

3.2 The imperfect pyrochlore model

The imperfect pyrochlore model is distinguished from the perfect pyrochlore model (A) by an extra degree of freedom in the occupancy of the 8b position which is no longer only a function of composition.

Both for stoichiometric and non-stoichiometric pyrochlore:

$$n_0(8a) + 6n_0(48f) + n_0(8b) = 8 - 2x \quad (2)$$

and

$$n_0(8b) > 1 - 2x \quad \text{for } x < 0.5, \quad (3a)$$

$$n_0(8b) > 0 \quad \text{for } x \geq 0.5. \quad (3b)$$

Since in the defect fluorite structure 8a, 48f, and 8b positions are equivalent, one can state from the excess 8b occupancy that the imperfect pyrochlore is a pyrochlore having a partially fluorite-like character.

3.3 The hybrid phase model

An extension of the imperfect pyrochlore model mentioned above is the hybrid phase model. Description of a classical two-phase model for the non-stoichiometric pyrochlore phase $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ according to Rouanet [11] is not possible because such a two-phase model would imply two distinct phases (fluorite and pyrochlore) separated by non-coherent boundaries each with its own lattice parameter dependent on composition [1].

The hybrid phase model used here implies a dispersion of relatively small volumes with fluorite structure having coherent boundaries with a perfect pyrochlore matrix. The hybrid phase system is a thermal equilibrium state in a certain temperature range and can be described with only one free energy function. Hence the hybrid phase concept represents a relatively stable condition intermediate to the classical concepts of homogeneous solid solution and a two-phase mixture [13 to 16]. It must be emphasized here that our description only relates to the anion sublattice, whereas the cation sublattice is supposed to be almost completely ordered.

Refinements of stoichiometric and non-stoichiometric pyrochlores on the basis of the hybrid phase model can be done because the defect fluorite structure (space group Fm3m) is so closely related to the pyrochlore structure (space group Fd3m) that the fluorite structure can be described as a completely disordered and hence highly imperfect pyrochlore, however, with the $x(48f)$ parameter fixed at 0.375.

The site relationships are:

$$(16c + 16d)_{\text{Fd3m}} \equiv 4a_{\text{Fm3m}} \quad \text{for cations,} \quad (4a)$$

$$\left. \begin{aligned} (8a + 8b + 48f)_{\text{Fd3m}} &\equiv 8c_{\text{Fm3m}} \\ x(48f) &= \frac{3}{8} \end{aligned} \right\} \text{for anions.} \quad (4b)$$

Hence it follows that the anion sublattices of both fluorite and pyrochlore phases can be described using crystallographic sites in Fd3m.

It now follows that the hybrid phase defined as above can be described in Fd3m with four possible sites for the oxygen ions. The occupation factors of these sites depend then only on the fractions u and $(1 - u)$ of pyrochlore and fluorite phase in the hybrid phase, respectively.

In the fluorite fraction, sites 8a, 8b, and 48f with $x(48f) = 0.375$ are randomly occupied. In the pyrochlore fraction the 8a and 48f sites with $x(48f) > 0.375$ are completely occupied, whereas 8b is vacant. The occupation factors of the four sites in each of the components of the hybrid phase and their overall values from which the hybrid phase composition parameter u can be refined, are shown in Table 1.

Compared to the imperfect pyrochlore model (B) the hybrid phase model (C) has one extra site but also only one occupation parameter for all oxygen sites and hence both models have the same number of parameters to be refined.

Table 1

Occupancy factor n_0 of oxygen sites in hybrid phases $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ in space group Fd3m as a function of composition parameter x and pyrochlore fraction u

site in Fd3m	n_0 in pyrochlore component	n_0 in fluorite component	overall n_0 in hybrid phase
8a	1	$\frac{8-2x-7u}{8(1-u)}$	$\frac{1}{8}u + \left(1 - \frac{x}{4}\right)$
8b	0	$\frac{8-2x-7u}{8(1-u)}$	$\left(1 - \frac{x}{4}\right) - \frac{7}{8}u$
48f($x(48f) \neq \frac{3}{8}$)	1	—	u
48f($x(48f) = \frac{3}{8}$)	—	$\frac{8-2x-7u}{8(1-u)}$	$\left(1 - \frac{x}{4}\right) - \frac{7}{8}u$

4. Results and Discussion

For the structure refinement of the neutron diffraction data the profile method [17] has been applied. The coherent scattering lengths used are $b(\text{Nd}) = 0.77$, $b(\text{Zr}) = 0.71$, and $b(\text{O}) = 0.580 \times 10^{-12}$ cm.

The quantity χ_r^2 given in the tables is defined as $\chi_r^2 = \sum w_i [y_i(\text{obs.}) - y_i(\text{calc.})/k]^2/\nu$, where $y_i(\text{obs.})$ and $y_i(\text{calc.})$ are the observed and calculated intensities for the i -th measuring point, w_i its statistical weight, and ν the number of points minus number of parameters.

Table 2

Refinement of $\text{Nd}_{0.502}\text{Zr}_{0.498}\text{O}_{1.749}$ as a perfect pyrochlore (A), an imperfect pyrochlore (B), and a hybrid phase (C)

parameter	refinement model		
	A	B	C
$n_0(8a)$	1.0	0.978(9)	0.9936(1)
$n_0(48f)$	1.0	0.997(2)	0.949(2)
$n_0(8b)$	0.0	0.039(9)	0.044(2)
$n_0(48f) (x(48f) = \frac{3}{8})$	—	—	0.043(2)
u	—	—	0.949(2)
\bar{B}	0.19(7)	0.27(7)	0.17(6)
$x(48f)$	0.4154(2)	0.4157(2)	0.4174(2)
a_0	10.6836(4)	10.6836(3)	10.6836(3)
χ_r^2	10.90	10.20	9.20

a_0 the lattice constant of the pyrochlore cell (see also Tables 3 and 4).

4.1 Stoichiometric pyrochlore ($\text{Nd}_{0.502}\text{Zr}_{0.498}\text{O}_{1.7749}$)

The stoichiometric pyrochlore composition was refined in either of the three models using an overall temperature factor \bar{B} . The results are given in Table 2.

It is seen that refinement as an imperfect pyrochlore (B) or a hybrid phase (C) gives only a small improvement in χ_r^2 compared with the perfect pyrochlore phase model (A). When there is some fluorite character this is expressed as no more than 4% occupation of the 8b sites according to model B and also as not more than 5% fluorite in a stoichiometric pyrochlore according to model C.

From Fig. 1 a and b it is seen that for the stoichiometric pyrochlore the results based on the models B and C do not differ significantly from the result for model A ($n_0(8b) = 0$ and $u = 1$ in Fig. 1 a and b, respectively).

So stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ can simply be considered as a perfect pyrochlore having only some intrinsic oxygen defects of which the concentration is certainly not larger than 5% of the number of anion 8b sites.

4.2 Hypostoichiometric pyrochlore ($\text{Nd}_{0.441}\text{Zr}_{0.559}\text{O}_{1.7795}$)

For this composition the refinement results are given in Table 3.

By comparing the χ_r^2 -values it is now evident that the imperfect pyrochlore model (B1) gives a significant improvement compared to the perfect pyrochlore model (A).

The occupation factor for oxygen at the 8b site calculated from model B is 28% ($n_0(8b) = 0.278$) instead of a value of 12% calculated from model A.

With individual temperature factors (B2) an even better improvement can be obtained for the imperfect pyrochlore model and though $n_0(8b)$ now decreases to 23%, it is still twice as much as the value expected for a perfect pyrochlore.

Using overall temperature factors, the best refinement result for the hypostoichiometric pyrochlore phase is obtained with the hybrid phase model refinement (C1).

With a volume fraction of about 18% fluorite component ($u = 0.824$) in the hybrid phase, the hypostoichiometric phase appears to have a considerable amount of "fluorite character". The improvement of the refinement results achieved with model C1 ($\chi_r^2 = 8.11$) compared to those based on model B1 ($\chi_r^2 = 9.3$) is in our opinion significant. This is based on the argument that independent refinement on the four oxygen sites of model C constraining the occupation factors for the total oxygen content (refinement C2) gives no further improvement compared to C1 in spite of two extra refinement parameters.

In Fig. 2 a and b it is shown that both for models B and C values of χ_r^2 are very sensitive to changes in the values of $n_0(8b)$ and u , respectively, and hence the results

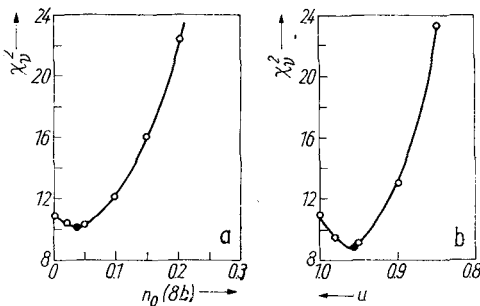


Fig. 1. a) χ_r^2 vs. the occupation factor of the 8b site for $\text{Nd}_{0.502}\text{Zr}_{0.498}\text{O}_{1.7749}$. The black dot indicates the minimum in the curve. b) χ_r^2 vs. the pyrochlore fraction u in the hybrid phase of $\text{Nd}_{0.502}\text{Zr}_{0.498}\text{O}_{1.7749}$.

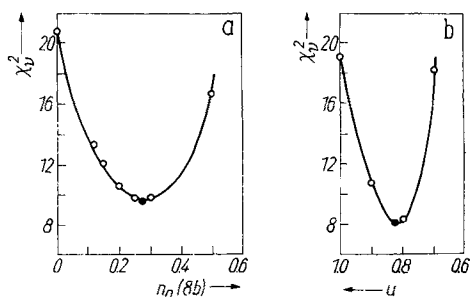


Fig. 2. a) χ_r^2 vs. the occupation factor of the 8b site for $\text{Nd}_{0.441}\text{Zr}_{0.559}\text{O}_{1.7795}$. b) χ_r^2 vs. the pyrochlore fraction u in the hybrid phase of $\text{Nd}_{0.441}\text{Zr}_{0.559}\text{O}_{1.7795}$

obtained with models B and C differ significantly from the perfect pyrochlore model (A) whereas the results favour model C over model B.

Table 3
Refinement of $\text{Nd}_{0.441}\text{Zr}_{0.559}\text{O}_{1.7795}$

parameter	refinement model				
	A	B1	B2	C1	C2
$n_0(8a)$	1.0	1.00(1)	0.96(2)	0.9929(7)	0.99(1)
$n_0(48f)$	1.0	0.974(3)	0.989(5)	0.824(6)	0.853(9)
$n_0(8b)$	0.118	0.28(1)	0.23(2)	0.169(5)	0.23(1)
$n_0(48f)$ ($y(48f) = \frac{3}{8}$)	—	—	—	0.169(5)	0.127(9)
u	—	—	—	0.824(6)	—
\bar{B}	1.05(1)	0.87(9)	—	0.24(9)	0.43(9)
B_{cations}	—	—	0.29(8)	—	—
$B_0(8a)$	—	—	0.5(4)	—	—
$B_0(48f)$	—	—	1.5(1)	—	—
$B_0(8b)$	—	—	2.1(1.6)	—	—
$x(48f)$	0.4090(3)	0.4104(3)	0.4110(2)	0.4172(4)	0.4157(5)
a_0	10.6242(6)	10.6244(5)	10.6243(4)	10.6243(4)	10.6243(4)
χ_r^2	13.5	9.3	6.0	8.11	7.53

A the perfect pyrochlore model.

B1 the imperfect pyrochlore model with overall temperature factor.

B2 the imperfect pyrochlore model with individual isotropic temperature factors.

C1 the hybrid phase model.

C2 the "hybrid phase model" with all oxygen positions independently refined.

B_{cations} the isotropic temperature factor for cations (see also Table 4).

$B_0(8a)$, $B_0(48f)$, $B_0(8b)$ the individual isotropic temperature factors for oxygen ions at 8a, 48f, and 8b sites, respectively (see also Table 4).

4.3 Hyperstoichiometric pyrochlore ($\text{Nd}_{0.534}\text{Zr}_{0.466}\text{O}_{1.773}$)

The refinement results for this composition are given in Table 4.

As there is now oxygen deficiency compared with the stoichiometric case, it is expected that for the perfect pyrochlore model (A) $n_0(8b) = 0.0$ and that the extra oxygen vacancies are at 8a and 48f sites. However, it is now surprising that the imperfect pyrochlore model B ($\chi_r^2 = 6.39$) gives far better results than model A ($\chi_r^2 = 9.52$). From model B it turns out that as much as 17% oxygen occupies the 8b

Table 4
Refinement of $\text{Nd}_{0.534}\text{Zr}_{0.466}\text{O}_{1.733}$

parameter	refinement model			
	A	B1	B2	C
$n_0(8a)$	1.0	1.01(1)	0.93(2)	0.9742(7)
$n_0(48f)$	0.9885	0.958(3)	0.976(6)	0.862(5)
$n_0(8b)$	0.0	0.17(1)	0.15(2)	0.112(5)
$n_0(48f) (x(48f) = \frac{3}{8})$	—	—	—	0.112(5)
u	—	—	—	0.862(5)
\bar{B}	0.66(9)	0.57(8)	—	0.01(8)
B_{cations}	—	—	-0.02(7)	—
$B_0(8a)$	—	—	-0.8(3)	—
$B_0(48f)$	—	—	1.2(1)	—
$B_0(8b)$	—	—	11.(4)	—
$x(48f)$	0.4112(3)	0.4130(3)	0.4131(2)	0.4175(3)
a_0	10.7174(5)	10.7175(4)	10.7177(3)	10.7177(4)
χ_r^2	9.52	6.39	3.6	4.87

A the perfect pyrochlore model.

B1 the imperfect pyrochlore model with overall temperature factor.

B2 the imperfect pyrochlore model with individual isotropic temperature factors.

C the hybrid phase model.

site ($n_0(8b) = 0.171$). The significance of this result is demonstrated in Fig. 3a where a steep minimum appears in the χ_r^2 versus $n_0(8b)$ curve.

As for hypostoichiometric pyrochlore, also in this case refinement as a hybrid phase (C) was tried. It appears that the best refinement result, even better than for model B, is achieved for $u = 0.86$ and hence with as much as 14 vol% fluorite phase in the hybrid phase. In Fig. 3b it is shown that the refinement is very sensitive to variations of u .

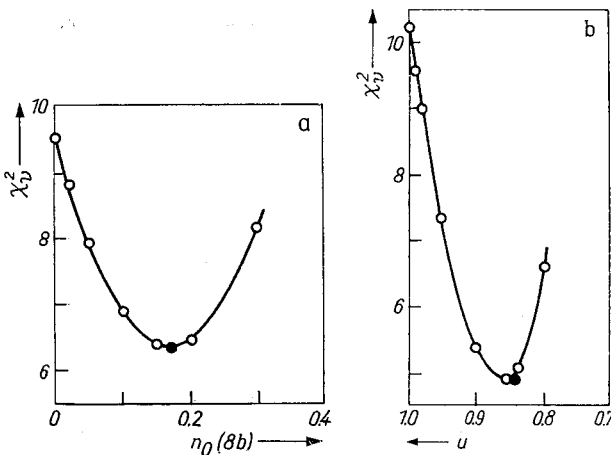


Fig. 3. a) χ_r^2 vs. the occupation factor of the 8b site for $\text{Nd}_{0.534}\text{Zr}_{0.466}\text{O}_{1.733}$. b) χ_r^2 vs. the pyrochlore fraction u in the hybrid phase of $\text{Nd}_{0.534}\text{Zr}_{0.466}\text{O}_{1.733}$

No reflections from the C-type rare-earth (Tl_2O_3) structure (space group Ia3) can be detected in the neutron diffraction pattern of this composition. This does not agree with the phase diagram given by Rouanet [11].

The refinement results for model B with individual temperature factors (B2) confirm the results obtained with an overall temperature factor (B1). Attention should be paid to the fact that (physically meaningless) negative temperature factors for cations and 8a anions are found. Negative values for the 8a temperature factors are reported in X-ray powder diffraction studies by several investigators [7, 8] and are also found in preliminary X-ray investigations on the single-crystal pyrochlore phase $\text{Gd}_{0.52}\text{Zr}_{0.48}\text{O}_{1.74}$ [9].

4.4 Defect fluorite ($\text{Nd}_{0.257}\text{Zr}_{0.473}\text{O}_{1.872}$)

Refinement of this composition both as a perfect defect fluorite structure with oxygen ions on their usual positions and as a perfect pyrochlore structure gave equally poor results ($\chi_r^2 \approx 35$).

It is likely that in this case we have relaxations of O^{2-} from their ideal fluorite positions along $\langle 100 \rangle$ directions as is found for yttria stabilized zirconia [3, 5, 6]. It is remarkable that with X-ray diffraction no superstructure reflections were found, but that neutron diffraction revealed some background modulations at the positions of the strong pyrochlore superstructure reflections 331, 442, and 511/333. It is likely that these modulations have their origin in small pyrochlore domains in the defect fluorite matrix.

If this interpretation is correct it accounts together with the results for non-stoichiometric pyrochlore for the continuity of conductivity observed in this type of system [1] and then redefines the fluorite-pyrochlore phase boundary as a boundary separating a fluorite matrix with pyrochlore regions and a pyrochlore matrix with fluorite regions.

4.5 Diffraction measurements at 600 °C

The samples having 44.1 and 53.4 mol% $\text{NdO}_{1.5}$ have also been measured at 600 °C. Refinements have been made on the basis of the imperfect pyrochlore model.

The results clearly show that the oxygen defect structure is frozen in at least up to 600 °C as the occupancy parameters of the oxygen sites do not differ within standard deviation from room temperature results. No essential differences exist in the defect structure at room temperature and at 600 °C and therefore refinements based on model C are not performed. $x(48f)$ shifts to somewhat higher values, e.g. for $x = 0.441$, $x(48f) = 0.4123(3)$ at 600 °C and 0.4104(3) at room temperature and for $x = 0.534$, $x(48f) = 0.4159(3)$ at 600 °C and 0.4130(3) at room temperature.

The pre-exponential factor for conductivity contains a contribution from the concentration of mobile species and this concentration depends on the oxygen defect structure. Therefore, the similarity of defect structure at 600 °C and room temperature is consistent with the observation that the value of the pre-exponential factor for conductivity is independent of temperature up to at least 600 °C.

4.6 $x(48f)$ as a function of concentration

The values of $x(48f)$ of the pyrochlore compositions refined as single-phase imperfect pyrochlores (B) and hybrid phases (C) are given in Table 5 and show that the calculated values of $x(48f)$ are consistent with model expectations. If calculated from the single-phase imperfect pyrochlore model (B), $x(48f)$ is maximum for stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ where 8b positions are not or only slightly occupied. This behaviour is expected because the $x(48f)$ shift is in the direction of the vacant 8b site and hence, when part of the 8b sites are occupied, local variations of $x(48f)$ occur in the sample.

Table 5

The space group parameter $x(48f)$ as a function of $\text{Nd}_{1.5}$ content

mol% $\text{NdO}_{1.5}$	$x(48f)$ calculated for the imperfect pyrochlore model (B)	$x(48f)$ calculated for the hybrid phase model (C)
44.1	0.4104(3)	0.4172(4)
50.2	0.4157(2)	0.4174(2)
53.4	0.4130(3)	0.4175(3)

When refined as a hybrid phase it is expected that for all compositions, $x(48f)$ has the same value in the pyrochlore component of the hybrid phase. This is observed indeed from Table 5 and, for the perfect pyrochlore phase $\text{Nd}_2\text{Zr}_2\text{O}_7$, $x(48f)$ turns out to be 0.4174(4).

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