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Phase relationships in the zirconia–yttria system

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Metastable and equilibrium phase relationships in the system ZrO_2:$YO_{1.5}$ have been studied by X-ray diffraction. The conditions for the retention of a zirconia-rich tetragonal phase at ambient temperature are established. The existence of a miscibility gap, closed below the solidus temperature, in the yttria-rich solid solution region is proposed. Some evidence for partially ordered phases is presented.

1. Introduction

The first detailed study of the zirconia–yttria system was that of Duwez *et al.* [1]: this was followed by that of Fan *et al.* [2] which differed markedly from that of Duwez *et al.* and indicated the existence of a pyrochlore with the composition $Y_2Zr_2O_7$. Later Lefevre [3], in a detailed study of the zirconia rich region, reported the occurrence of a tetragonal phase stable at room temperature; this phase, not previously reported, has since been observed by others [4-6].

The liquidus has been determined by Rouanet [7] and Noguchi *et al.* [8] whose results are in good general agreement and who both found a eutectic point at about 87 mol% $YO_{1.5}$. (Compositions are expressed throughout in mol% yttria taken as $YO_{1.5}$.) An alternative version of the liquidus due to Skaggs *et al.* [9] has a peritectic point at 86 mol% $YO_{1.5}$.

A recent paper by Srivastava *et al.* [10] presents some new data on the zirconia–yttria system: it also includes a critical review of the literature and presents a modified phase diagram. However, it leaves certain discrepancies unresolved, and in particular it fails to account for the undoubted occurrence in the zirconia-rich region of a tetragonal phase at room temperature.

In view of the interest in yttria-stabilized zirconia as a high performance ceramic, it would be useful to resolve these ambiguities and this paper describes the results of X-ray diffraction studies on specimens prepared by various methods. Metastable as well as equilibrium states have been studied, and this has enabled some apparent inconsistencies in previously published work to be resolved. In the zirconia-rich region the equilibrium diagram presented differs only a little from that of Srivastava *et al.* [10] but the differences are critical in determining the conditions for the formation of a tetragonal phase at room temperature. In the yttria-rich region more extensive changes are proposed, including the introduction of a new miscibility gap in the yttria solid solution (type C rare earth oxide structure) region.

No extensive literature survey is included, since this has been adequately covered by Srivastava *et al.* [10], and references are restricted largely to work which is relevant to the differences between the conclusions of this paper and those of Srivastava *et al.* [10].

Because there are significant discrepancies between different studies it may be worth noting briefly the major problems associated with the determination of true equilibria in the zirconia–yttria system. At temperatures above 2000°C, direct studies of crystal structure are difficult, so that many X-ray studies have been carried out at room temperature on specimens cooled from a high temperature: unless this cooling is very rapid the compositions and proportions of the phases present may change during cooling. Even if quenching is sufficiently rapid to prevent compositional changes, structural changes may still occur and complicate the interpretation of the results. Pure zirconia has two structural transformations on cooling from its melting point, cubic to tetragonal at about 2340°C [7] and tetragonal to monoclinic at about 1170°C [10]; yttria transforms from hexagonal to cubic at about 2300°C on cooling [7, 11]. In the pure oxides, none of the high temperature phases can be retained by quenching to room temperature.

At low temperatures, below about 1200° C, the converse problem arises since cation diffusion becomes so slow that equilibrium is attained with difficulty, if at all. This is relevant to the interpretation of calorimetric studies which usually provide information about transitions between metastable rather than equilibrium states: nevertheless valuable inferences may be drawn from such data.

Finally, there is a difficulty associated with the existence of metastable states. Even at temperatures high enough to ensure substantial cation mobility, the phases observed may depend on the choice of starting material if there is an energy barrier to mixing or unmixing. Only if identical results are obtained with initially homogeneous materials (e.g. co-precipitates, quenched melts) and initially inhomogeneous materials (e.g. physically mixed oxides) can equilibrium be regarded as proven. For practical reasons less rigorous standards are often adopted.

2. Experimental technique

2.1. Materials

The materials used were zirconium dioxide (Ugine Kuhlmann, hafnium free, > 99.9%), yttrium oxide (Rare Earth Division: American Potash and Chemical Corporation, > 99.9%: Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3 < 0.1% total) and "zirconium carbonate" paste (Magnesium Elektron Ltd, HfO_2 ca. 2 wt %, Y_2O_3 < 0.01 wt % in ZrO_2). The zirconium carbonate was dissolved in analytical grade nitric acid to provide zirconyl nitrate solution for coprecipitation.

2.2. Sample preparation

Mixed oxide samples were prepared by grinding the components together in an agate mortar followed by pelleting in a steel die: the pellets were then heat-treated in a furnace at the required temperature, or melted in argon using an electric arc furnace with a water-cooled copper hearth. Arc-melted samples were black due to oxygen deficiency but annealing for a few hours in air at 1000° C restored the normal colour: no differences were found between annealed arc-melted samples and some melted in air in a solar furnace. Melts typically had a mass of 0.25 g and were cooled to 700° C in 15 sec: thus the average cooling rate is about 100° C sec^{-1} but in the critical high temperature range the cooling rate could be close to 1000° C sec^{-1}.

Co-precipitates were prepared by stirring mixed zirconyl nitrate and yttrium nitrate (yttrium oxide dissolved in nitric acid) solutions into aqueous ammonia. The precipitates were washed, dried, and calcined for 24 h at 1200° C before being subjected to any further heat-treatment.

Heat-treatments up to 1700° C were carried out in air, using a globar furnace up to 1400° C and a molybdenum wound furnace with protected windings above that temperature. A few high temperature treatments at 2000° C utilized a specially designed gas fired furnace which permitted samples to be quenched into brine with a quenching time of about 5 sec.

2.3. X-ray studies

The phases present at room temperature were determined using a Guinier-Hagg focusing camera with Cu$K\alpha$ radiation. To enable accurate lattice parameters to be determined some thoria was included in each specimen as a standard. (The lattice parameter of the thoria had been accurately determined as 5.5972 ± 0.0001 Å at 26° C, relative to Cu$K\alpha_1$ = 1.540 51 Å, using a 19 cm powder camera). The parameters determined with the Guinier camera typically had estimated standard deviations of 0.01%. Some studies of partial ordering were made on single crystals using the Weissenberg and back-reflection Laue techniques.

3. Results

3.1. Homogeneous phases

Homogeneous zirconia–yttria mixtures were prepared by co-precipitation with no heat-treatment after calcination at 1200° C, and by arc melting followed by rapid quenching. These are, in general, metastable rather than equilibrium phases, but a knowledge of the room temperature structures and lattice parameters is necessary to interpret the results obtained after high temperature equilibration.

Samples in the range pure zirconia to 3 mol% $YO_{1.5}$ were monoclinic. The lattice parameters for 3 mol% $YO_{1.5}$ were a = 5.159 Å, b = 5.211 Å, c = 5.321 Å and β = 99.16°, compared to a = 5.147 Å, b = 5.206 Å, c = 5.135 Å and β = 99.23° measured for pure zirconia. The volume increase in 3 mol% $YO_{1.5}$ is thus about 0.5%.

4 and 5 mol% $YO_{1.5}$ could not be prepared in homogeneous form and were invariably a mixture of monoclinic and tetragonal phases. The proportions of the two phases were rather variable: this may arise from sample inhomo-

geneity which is quite likely in the arc-melted specimens, or alternatively grain size may influence structure in this transitional region.

From 6 to 11 mol% $YO_{1.5}$ the structure was tetragonal, while from 12 to 13 mol% $YO_{1.5}$ there was a second ambiguous range in which specimens could be tetragonal, face centred cubic (fluorite structure), or (rarely) a mixture of the two. Arc-melted samples were generally tetragonal, initially, but those with compositions of 12 and 13 mol% $YO_{1.5}$ transformed completely to cubic after annealing at 1600°C for 7 days, without any detectable separation of a second phase. This suggests that physical factors such as strain or grain size may influence the compositional range of the tetragonal phase. The lattice parameters for the tetragonal samples, and some low yttria cubic samples, are shown in Fig. 1a: the data of Lefevre [3] are included for comparison and the agreement is excellent.

Electron micrographs of tetragonal crystals showed these to be multiply twinned on a scale of a few hundred Ångstroms. The crystallite axes were parallel to the axes of the parent fluorite matrix from which the tetragonal grains are considered to develop by a diffusionless transformation. Electron diffraction patterns were consistent with the tetragonal phase having the structure of pure zirconia at 1250°C determined by Teufer [12], but because of the twinning it was not possible to establish this relationship unequivocally. While it is probable that the tetragonal phase has the Teufer structure the lattice parameters in this paper refer to a non-primitive cell used by Ruff and Ebert [13] and Lefevre [3] which has twice the volume of Teufer's primitive cell: this choice emphasizes the relationship between the tetragonal and fluorite structures.

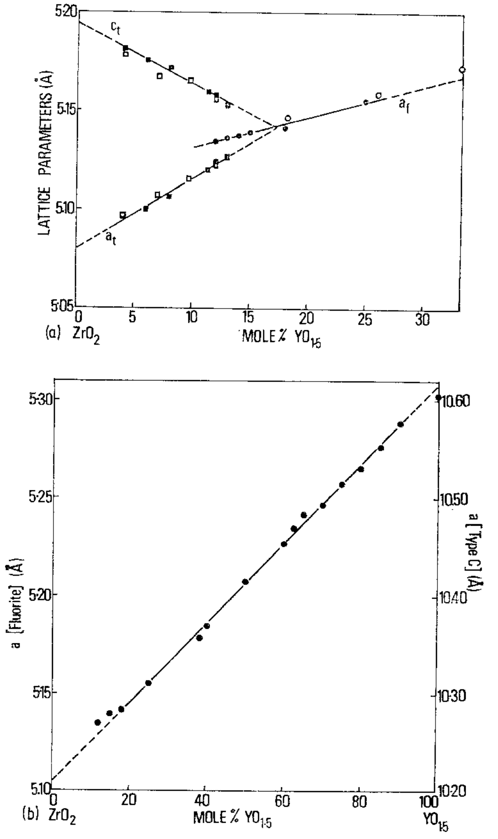

Figure 1 Lattice parameters at room temperature for homogeneous zirconia–yttria phases. (a) 0 to 33 mol % $YO_{1.5}$, (b) 12 to 100 mol % $YO_{1.5}$. ■, □ tetragonal ●, ○ cubic: open symbols from data of Lefevre [3].

All specimens containing more than 13 mol% $YO_{1.5}$ were cubic, but there was an apparently continuous transition from the fluorite structure at low yttria content to the type C rare earth oxide structure (i.e. the yttria structure) at high yttria content, with a consequent doubling of the lattice parameter. For the co-precipitated samples this transition is indicated by the appearance in the X-ray diffraction patterns of very weak lines characteristic of the type C structure which increase in intensity as the yttria content is increased. These additional lines are quite sharp and the lattice parameter determined from them which varies linearly with composition is within experimental error twice that of the fluorite cell.

With arc-melted samples, the continuous transition is less certain. Weak diffuse type C lines are apparent in Guinier photographs of 62.5 and 65 mol% $YO_{1.5}$ samples, and from 70 mol% $YO_{1.5}$ upwards these lines are sharp enough to measure reliably. For both the 70 and 75 mol% $YO_{1.5}$ compositions there were small but significant discrepancies between the parameters of the fluorite cells, and those of the fluorite sub-cells of the type C phase: these discrepancies were not sufficient to cause observable splitting of those reflections which are common to both the fluorite and type C structures. Electron diffraction studies confirm that these samples are not truly homogeneous. Fig. 2 is a dark-field electron micrograph imaged with a type C non-fluorite reflection; the light regions have the type C structure and are embedded in a coherent matrix of fluorite type material. This inhomogeneity may arise from slight compositional fluctuations which are

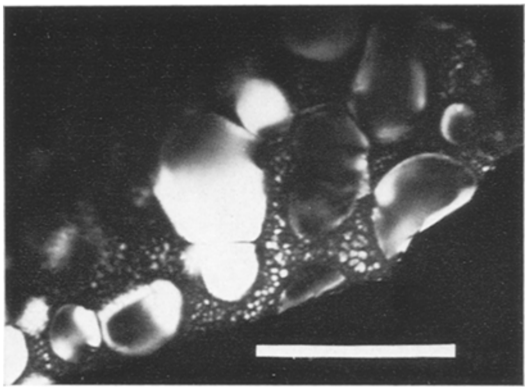

Figure 2 Dark-field electron micrograph of 75 mol% $YO_{1.5}$ arc melted and quenched, imaged with type C reflection. Light regions have the type C rare earth oxide structure, and are embedded in a coherent fluorite type matrix. Bar indicates 1 μm.

difficult to avoid in specimens quenched from the melt.

Arc-melted samples with compositions around 85 mol% $YO_{1.5}$ also tended to segregate into two phases, but in this case the two phases both had the type C structure. This point will be discussed in more detail in a subsequent section.

The lattice parameters for the cubic solid solutions are presented in Fig. 1b. The parameter for the fluorite cell, or sub-cell for the type C structure, can be expressed as

$$a(\text{Å}) = 5.104 + 0.204x, \text{ for } 0.18 < x < 0.90$$

where x is the mole fraction of $YO_{1.5}$ in ZrO_2. There is generally good agreement between these results and the data of Lefevre [3], Rouanet [7], Noguchi *et al.* [8] and Steele and Fender [14]. By comparison the parameters determined by Duwez *et al.* [1] for the fluorite solid solution range appear consistently low.

3.2. Equilibrium phases: the zirconia-rich region

Samples containing from 3 to 25 mol% $YO_{1.5}$ were prepared by arc melting, by co-precipitation and by sintering of the mixed oxides. These were heat-treated for 4 weeks at 1400°C, 1 week at 1600°C, 2 days at 1700°C or 2 h at 2000°C. Identical results were obtained with co-precipitates and mixed oxides after these times, indicating that equilibrium was established. Arc melted samples were considerably less reactive and transformed so slowly that even after grinding and heating equilibrium was not generally attained. Except for the 2000°C specimens which were rapidly quenched, specimens were cooled in the furnace at 200°C h^{-1} to 1400°C and then withdrawn.

At room temperature samples containing more than 15 mol% $YO_{1.5}$ were single phase with the fluorite structure. Samples with less yttria were two phase: one phase was monoclinic with the baddelyite structure (i.e. the low temperature zirconia structure) while the other was either fluorite or tetragonal, depending on the equilibration temperature. The proportions of the phases depended on composition but the lattice parameters depended only on the equilibration temperature. By determining the lattice parameters of the cubic or tetragonal phase and comparing these with those obtained with homogeneous samples (Fig. 1a) the lower limit of the fluorite solid solution has been determined quite accurately at 1400, 1600 and 2000°C. The upper limit of composition of the tetragonal solid solution (which becomes monoclinic at room temperature) has been estimated from the proportion of monoclinic to cubic or tetragonal. The phases found (at room temperature) and the boundaries determined are illustrated in Fig. 3.

It must be stressed that the structures recorded at room temperature are not in general those existing at the equilibration temperature. Consider, for example, samples containing 6 mol% $YO_{1.5}$ equilibrated at various temperatures and then quenched to room temperature sufficiently rapidly to prevent cation diffusion. Above about 2200°C such a sample will be single phase with the fluorite structure, and on quenching will undergo a diffusionless transformation to a multiply twinned tetragonal phase. At 2000°C the equilibrium is a two-phase mixture of tetragonal solid solution containing about 2 mol% $YO_{1.5}$ and fluorite solid solution containing about 8 mol% $YO_{1.5}$; when this is quenched the tetragonal phase transforms to monoclinic and the fluorite phase to tetragonal. At 1400°C the equilibrium is again two phase with a tetragonal phase containing about 4 mol% $YO_{1.5}$ and a fluorite phase containing about 14 mol% $YO_{1.5}$; on quenching the tetragonal phase transforms to monoclinic but the fluorite phase now contains sufficient yttria to retain that structure at room temperature and does not undergo any transformation.

3.3. Equilibrium phases: the yttria-rich region

Samples containing from 70 to 90% mol

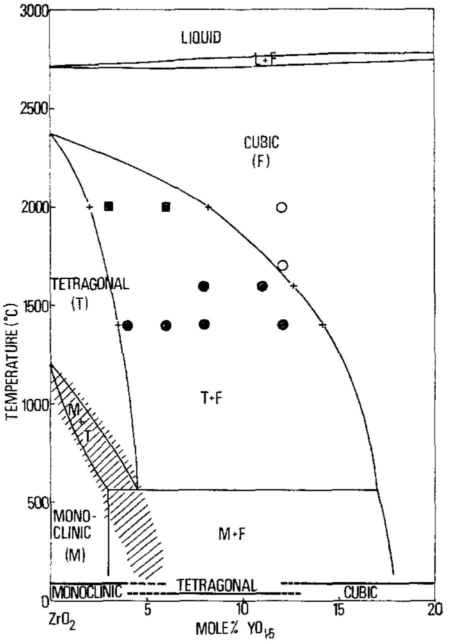

Figure 3 Phase diagram for the zirconia rich portion of the zirconia–yttria system. Non-equilibrium homogeneous phases are indicated at lower margin. Phases found at room temperature are indicated thus: △ monoclinic, □ tetragonal, ○ cubic, ■ monoclinic + tetragonal, ● monoclinic + cubic. Hatched region indicates non-equilibrium monoclinic-tetragonal transition.

$YO_{1.5}$ prepared by arc melting, co-precipitation or sintering of the mixed oxides were heat-treated at 1600°C for one week. The phases present at room temperature and their lattice parameters are shown in Table I. It will be seen that there are discrepancies between samples prepared in different ways showing that true equilibrium was not established. Nevertheless, tentative conclusions may be drawn which suggest that the phase relationships in this region may be more complicated than was indicated by Duwez *et al.* [1].

The most significant feature of Table I is that it indicates the existence of two type C phases with slightly different lattice parameters. This was particularly clear in the arc-melted 85 mol% $YO_{1.5}$ in which every line of the type C pattern appeared as a clearly resolved doublet. Also since the relative intensity of the components of each doublet was the same for all reflections both phases must have the same structure. Since zirconium and yttrium have almost identical X-ray scattering factors, cation order cannot easily be detected in this system by X-ray methods so that one of the type C phases could be cation ordered, and this is theoretically possible at the composition 75 mol% $YO_{1.5}$. However, an arc-melted sample of hafnia: 85 mol% yttria gave a virtually indistinguishable pattern of doublets and in this system cation ordering would cause significant intensity changes. Thus it seems probable that the two type C phases differ only in composition.

It is not clear whether this miscibility gap corresponds to equilibrium since the co-

TABLE I Phases present at 1600°C in zirconia–yttria

Composition (mol % $YO_{1.5}$)	Sample	Phases	Lattice parameters (Å)		
			F	½ C′	½ C
70	a.m.	F + C′	5.2419	5.2589	
	m.o.	F + C′/C	5.2391		5.2797*
75	a.m.	F(v.w.) + C′	not measured	5.2579	
	co-ppt.	F + C′	5.2396	5.2619	
80	a.m.	C′ + C(w.)		5.2657	not measured
	m.o.	F + C′/C	5.2372		5.2782*
	co-ppt.	F(v.w.) + C′	not measured	5.2651	
85	a.m.	C′ + C		5.2664	5.2875
	m.o.	F(v.w.) + C	5.2365		5.2850
	co-ppt.	C/C′			5.2742
90	a.m.	C			5.2882

a.m. = arc melted; m.o. = mixed oxides; co-ppt. = co-precipitates; F = fluorite; C′ = type C "small" cell; C = type C; w. = weak; v.w. = very weak.

*Denotes a broad set of reflections, possibly doublets arising from unresolved C′ and C.

precipitated sample of 85 mol% $YO_{1.5}$ gave a sharp diffraction pattern and had a lattice parameter intermediate between that of C and C′, where C′ designates the type C phase with the smaller parameter. In the mixed oxides with compositions 70 and 80 mol% $YO_{1.5}$ the type C lines were unusually broad with square rather than Gaussian profiles, which suggest unresolved doublets.

When heat-treated samples of arc-melted and mixed-oxide samples were ground together and annealed for a further week at 1600°C the resultant material contained all three phases F, C′ and C. Since cation diffusion is quite rapid under these conditions it seems that there may be some potential barrier to equilibrium. Further work on this aspect of the zirconia-yttria system is in progress.

On the basis of the lattice parameters in Table I it is proposed that at 1600°C the fluorite solid solution extends from 13 to 66 mol% $YO_{1.5}$ and the two phase F + C′ region runs from 66 to 77 mol% $YO_{1.5}$. There is then a narrow single phase C′ region followed by a two phase C + C′ region from 79 to 90 mol% $YO_{1.5}$. Above 90 mol% $YO_{1.5}$ the system has a single phase solid solution of zirconia in yttria. Since there is no structural difference between C′ and C, and little size difference it seems likely that the C′ + C region does not extend to the solidus. Fig. 4 which embodies these results shows the proposed phase diagram for the yttria-rich region of the zirconia–yttria system.

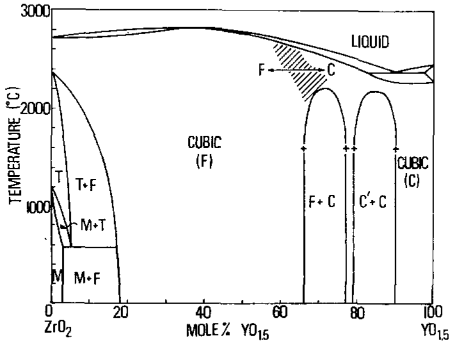

Figure 4 Phase diagram for the zirconia–yttria system. Hatched region represents the apparently continuous fluorite-type C transition.

3.4. Ordered phases

It was noted above that X-ray powder patterns of 62.5 mol% $YO_{1.5}$ showed diffuse type C reflections. Fig. 5a is a back-reflection Laue photograph of an arc melted single crystal of this composition: the prominent diffuse reflections can be indexed in terms of the type C structure. This was confirmed by Weissenberg photographs which showed sharp fluorite and diffuse type C reflections.

Corresponding patterns from 50 and 25 mol% $YO_{1.5}$ are shown in Fig. 5b and c but now the diffuse intensity cannot be so easily explained. The inner ring of three pairs of diffuse reflections in Fig. 5b corresponds to a much larger unit cell than would arise from either type C or pyrochlore ordering. The 25 mol% $YO_{1.5}$ pattern is similar to that from ZrO_2: 17 mol% CaO shown in Fig. 5d, and the diffuse intensity in the latter system, arises from domains of ϕ_1 ordering, where ϕ_1 has a large monoclinic cell with composition $CaZr_4O_9$ [15].

Attempts to increase the degree of order by heat-treatment at a variety of temperatures failed. However, the clear evidence for short range order suggests that ordered phases should exist but may only be stable at low temperatures where low cation mobility impedes their formation.

4. Discussion

4.1. The liquidus

Studies by Rouanet [7] and Noguchi *et al.* [8] indicate that as the yttria content increases the liquidus temperature of a binary mixture initially rises slightly reaching a rather flat maximum at about 40 mol% $YO_{1.5}$ and then falls to a eutectic point at 90 mol% $YO_{1.5}$. This eutectic is associated with the cubic to hexagonal transition which occurs in yttria at 2300°C [11]. Anomalies found by Noguchi *et al.* in the zirconia-rich region are comparable with their estimated errors and may perhaps be disregarded. Liquidus measurements on the analogous systems ZrO_2:Er_2O_3 [7], ZrO_2:Yb_2O_3 [7], HfO_2:Er_2O_3 [16] and HfO_2:Y_2O_3 [17] are all remarkably similar in general form and all show a eutectic point at about 90 mol% rare earth oxide.

The one divergent report is that of Skaggs *et al.* [9] who found a peritectic in the zirconia–yttria system. In the absence of any supporting evidence for the peritectic, it seems preferable to adopt the eutectic endorsed by the bulk of the work in this field. The phase diagrams in Figs. 3 and 4, therefore, utilize the results of Rouanet

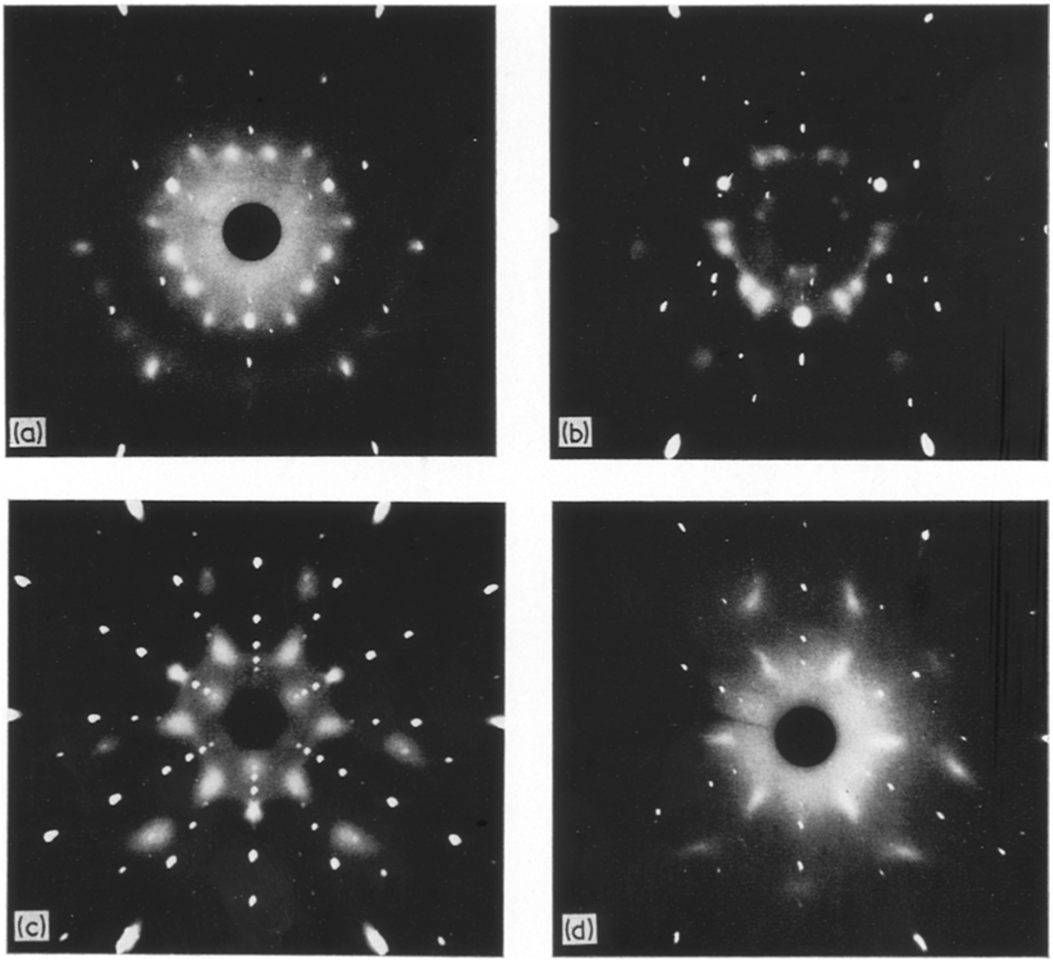

Figure 5 Back-reflection Laue photographs normal to [111]. Unfiltered Cu radiation at 17 kV. (a) ZrO_2:62.5 mol% $YO_{1.5}$. (b) ZrO_2:50 mol% $YO_{1.5}$. (c) ZrO_2:25 mol% $YO_{1.5}$. (d) $ZrO_2$17 mol% CaO.

for the liquidus. Since the eutectic is associated with a phase change in pure yttria the form of the liquidus provides no evidence for any miscibility gaps extending to the solidus, rather it implies a continuous transition from fluorite to type C at high temperature.

4.2. The zirconia-rich region

The phase diagram proposed for this region (Fig. 3) is based on the experimental results described in this paper, together with the accepted monoclinic to tetragonal and tetragonal to cubic (fluorite) transitions in pure zirconia. The form of the liquidus indicates that the fluorite solid solution range is continuous at sufficiently high temperatures in this region. Calorimetric [5, 10], dilatometric [1] and X-ray data [10] all show that the monoclinic to tetragonal transition temperature is progressively lowered relative to that in pure zirconia by the addition of up to about 5 mol% $YO_{1.5}$.

Srivastava *et al.* [10] state that there is a eutectoid transformation at about 565° C and 7.5 mol% $YO_{1.5}$. Since it is virtually impossible to establish equilibrium in this system at so low a temperature this conclusion is dubious; nevertheless, it is difficult to construct a plausible diagram which does not have a eutectoid in this vicinity. Consequently, the proposed diagram agrees substantially with that of Srivastava *et al.* [10] except that the lower limit of fluorite solid solution is more precisely determined and shown to vary significantly with temperature between 1400 and 2000° C. This variation was not observed by Srivastava *et al.* [10] or Duwez *et al.* [1] since their cooling rates from 2000° C were too slow to retain the high temperature equilibrium. An important conclusion from this variation is that fluorite solid solutions with compositions in the range 6 to 12 mol% $YO_{1.5}$ can be prepared at temperatures above 2200 to 1700° C which if cooled rapidly will be tetragonal at room temperature. Slow cooling results initially in the separation of tetragonal and cubic phases, and the tetragonal phase transforms to monoclinic at a lower temperature. Thus the tetragonal phase, which is essentially metastable, is observed only on rapid cooling from high temperatures [3, 18].

4.3. The yttria-rich region

The diagram presented in Fig. 4 includes a miscibility gap in the type C yttria solid solution which has not be observed previously. However, the lattice parameters reported by Noguchi *et al.* [8] for the two phases present in 82.4 mol% $YO_{1.5}$ quenched from the melt, 5.260 Å and 10.555 Å, could correspond to an incompletely resolved mixture of two type C phases, rather than a mixture of fluorite and type C phases as they suggest.

It is emphasized that this new miscibility gap is tentative since it may be a metastable rather than an equilibrium feature. Similar gaps in type C regions have been found by Perez y Jorba in the ZrO_2:Gd_2O_3 and ZrO_2:Dy_2O_3 systems [19].

The miscibility gap between the fluorite and type C phases is well established. Its upper limit has been adjusted relative to that of Duwez *et al.* [1] to allow for the insertion of the C′-C region.

Both gaps have been closed below the solidus temperature since the form of the liquidus adopted gives no grounds for doing otherwise. Against this, it is observed that specimens cooled from the melt do show some segregation into F + C′ and into C′ + C but this may occur at sub-solidus temperatures and arise from inadequate quenching. Rouanet [7] for example did not observe segregation, and Perez y Jorba likewise reports a continuous F to C transition in ZrO_2:Gd_2O_3 and ZrO_2:Dy_2O_3 co-precipitated samples quenched from 2000° C [19].

4.4. Ordered phases

There is no unequivocal evidence for any ordered phase in the zirconia-yttria system. Fan *et al.* [2] found X-ray diffraction evidence for a pyrochlore, $Y_2Zr_2O_7$, but this work has been comprehensively criticized by Smith [20] who used neutron diffraction, which is much more sensitive to cation ordering in this system, and found no sign of pyrochlore ordering. An attempt by Barker [21] to form a pyrochlore by extended annealing at 950° C also failed. Dulcot *et al.* [22] have reported an ordered structure with the composition $Y_2Hf_7O_{17}$ in the hafnia–yttria system: its structure was not determined, however, and there is as yet no evidence for an analogous phase in zirconia–yttria.

Nevertheless, the well-defined diffuse reflections obtained from samples in the fluorite solid solution composition range (Fig. 5b and c), is clearly indicative of short or medium range order. Therefore, it seems likely that ordered phases will be discovered in the zirconia–yttria system when the correct conditions of time, temperature and composition are established.

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