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On the continuous transition between two structure types in the zirconia — gadolinia system

A continuous transition between the fluorite and type C rare earth oxide structures at high temperature has been reported by Perez y Jorba *et al.* [1, 2] in the systems ZrO_2 with Gd_2O_3, Dy_2O_3 and Yb_2O_3. At low temperatures there was a miscibility gap between the fluorite and type C phases, while at intermediate temperatures two type C phases coexisted. Similar results were reported in the $ZrO_2-Y_2O_3$ system [3], but these were later shown to be artefacts arising from imperfect equilibration [4]. The continuous structural transition has also been observed directly by Rouanet using high temperature X-ray diffractometry in the systems ZrO_2 with Y_2O_3, Er_2O_3 or Yb_2O_3 [5].

Since a continuous change of equilibrium structure with composition or temperature would be of theoretical interest, it was decided to re-examine one of the cases cited above. The $ZrO_2-Gd_2O_3$ system was selected as it is well documented, and the relevant regions of the phase diagram are readily accessible experimentally.

The general techniques used have been described previously [3, 4]. Oxides of 99.9% purity were used, and samples were prepared by mixing the oxides, by arc melting mixed oxides, and by coprecipitation. Pellets weighing about 250 mg were equilibrated in air for 2 weeks at 1450° C or for 4 days at 1650° C, or in a gas-fired furnace for 5 h at 1850° C; they were then removed quickly from the furnaces.

A single composition was studied, ZrO_2 :80 mol $\% GdO_{1.5}$, since this should exhibit the three regimes indicated by Perez y Jorba *et al.* at 1450, 1650 and 1850° C respectively. In fact, X-ray diffraction patterns recorded with a Guinier camera using both Cu and CrKα₁ radiations, the latter to avoid GdL fluorescence, showed that all the samples were essentially mixtures of fluorite and type C phases. In general the patterns were very sharp, indicating little if any phase separation during cooling. However the samples equilibrated at 1850° C did show, in addition to the sharp fluorite and type C reflections, some weak, diffuse reflections corresponding to a second type C phase, and also contained a trace of $B-Gd_2O_3$ phase.

The lattice parameters and estimated compositions of the major phases found are given in Table I: There were no significant variations attributable to the different initial sample preparations so that the values are the means for the three types. Compositions were estimated by linear interpolation between the cell volumes of the pure components as proposed by Zen [6] for example. This was justified here by measurements on 70 and 90 mol $\% GdO_{1.5}$ samples, which were single phase fluorite and type C respectively: In both cases the difference between the nominal and estimated compositions was less than 0.5 mol %.

The limits of the two phase field based on these results are shown in Fig. 1, which also indicates

TABLE I Phase data determined at room temperature for ZrO_2 : 80 mol $\% GdO_{1.5}$ equilibrated at high temperature

Equilibrium temperature (° C)	Lattice parameter (Å)		Composition (mol $\% GdO_{1.5}$)	
	Fluorite	Type C*	Fluorite	Type C
1450	5.322	5.367	69.9	86.1
1650	5.328	5.368	72.0	86.4
1850†	5.340	5.371	76.5	87.4

Standard deviations of lattice parameters are about 0.001 Å.

*The parameter quoted is that of the fluorite sub-cell, i.e. half that of the type C cell.
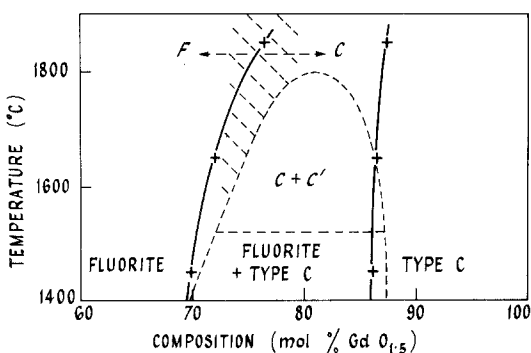
†A trace of $B-Gd_2O_3$ solid solution was present also.

Figure 1 Extent of the fluorite type C two-phase field in the ZrO_2–Gd_2O_3 system. Broken lines and italic lettering indicate boundaries and phases reported by Perez y Jorba *et al.* [1].

the boundaries reported by Perez y Jorba *et al.* [1]; there are apparent inconsistencies between the two sets of data. A feature of the diagram proposed here which may explain these differences is the variation with temperature of the fluorite limit of the two-phase field. When a sample equilibrated at a high temperature in the fluorite field close to this limit is cooled, it enters the two-phase region and becomes unstable. Rapid cooling inhibits cation migration over the distances required for discrete phase separation; however type C micro-domains coherent with the fluorite matrix do form, since this involves only short diffusion distances, giving rise to diffuse type C reflections in addition to the sharp fluorite reflections. The composition of the microdomains is probably about that of the equilibrium type C phase, but the lattice parameter is constrained elastically to conform to that of the matrix. In samples quenched from 1850° C the microdomains were observed by dark-field electron microscopy and had a maximum dimension of about 50 Å [7]. It must be emphasized that the presence of these microdomains at room temperature does not establish that type C order was present at the equilibration temperature.

The size of the microdomains in samples quenched into the two-phase field may reasonably be assumed to increase with increasing Gd_2O_3 content. Consequently the sharpness and intensity of the type C reflections will also increase, and

patterns recorded at room temperature will show an apparently continuous variation of structure type with composition. Conversely, when such quenched samples are heated, the type C reflections will weaken as the microdomains dissolve, and will disappear at a temperature which will increase with Gd_2O_3 content: This has been observed by Rouanet and Foëx [8].

The co-existence of two type C phases is similarly explained. When a sample, equilibrated at high temperature in the two-phase region, is cooled, the original type C phase will be retained and the fluorite phase will exhibit coherent precipitation. In this case the extra type C reflections may be fairly sharp as the fluorite phase has the maximum Gd_2O_3 content possible at the equilibration temperature.

It is concluded therefore that the continuous transition between two structure types, and also the coexistence of two type C phases in the zirconia–gadolinia system are not characteristic of true equilibrium, but arise from the formation of coherent microdomains when solid solutions rich in gadolinia are cooled rapidly from high temperatures.

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