

# Phase relationships in the yttria-rich part of the yttria-zirconia system

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Phase equilibria in yttria-zirconia mixtures containing not less than 50 mol %  $YO_{1.5}$  have been studied between 1200 and 2200° C. The solubility of zirconia in yttria is shown to decrease with increasing temperature: the miscibility gap between the zirconia (fluorite) and yttria (type C rare earth) solid solutions extends from 64 to 75 mol %  $YO_{1.5}$  at 1400° C, from 66 to 79% at 1700° C and from 73 to 85% at 2000° C. An ordered fluorite-related phase with the ideal formula  $Zr_3Y_4O_{12}$  and a narrow homogeneity range, which disorders at about 1370° C, is reported.

## 1. Introduction

There have been a number of studies of the yttria-zirconia system since the pioneering work of Duwez *et al.* [1], one of the most recent being that of Srivastava *et al.* [2] which included a critical review of the previous work on the system. Except for that of Duwez *et al.*, work on sub-solidus equilibria has concentrated on the zirconia-rich region as yttria-stabilized zirconia is a commercially significant material both as a refractory and as a solid electrolyte.

A previous paper by the present author [3] reported principally on the zirconia-rich region, but included some data on the yttria-rich region also. In particular it was noted that under certain conditions two type C rare earth (i.e. yttria solid solution) phases co-existed, suggesting that there was a miscibility gap in the yttria solid solution region: such gaps have been reported by Perez y Jorba [4] in several zirconia-rare earth oxide systems. However, the evidence for the gap was not wholly consistent so that it was suggested that this might be a metastable configuration.

This paper describes experiments on yttria-rich yttria-zirconia mixtures, using both mixed oxides and co-precipitates to establish that equilibrium was attained, and employing rapid cooling from high temperatures in an attempt to retain that equilibrium. Experimentally it was not possible to retain the equilibrium from 2200° C, the highest

temperature used, so that the results for that temperature are tentative.

A significant feature of the results obtained is the decrease in the solubility of zirconia in yttria as the temperature increases. This decrease enables the sub-solidus boundaries to be correlated with the liquidus measurements of Rouanet [5] in a satisfactory fashion without the need to invoke a continuous transition between the fluorite and type C solid solutions at high temperatures.

The miscibility gap in the type C region suggested by the co-existence of two type C phases has not been confirmed. However the co-existence of these phases can now be explained as a metastable state which occurs in samples initially treated at high temperatures, arising from the variation with temperature of the solubility of zirconia in yttria.

Finally, the existence of an ordered phase in the system, stable only below about 1370° C, has been established. This is not the pyrochlore sought unsuccessfully in this system [6, 7] and in yttria-hafnia [8], but is a  $\delta$ -phase with the ideal formula  $Zr_3Y_4O_{12}$  (57 mol %  $YO_{1.5}$ ) and a narrow homogeneity range.

## 2. Experimental technique

The general details of sample preparation, heating and X-ray diffraction analysis have been described in a previous paper [3].

The compositions studied in the work described here ranged from 65 to 90 mol% yttria (as  $YO_{1.5}$ ) by steps of 5 mol%, together with 50 and 57.14 mol% for low temperature ordering experiments. Experiments in 1400, 1700 and 2000°C were performed with both mixed oxide and co-precipitated samples: unless otherwise noted the remaining experiments utilized mixed oxides only.

The samples were held at the required temperature for long enough to establish equilibrium and then withdrawn from the furnace as quickly as possible and allowed to cool to room temperature before being examined by X-ray diffraction. Heating at 1950°C and above was carried out in a special gas furnace which enabled the samples to be quenched in cold water within a few seconds of leaving the hot zone: to avoid contamination the samples were totally enclosed during heating in a cell of zirconia-80 mol% yttria, constructed to disintegrate on quenching. The heating times were about 4 weeks at 1400°C, 2 days at 1700°C, 4 h at 1950 and 2000°C and 2 h at 2200°C.

The phases present at room temperature and their lattice parameters were determined using a Guinier camera with thoria ( $a = 5.5972 \text{ \AA}$ ) as an internal standard. Statistical analysis of many measurements indicated that when only a single, well crystallized phase was present the accuracy of parameter determination was about 0.01%. In the two-phase samples, where the individual patterns were often less sharp and the parameters were dependent on equilibration temperature, the accuracy was rather less, typically about 0.03%.

Regression analysis of all the available data on single-phase samples, including some used in the previous work [3], indicated that the lattice parameter of the fluorite solid solutions and of the fluorite sub-cell in the type C (i.e. yttria) solid solutions could be related to the composition by one of the following expressions,

$$a(\text{\AA}) = 5.096 + 0.221x \quad 0.40 \leq x < 0.65$$

or

$$a(\text{\AA}) = 5.125 + 0.176x \quad 0.65 \leq x \leq 0.90$$

where  $x$  is the mole fraction of  $YO_{1.5}$ . These relations were then used to determine the composition of the individual phases in the two-phase samples. It may be noted that the lattice parameter of 90 mol% yttria, the only composition which was single phase at all the temperatures

used, was independent of equilibration temperature from 1400 to 2200°C.

### 3. Results

Three distinct phases were found in this system. Two are solid solutions with extensive stability fields; one is a solution of yttria in zirconia and has the fluorite structure, and the other, a solution of zirconia in yttria, has the type C rare earth oxide structure. The third phase is a compound with the formula  $Zr_3Y_4O_{12}$  and is stable only at low temperature. The relationships between these phases are shown in Fig. 1.

#### 3.1. Equilibrium between 1400 and 2000°C

Samples equilibrated at 1400, 1700, 1950 and 2000°C were examined by X-ray diffraction. The

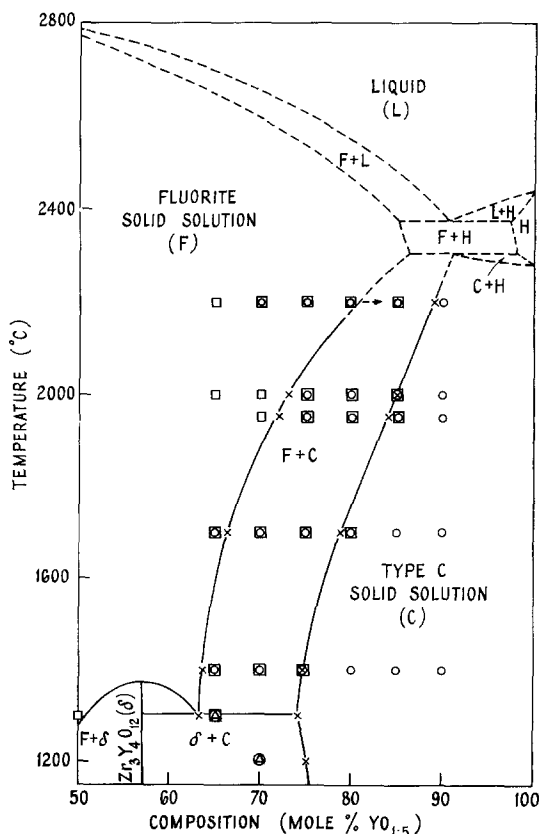


Figure 1 Phase diagram of the yttria-rich yttria-zirconia system. Phases present at room temperature: □ fluorite solid solution; ○ type C solid solution; △  $\delta$ -phase  $Zr_3Y_4O_{12}$ ; (combinations of symbols indicate multi-phase samples). × limits of solid solubility derived from lattice parameters. Boundaries above 2200°C after Rouanet [5].

phases found and their lattice parameters, which are the mean values from mixed oxide and co-precipitated samples, are set out in Table I. There were no significant differences between the two types of sample, which is evidence that equilibrium was attained. In the two-phase samples the parameters depend on the limits of the two-phase field, and hence on the equilibration temperature, but not on the overall composition. The mean values of the limiting parameters at each temperature, together with the compositions deduced therefrom, are shown in the lower part of Table I.

In general there was good agreement between the extent of the two-phase field deduced from the lattice parameters and the phases actually observed. There were minor discrepancies, particularly at 1700°C, where two phases were found in samples which should have been single phase on the basis of the lattice parameter measurements. However, in each case the minor phase was present only in small amount, and the assumption of a linear relationship between parameter and composition is an approximation, so that these discrepancies are not considered significant. The results with the 85 mol% yttria samples at 1950 and 2000°C were more anomalous, as the lattice parameters indicated a more yttria-rich upper limit to the two-phase field than that derived from the 75 and 80 mol% samples. This anomaly, while not large, occurred with mixed oxides and co-precipitates, was apparently reproducible and is

outside the probable limits of experimental error. It is possible, therefore, that at these high temperatures the equilibrium phases were not completely retained on quenching.

### 3.2. Experiments at 2200°C

Two batches of samples were equilibrated at 2200°C. Although the samples weighed only about 150 mg each and were apparently well quenched the subsequent X-ray analysis showed that the high temperature equilibrium was not retained. The phases present, their measured lattice parameters and estimated compositions are shown in Table II. The values are the mean of the two batches which differed only slightly.

The patterns from the 90 mol% yttria were very sharp and corresponded to type C only, which suggests that this composition is single phase at 2200°C and at temperatures immediately below this, since there was no sign of segregation during cooling. The samples containing from 70 to 85 mol% yttria showed separation into fluorite and type C phases, but the parameters of these phases varied with overall sample composition which indicates clearly that equilibrium was not retained on quenching.

Some conclusions may be drawn however. The presence in the 85 mol% sample of a type C phase containing 89 mol% yttria indicates that the upper limit of the two phase field in the vicinity of 2200°C is not less than 89 mol% yttria. Taken in

TABLE I Phases present, lattice parameters (Å) and miscibility gap in yttria-rich yttria-zirconia mixtures

Composition (mol % YO <sub>1.5</sub> )	Equilibration temperature (°C)							
	1400		1700		1950		2000	
	Fluorite	Type C	Fluorite	Type C	Fluorite	Type C	Fluorite	Type C
65	5.237	5.255	5.242	5.262			5.241	Not present
70	5.237	5.257	5.242	5.262	5.247	Not present	5.247	Not present
75	5.238	5.258	5.243	5.264	5.252	5.272	5.252	5.272
80	Not present	5.265	5.241	5.266	5.252	5.272	5.253	5.273
85	Not present	5.275	Not present	5.274	Very weak	5.275	5.255	5.279
90	Not present	5.284	Not present	5.284	Not present	5.284	Not present	5.284
<i>Limits of two-phase field</i>								
Parameter	5.237	5.257	5.242	5.264	5.252	5.273	5.254	5.275
Composition	64%	75%	66%	79%	72%	84%	73%	85%

Note: lattice parameters for the type C solid solutions are quoted in terms of the fluorite sub-cell, i.e. half the true lattice parameter.

TABLE II Phases, lattice parameters and compositions in samples quenched from 2200° C

Overall composition (mol% YO <sub>1.5</sub> )	Fluorite		Type C	
	Parameter (Å)	Composition (mol% YO <sub>1.5</sub> )	Parameter (Å)	Composition (mol% YO <sub>1.5</sub> )
65	5.242	66	Not present	
70	5.248	70	Diffuse	
75	5.256	75	5.266	80
80	Diffuse		5.272	84
85	Very diffuse		5.282	89
90	Not present		5.284	90

conjunction with the observation that 90 mol% lies in the single-phase region, this defines the upper limit of the two-phase field tolerably well.

The lower limit of the two-phase field is much less certain. The type C phase in the 80 mol% sample contains about 84 mol% yttria, considerably less than the 89 mol% postulated above as the likely upper limit of the two-phase field at 2200° C, and slightly less even than the content at 2000° C, i.e. 85 mol% yttria. This suggests that this type C phase segregated during cooling and that at 2200° C 80 mol% may be single phase with the fluorite structure: similar considerations apply to the 75 mol% sample. However, this can hardly explain the presence of the type C phase in the 70 mol% sample since this composition was single-phase fluorite when quenched from 1950 and 2000° C. This may indicate small composition changes or sample inhomogeneity arising from differential evaporation or from solid state diffusion, so that the results at this temperature should be treated with caution. Nevertheless, it is tentatively concluded that the single-phase fluorite field extends to at least 80 mol% yttria at 2200° C.

### 3.3. Equilibrium below 1400° C

In an attempt to determine the extent of the miscibility gap at low temperatures, mixed oxide and co-precipitate samples containing 70 mol% yttria were heated at 1200° C for 4 months with grinding and pelleting at monthly intervals. Equilibrium was not achieved since at the end of that time the two samples gave different diffraction patterns of indifferent quality: for the mixed oxides the pattern indicated unreacted yttria together with a  $\delta$ -phase, while the co-precipitate contained a type C solid solution containing about 75 mol% yttria and the  $\delta$ -phase. In view of the greater reactivity

of co-precipitated samples the latter is more likely to indicate the true equilibrium.

The  $\delta$ -phase, a designation used originally by Lefèvre in his work on the zirconia-scandia system [9], has a rhombohedral fluorite-related structure with 1.75 fluorite sub-cells in the unit cell. It has the ideal formula  $M_7O_{12}$  and has been reported in many binary oxide and some more complex systems [10–12], but not previously in the zirconia-yttria system; its formula would be  $Zr_3Y_4O_{12}$  corresponding to an ideal composition of 57.14 mol% yttria.

It should be mentioned that, while the fluorite-related  $M_7O_{12}$  phase has usually been designated  $\delta$ , Hyde *et al.* [13] denoted this phase in the praseodymium-oxygen system by  $\iota$  and called  $Pr_{11}O_{20} \delta$ , so that confusion is possible.

To further investigate the conditions for the occurrence of the  $\delta$ -phase, mixed oxide samples containing 50, 57.14 and 65 mol% yttria were heated at 1300° C with monthly regrinding. After 3 months the 50 mol% samples were fluorite solid solution only and the 57.14 mol% sample was  $\delta$ -phase only. The 65 mol% sample was a mixture of fluorite solid solution containing 63 mol% yttria, type C solid solution containing 74 mol% yttria and the  $\delta$ -phase: these three phases continued to co-exist without perceptible change even after thorough regrinding under acetone and a further month at 1300° C. This implies that 1300° C is close to the temperature below which the fluorite solid solution decomposes into  $\delta$ -phase and type C solid solution: since the fluorite phase has a composition between those of the  $\delta$ -phase and the type C phase this decomposition is eutectoidal as indicated in Fig. 1.

By heating small samples of the  $\delta$ -phase to successively higher temperatures the transition to a disordered fluorite structure has been found to

occur between 1360 and 1380° C. At 1380° C disordering is quite slow and takes several weeks to reach completion.

The lattice parameters of the  $\delta$ -phase in the hexagonal representation were  $a = 9.7345 \text{ \AA}$  and  $c = 9.1092 \text{ \AA}$ . Furthermore, within experimental error, they were the same in the pure  $\delta$ -phase and in the 65 mol% mixture which suggests that  $Zr_3Y_4O_{12}$  may be a line compound, or has at most a narrow homogeneity range.

#### 4. Discussion

The conclusions from this work, illustrated in Fig. 1, which differ from those of previous studies are the marked variation with temperature of the position of the miscibility gap between the fluorite and type C phases, and the existence at low temperature of an ordered phase which is not a pyrochlore.

The solubility of zirconia in yttria decreases markedly with increasing temperature, from about 25 mol% at 1400° C to 15 mol% at 2000° C and perhaps as little as 11 mol% at 2200° C. This decrease is in contradiction to the work of Duwez *et al.* [1], and also with that of Stacy and Wilder [14] on the yttria-hafnia system which might be expected to be analogous. The miscibility gap reported by Duwez *et al.* at 2000° C, 72 to 87 mol% yttria when expressed at  $YO_{1.5}$ , is in fair agreement with that reported here, particularly when the difference in the cooling rates is considered. The major discrepancy is at lower temperatures, and it is considered that the work reported here, which utilized mixed oxides and coprecipitates and continued heat-treatments until both gave the same results, is more reliable.

Also the decreasing solubility of zirconia at higher temperatures appears to accord well with the very high temperature data of Rouanet [5] who reports a miscibility gap from 82 to 97 mol% yttria at the solidus temperature. The phase boundaries above 2200° C in Fig. 1 are based on Rouanet's work, slightly modified to conform with thermodynamic requirements if there is not to be a continuous transition between the fluorite and type C structures. Such continuous transitions may not be impossible but convincing examples are hard to find. It must be stressed though that the detail in this region is hypothetical only and, while it appears consistent with the experimental evidence, alternatives are possible.

Finally, the form of the miscibility gap shown in Fig. 1 explains the appearance under certain

conditions of two co-existing type C phases. This was reported previously [3] when arc-melted samples containing from 80 to 90 mol% yttria were annealed at 1600° C, although the possibility that this was a metastable situation was emphasized. When samples in this composition range are equilibrated at very high temperatures or are cooled rapidly from the melt there is a tendency for two phases to separate, one a type C phase containing say 90 mol% yttria and the other a fluorite phase containing say 80 mol% yttria. Rapid cooling inhibits cation diffusion, but anion diffusion continues so that the 80 mol% fluorite phase undergoes anion ordering and develops the type C structure also, as this composition is in the type C field at room temperature. Because arc-melted samples are relatively stable unless they are exceptionally well ground and annealed, the main effect of moderate annealing times at 1600° C is to improve the crystallinity and make the two type C phases more readily detectable.

The ordered phase,  $Zr_3Y_4O_{12}$ , formed slowly at both 1200 and 1300° C, but Rossell [15] has not been able to prepare the phase consistently under apparently similar conditions: this discrepancy is not understood. The  $\delta$  structure appeared to be stable up to 1360° C, but as the disordering is very sluggish the true transition temperature could be lower than that indicated. In material which was yttria-rich relative to the ideal  $\delta$  composition, the  $\delta$ -phase was in equilibrium with type C solid solution of zirconia in yttria. Since the  $\delta$ -phase composition lies in the metastable continuation of the fluorite solution field there must be a eutectoid of the general form shown.

The existence of an ordered phase in this system had been postulated previously on the basis of certain diffuse reflections in back-reflection Laue photographs from arc-melted specimens [3]. However, until the detailed structure of  $Zr_3Y_4O_{12}$  is determined it is not possible to say whether this phase adequately explains the observed diffuse reflections. Indeed there is some evidence that the  $\delta$ -phase does not account for the diffuse scattering observed in electron diffraction [15], so that other ordered phases may still remain to be discovered.

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