JOURNAL OF SOLID STATE CHEMISTRY 7, 448–453 (1973)

A High-Temperature Neutron Diffraction Study of Pure and Scandia-Stabilized Zirconia

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Received November 6, 1972

A high-temperature neutron diffraction apparatus has been used to study a section of the zirconia–scandia system; the purpose was to determine whether this technique can be generally applied to phase equilibria studies. The structure of the tetragonal form of zirconia at 1200°C has been confirmed, and the parameters obtained were $z(4d) = 0.188 \pm 0.002$, $B_0 = 2.50$ Å^2, $B_{Zr} = 0.80$ Å^2, and $R = 0.045$. The effect of substituting scandia into the tetragonal zirconia structure was studied and the transformation of the ordered low-temperature β-phase to a grossly nonstoichiometric fluorite phase was also observed.

Introduction

Cubic stabilized zirconia phases (CSZ) are ionic conductors over wide ranges of temperature and oxygen partial pressures. Substitution of various di- and trivalent cation oxides into the zirconia lattice results in an increase in conductivity with increasing dopant content (*1*). The conductivity reaches a maximum at ca. 15 mole % dopant content, with a subsequent decrease in conductivity if the dopant concentration is further increased. X-ray (*2*), density (*3*), and other studies have shown that a vacancy mechanisn is responsible for the transport of anions through the oxygen sublattice. Of the numerous CSZ phases studied the zirconia–scandia system contains the composition of highest ionic conductivity (*4*), but it is not clear in this system whether the maximum in the conductivity-composition diagram is due to the existence of a particular structural type, or to the same mechanism as occurs in other CSZ systems. Interpretation of the conductivity data is complicated by the contradictory nature of the published phase diagrams for the zirconia–scandia system, as shown in Fig. 1. This diagram shows the results of the three latest, and most thorough, of the studies of this system (*5–7*). Part of this ambiguity stems from the fact that many of the samples were quenched from elevated temperatures, and did not necessarily represent equilibrium states.

Short-range ordering of the oxygen vacancy sites might be expected to occur in disordered nonstoichiometric phases MO_{2-x}. Complete ordering of oxygen vacancies has been observed at certain concentrations in this and other related systems, but the diffraction effects due to partial ordering, or to relaxation of the oxygen lattice, would be difficult to detect by powder X-ray diffraction since the ratio of atomic scattering factors for zirconium and oxygen is ca. 5:1. However, the corresponding neutron scattering lengths are in the ratio of 1.2:1, so that neutron diffraction could possibly resolve oxygen ordering. A study at temperature by neutron diffraction of selected regions of the zirconia–scandia system could clarify the phase diagram and might allow meaningful discussion of the effects of doping on conductivity. It should be stressed that in this system there is so far no evidence (*7*) to indicate cation ordering, so that all diffraction effects should be due to a combination of the relaxation of the anions and cations from ideal fluorite sites, or ordering of vacancies and oxygens within the anion sublattice.

As the systems of interest to this study are subtraction structures obtained by removal of anions from a fluorite oxide, compositions are

Printed in Great Britain

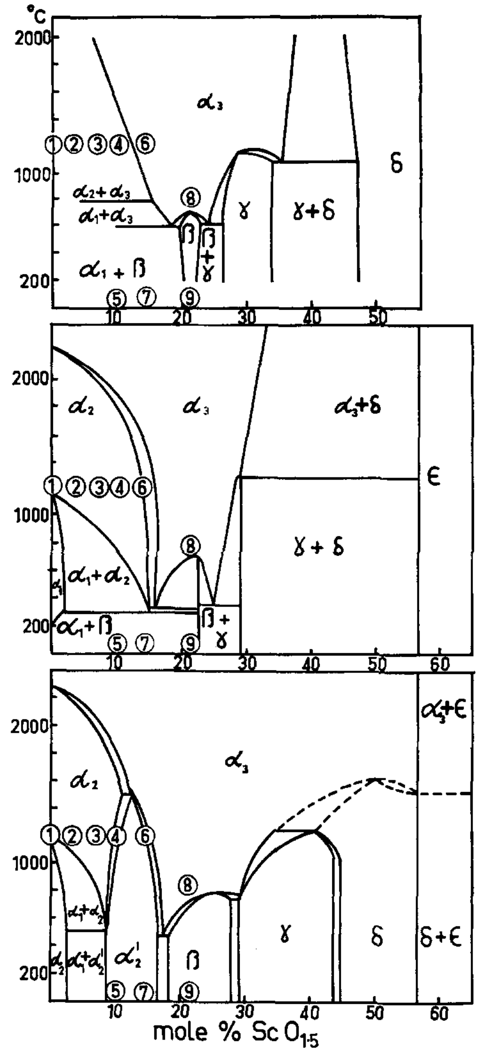

FIG. 1. The system ZrO_2–Sc_2O_3. Top: Spiridonov, Popova, and Popilskii (*5*); center: Thornber, Bevan, and Graham (*7*); bottom: Ruh (*6*). The superimposed circles represent the compositions of the samples, and the temperature at which the samples were examined, in this study.

reported in terms of $ScO_{1.5}$ content. For this reason the results of Refs. (*5* and *6*) have been recalculated on this basis for inclusion in Fig. 1.

The Phases of Zirconia

1. The Monoclinic Structure

The low-temperature stable form of zirconia is monoclinic as represented by the naturally occurring mineral baddeleyite. In this structure the cations are in sevenfold coordination (*8*); it has been described as distorted fluorite (*9*). HfO_2 (*10*) and ScOF (*11*) are the only other compounds with this structure. On heating monoclinic zirconia a martensitic transformation occurs with substantial volume contraction (*12*). The transformation monoclinic ⇌ tetragonal involves a considerable degree of hysteresis. The monoclinic structure can accept only a small proportion of altervalent cation oxides into its structure. Substitution of this type causes a sharp drop in the temperature of the martensitic transformation. In the diagrams of Fig. 1 monoclinic zirconia and its related solid solution phase are designated as the α_1 region.

2. Tetragonal Zirconia

The high-temperature stable form of zirconia is tetragonal, α_2. For pure zirconia this structure cannot be obtained at low temperatures by quenching. This structure is derived from a fluorite oxide by elongating one of the three initially equal crystallographic axis with respect to the other two (*13*) and displacing oxygen alternatively above and below their ideal positions in the (001) plane [Teufer (*14*)]. The relationship of the two structures is made clear by

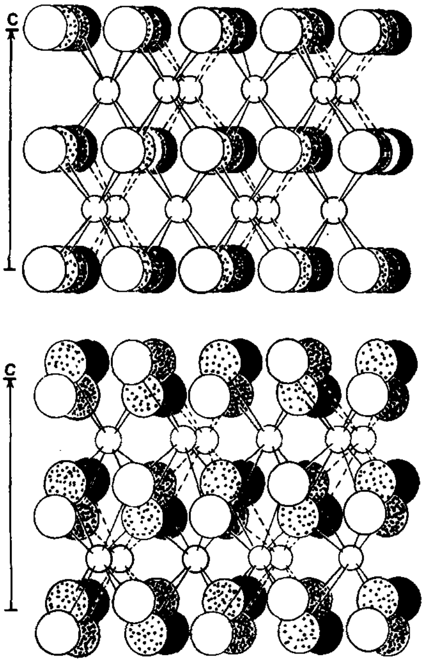

FIG. 2. Tetragonal zirconia, and relation to fluorite. Top: *tetragonally distorted fluorite*; bottom: *the tetragonal structure of zirconia.*

the projection in Fig. 2. If the c/a ratio of the high-temperature structure was reduced to $\sqrt{2}$, the cation sublattice would be identical to that present in a cubic fluorite oxide; the rumpling of the oxygen planes decreases to zero as the oxygen z parameter approaches 0.250. For $z = 0.250$ and $c/a = \sqrt{2}$ a cubic fluorite structure is obtained.

The space group of the tetragonal structure is $P4_2/nmc_1$ and the oxygen atoms are in positions $4(d)$, which allows a variable z parameter. The α_2' phase suggested by Ruh (*6*) is also tetragonal, but a different space group is involved which places the anions in special positions with fixed parameters.

The rumpling of the pseudo-fluorite anion layers gives rise to a small number of relatively weak "oxygen only" peaks in an otherwise tetragonally distorted fluorite X-ray powder pattern, and these allow differentiation between the two space groups. The intensities of these peaks decrease rapidly with increasing dopant concentration, and an increase in the anion vacancy concentration has the effect of increasing the value of the $z(4d)$ parameter toward its limiting value of 0.250. In the X-ray case these peaks would become virtually unobservable in a powder diffraction pattern well before the limiting value was reached. One result of this effect is that the X-ray diffraction pattern of a sample for which $c/a = \sqrt{2}$ could be apparently indexed as cubic fluorite even though the true symmetry was tetragonal. In addition, a tetragonal phase having the α_2 structure could be wrongly assigned the α_2' structure. In neutron diffraction patterns however the relative intensity of the oxygen-only peaks is an order of magnitude larger (*15*).

The tetragonal structure of zirconia can accommodate a high degree of substitution by lower-valent cation oxides giving rise to what appear to be grossly nonstoichiometric phases. These phases can be retained at room temperature, and are referred to in Fig. 1 as the α_2 region.

3. Cubic Zirconia

On heating to 2300°C a cubic fluorite structure has been reported for pure zirconia. This structure was derived from an X-ray diffraction study (*16*). The α_3 region of Fig. 1 refers to a grossly nonstoichiometric cubic fluorite structure.

Experimental Methods

1. Sample Preparation

The zirconia used in this study was of 99.8% purity. The undoped zirconia sample used in the neutron diffraction study was in the form of a cylinder of dimension 4 × 1 cm diameter. The sample was prepared by isostatic pressing followed by firing for 1 day at 900°C. This resulted in a sample of approximately 70% of theoretical density. The scandia was of 97% purity, the impurities consisting almost completely of rare earths, and mixed oxide samples were prepared by coprecipitation from solution with ammonia. The resulting dried hydrous oxides were powdered and fired at 500°C for 30 min and the composition was determined by chemical analysis. The fine reactive powders so obtained were then isostatically pressed and refired at 1700° for 14 hr, and then cooled slowly. The resulting cylindrical specimens were of approximately 95% of theoretical density.

2. Diffraction Studies

The experiments were carried out at the HIFAR reactor located at the Australian Atomic Energy Research Establishment. A description of the neutron diffraction furnace will be published elsewhere (*17*). The mean neutron wavelength was 1.087 Å, and the diffractometer contained an analyzing crystal in the diffracted beam to obtain better resolution. The neutron scattering lengths used were taken from a recent compilation(*18*) and absorption corrections to the data were not considered necessary (*19*). Because of partial overlapping of neighboring peaks in the diffraction pattern the analysis was based upon intensities, so that the value minimized in the final calculation was of the form

$$R = \Sigma |I_o - I_c| / \Sigma I_c,$$

where I_o and I_c are the observed and calculated intensities, respectively.

The c and a values used for pure tetragonal zirconia were obtained from the compilation by Lang (*20*), and from the observed shifts of the peaks in the neutron diffraction patterns, c and a values were derived for the scandia containing samples.

Results

In the composition range investigated five phase regions have been reported. The neutron

TABLE I

Composition (mole % $ScO_{1.5}$)	Sample no.[a]	Temp. (°C)	z (4d) ±0.002	$B_{Zr,Sc}$ (Å^2)	B_o (Å^2)	R
0	1	1200	0.188	0.80	2.50	0.045
6.9	3	1200	0.202	1.18	3.25	0.057
10.0	4	1200	0.208	0.85	2.50	0.034
10.0	5	25	0.212	0.55	0.85	0.026
21.4	8	800	Cubic fluorite	2.1	5.0	0.125
21.4	9	25	β-Phase			

[a] The sample number is the number contained in the superimposed small circles in Fig. 1.

diffraction patterns were recorded at various temperatures, and the circles superimposed in Fig. 1 refer to the composition and temperature of the particular sample studied. The results are summarized in Table I.

2.1. Pure ZrO_2 at 1200°C. Parameters for tetragonal zirconia, the α_2 phase, were refined using Teufer's (*14*) values as a starting point. The final values obtained were $z = 0.188 \pm 0.002$, $B_0 = 2.50$ Å^2; $B_{Zr} = 0.80$ Å^2 and $R = 0.045$. The z parameter is close to that found by Teufer at 1250°C, but the neutron temperature factors are considerably lower than those found from X-ray analysis, as is normal. The low R value obtained is in part due to the comparatively small number of reflections used in the analysis. Table II lists the calculated and measured intensities, the standard deviation in the measured intensities and each individual $|I_o - I_c|$ value. It can be seen that, with the exception of the (220) and (123 + 301) reflections, the difference between the observed and calculated intensities is acceptable. One possible reason for the poor agreement between the calculated and measured value for the (220) reflection is that isotropic temperature factors were used in the calculations.

2.2. Samples of composition 3.2 and 14.5 mole % $ScO_{1.5}$ were also studied, however the neutron intensity data could not be satisfactorily refined. X-ray examination, at room temperature, showed these samples to be two-phase. This would imply that the single-phase structures obtained on annealing at 1700°C had decomposed into two-phase systems, due to the slow cooling rate. The subsequent reheating to 1200°C in the neutron diffraction furnace has not been sufficient to allow a single phase to reform, and the recorded neutron diffraction pattern is of two phases of similar "d" spacings, but evidently significantly different z values.

TABLE II

PURE ZIRCONIA AT 1250°C[a]

$h\,k\,l$	I_o	SD	I_c	$\lvert I_c - I_o \rvert$
1 0 1	1471	40	1480	9
0 0 2	—		2	2
1 1 0	144	17	157	13
1 0 2[b]	808	32	786	22
1 1 2 2 0 0	3771	64	3763	8
1 0 3 2 1 1	1177	38	1179	2
2 0 2	—		2	2
2 1 2[b]	434	26	462	28
0 0 4	—		69	69
2 2 0	482	27	631	149
1 0 4[b]	334	26	308	26
1 2 3 3 0 1	570	31	668	98

[a] I_o = observed intensity; I_c = calculated intensity; SD = standard deviations for I_o.

[b] Oxygen-only peaks.

2.3. The sample of 21.4 mole % $ScO_{1.5}$ content was studied at 800 and 25°C. At 800°C the neutron diffraction pattern could be indexed as cubic fluorite with no observable superstructure reflections. However, when the data was analyzed in terms of a defect fluorite (α_3) structure, parameters $R = 0.125$, $B_0 = 5.0$ Å^2 and $B_{Zr,Sc} = 2.1$ Å^2 were obtained. Considerable intensity modulated diffuse scattering was observed in the recorded pattern, similar to that reported in room temperature neutron diffraction studies of phases in the ZrO_2–CaO (*1*) and ZrO_2–Y_2O_3 (*20*) systems and indicating extensive clustering or short-range order. The large R value obtained is no doubt associated both with ordering tendencies and with significant relaxation of the oxygen ions from the ideal fluorite sites.

At 25°C the neutron diffraction pattern could be indexed in terms of the β-phase lattice parameters recorded by Thornber, Bevan, and Graham (*7*). These parameters were derived from a powder X-ray diffraction study, and Thornber suggested that the ideal composition of this phase is either

(a) $Zr_{50}Sc_{12}O_{118}$ (19.4 mole% $ScO_{1.5}$),
(b) $Zr_{48}Sc_{14}O_{117}$ (22.6 mole% $ScO_{1.5}$),
(c) $Zr_{46}Sc_{16}O_{116}$ (25.8 mole% $ScO_{1.5}$);

with (b) being the most likely. However, Spiridinov, Popova, and Popilskii (*5*) suggested the ideal composition is $Zr_7Sc_2O_{17}$ (22.2 mole% $ScO_{1.5}$). The structure of this phase is obviously fluorite derived, but could not be further elucidated from the neutron data.

Discussion

The upper two-phase diagrams shown in Fig. 1 indicate that a two-phase region $\alpha_1 + \beta$ exists for 3 to 20 mole % $ScO_{1.5}$ and that the tetragonal α_2 phase is unstable at low temperatures. In this study the only phases found in this region at low temperature were either $\alpha_1 + \alpha_2$, single-phase α_2, or $\alpha_2 + \beta$. In order to see whether this result was due to a kinetic effect the 10.0 mole % $ScO_{1.5}$ sample was annealed at 400°C for 12 wk. A subsequent X-ray diffraction pattern showed only a single-phase tetragonal structure. Ruh (*6*) reports that the tetragonal (α_2) phase transforms to the distorted fluorite tetragonal structure (α_2') at room temperature. No evidence for this transformation was found in this study, all room temperature tetragonal patterns were of the α_2 type.

Previous X-ray diffraction studies on a number of ZrO_2–M_2O_3 systems (*21*) (M = trivalent rare earth, or yttrium) has shown that the *a* and *c* parameters of the tetragonal α_2 structures vary linearly with the trivalent cation content, and that samples containing greater than 17 mole % of additive would have cubic structures.

In this study the relationship between the *z* parameter and the scandia content at 1200°C is close to linear of the form

$$z = 0.188 + 0.002 \times (\text{mole } \%\ ScO_{1.5}).$$

Assuming that an extrapolation of these results is valid, and that the equilibrium phase at this temperature is single-phase α_2, this relationship indicates that at 17 mole % of additive the *z* parameter would be significantly smaller than 0.250 even though the *c*/*a* ratio has become $\sqrt{2}$. Allowing for a standard deviation three times the quoted uncertainty in the *z* parameter, a nonlinear relationship between *z* and vacancy concentration is just possible, but even so in the range 10 to 17 mole % of additive the *z* parameter would have to increase dramatically to reach the value of 0.250 needed to give true cubic symmetry. This would indicate that there is no continuous transition from the tetragonal α_2 structure to the cubic fluorite structure as suggested in earlier studies of this system, and in Ref. (*5*), but that a two-phase region separates these two structure types.

Conclusion

The tetragonal structure reported for zirconia at 1200°C has been confirmed by neutron diffraction and it has been shown that this structure can accommodate a high degree of nonstoichiometry. This study does not agree in entirety with any of the previous three studies reported, and indicates that further studies are needed, preferably at temperature and with the accent on attaining true equilibrium. The cubic phase in this system contains a high degree of short-range order.

No evidence for long-range ordering within either the cation or anion sublattices was observable from analysis of the coherent Bragg scattering peaks in any of the samples studied, with the exception of the β-phase. However, extensive modulation of the neutron background indicated a considerable degree of short-range ordering to be present, the nature of which has not been determined.

It would seem that the technique described in this study could be also usefully employed to examine other zirconia-based phases, in particular the commercially important ZrO_2–CaO and ZrO_2–Y_2O_3 systems.

Acknowledgment

The members of the CSIRO involved in this study express their thanks to the Australian Atomic Energy Commision for the considerable help given, and in particular to Dr. M. Elcombe of that establishment. This work was initiated by the Engineering Ceramics and Refractories Section of the then Division of Applied Mineralogy, and completed while the authors were attached to the Engineering Ceramics and Refractories Laboratories of the Division of Tribophysics, CSIRO.

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