

# Solid-state reaction, microstructure and phase relations in the $ZrO_2$ -rich region of the $ZrO_2$ - $Yb_2O_3$ system

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Phase relations below 1700 °C in the  $ZrO_2$ -rich region of the zirconia–ytterbia system have been established using thermal expansion, room-temperature X-ray diffraction, precision lattice parameter measurements and microscopic observations. The solubility limits of ytterbia in both monoclinic and tetragonal zirconia were determined. A eutectoid reaction, tetragonal zirconia solid solution  $\rightarrow$  monoclinic + cubic zirconia solid solutions at  $400 \pm 20$  °C and 2.4 mol% ytterbia was found. The left-hand boundary of the cubic zirconia solid-solution field was redetermined between room temperature and about 1700 °C. Long-range ordering was present at 40 mol% ytterbia and the formation of an ordered phase,  $Zr_3Yb_4O_{12}$ , isostructural with  $M_7O_{12}$ -type compounds was found. Its thermal stability was established between room temperature and  $1630 \pm 10$  °C, in which it decomposes into cubic zirconia solid solution by an order–disorder reaction.

## 1. Introduction

The study of the  $ZrO_2$ -rich portion of several  $ZrO_2$ - $MO(M_2O_3)$  systems, mainly CaO, MgO and  $Y_2O_3$ , is very important not only from the point of view of the technological applications of zirconia solid solutions but also for a knowledge of the not very clear metastability phenomena that are present, which would lead to a better understanding of zirconia-based materials behaviour. An example of this is the many discrepancies to be found in the reported phase equilibrium diagram for these systems [1–8]. Concerning the  $ZrO_2$ - $Yb_2O_3$  system, in which the ionic radius of  $Yb^{3+}$  (0.086 nm) is quite near to that of the  $Y^{3+}$  cation (0.092 nm) [9], the phase distribution could be very similar to that present in the  $ZrO_2$ - $Y_2O_3$  system. If this is so, then it could contribute to clarify some of the above controversies. On the other hand, from a technological point of view a mixture of  $Y_2O_3$ + $Yb_2O_3$  oxides has been used for a fully stabilized zirconia electrolyte with improved ionic electrical conductivity [10]. Rouanet [11] studied the phase diagram for the  $ZrO_2$ - $Yb_2O_3$  system in the vicinity of the liquidus, and a cubic solid-solution domain in the whole  $Yb_2O_3$  concentration range was found. Recently, Stubican [12] reported a partial study of the  $ZrO_2$ - $Yb_2O_3$  system in which an ordered phase of the  $M_7O_{12}$  type ( $Zr_3Yb_4O_{12}$ ) seems to exist. Although a similar phase diagram to that of the  $ZrO_2$ - $Y_2O_3$  system was assumed, however no experimental data for the  $ZrO_2$ -rich region were reported.

The present study was undertaken to define the stability domain of Yb-doped tetragonal zirconia and the phase relations present in the  $ZrO_2$ -rich region of

the  $ZrO_2$ - $Yb_2O_3$  system. For the most part, solid-state reactions of coprecipitated hydroxides were taken as starting materials and, occasionally, some plasma-melted samples were used to determine the solubility limit of  $Yb_2O_3$  in monoclinic zirconia.

## 2. Experimental procedure

### 2.1. Compositions and starting materials

The composition range of 0 to 10 mol%  $Yb_2O_3$  was studied at increments of 0.5 mol%  $Yb_2O_3$ , and beyond that  $Yb_2O_3$  concentration the increments were of 2.5 mol%. Samples were prepared using Zr-tetra-butoxide and  $Yb(NO_3)_3 \cdot 5H_2O$  (99.99% pure), and coprecipitating the hydroxides by dropwise addition to a 6 M  $NH_4OH$  aqueous solution. The precipitate was filtered and thoroughly washed. After washing, the powder was calcined at 800 °C for 2 h in order to obtain a well-crystallized sample. Quantitative compositional analysis of calcined powders was carried out by Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES).

Powder batches were ball-milled in isopropyl alcohol for 2 h, dried, granulated and isopressed at 200 MPa. Cylindrical samples of 0.5 cm diameter and 1.0 cm long were used for the thermal expansion measurements. All the compositions were sintered at about 1700 °C for 4 h in air to promote equilibration and then furnace-cooled. These samples were used for the phase equilibrium studies, and mainly three series of samples were fired at 840 °C for 1000 h, 1290 °C for 336 h, and 1640 °C for 24 h and rapidly quenched by air-blasting. An additional series of samples in the

concentration range of 0 to 3 mol %  $\text{Yb}_2\text{O}_3$  were plasma-melted and water-quenched.

Beyond 10 mol %  $\text{Yb}_2\text{O}_3$ , only the high-temperature sintered samples were taken into account to be studied. Finally, on the composition containing 40 mol %  $\text{Yb}_2\text{O}_3$  ordering studies were carried out by annealing it for long periods of time ( $\geq 2$  months) in the temperature range of 1680 to 1000 °C.

## 2.2. Room-temperature X-ray diffraction analysis

The phases present in both furnace-cooled and quenched samples were identified at room temperature. An X-ray diffraction (XRD) spectrometer using Ni-filtered  $\text{CuK}$  radiation was used with a  $2\theta$  scanning speed of  $2^\circ \text{min}^{-1}$ . Lattice parameters were determined at room temperature using a  $2\theta$  scanning speed of  $0.25^\circ \text{min}^{-1}$  and Si ( $a = 0.54301 \text{ nm}$ ) as an internal standard. Sixteen peaks in the forward reflection region were used in the lattice parameter determinations, i.e. 1 1 1, 2 0 0, 2 2 0, 3 1 1, 2 2 2, 4 0 0, 3 3 1, 4 2 0, 4 2 2, 5 1 1, 3 3 3, 4 4 0, 5 3 1, 6 0 0, 6 2 0 and 5 2 3. The precision of the parameter measurements was estimated to be  $\pm 0.0005 \text{ nm}$  for compositions containing either the tetragonal, cubic or the tetragonal + cubic phases. The phase boundaries of the monoclinic and cubic zirconia fields were determined using both the disappearing phase method, and the precise lattice parameter measurements.

## 2.3. Thermal expansion measurements

In order to establish with precision the equilibrium temperature between tetragonal and monoclinic zirconia phases, the thermal expansion of solid-state reacted samples were measured with a high-temperature dilatometer between room temperature and 1200 °C, with heating and cooling rates of  $5^\circ \text{C min}^{-1}$  and using  $\text{Al}_2\text{O}_3$  as a reference material.

## 2.4. Microstructural studies

The phase boundaries of the tetragonal and tetragonal + cubic phase fields were also determined from the microstructure observations using SEM. After sintering the samples were polished, thermal-etched, and then the microstructures were observed. These thermal-etched samples were successively annealed at lower temperatures, and the microstructure was observed again. Thus the first formation of cubic zirconia grains, and the disappearance of the tetragonal ones, in a composition theoretically located in the tetragonal + cubic zirconia field, would be better detected by microscopic observations. It is well known that very low concentration of a phase could not be detected accurately by using XRD analysis.

## 3. Results and discussion

### 3.1. The tetragonal–monoclinic transformation of zirconia

Since tetragonal–monoclinic transformation of low

$\text{Yb}_2\text{O}_3$ -doped zirconia takes place with a large volume change, the temperature for such a transformation,  $M_s$ , could be determined by measuring the change in length occurring in a previously sintered sample during heating and cooling. On the other hand, as the monoclinic–tetragonal transformation is a progressive process, then the contraction which occurs on heating takes place in an extended temperature interval, and therefore it is very difficult to measure with precision the transformation temperature,  $A_s$ . In contrast, the expansive reverse transformation on cooling was well defined in a very short temperature range, and thus it could be measured with great precision. Typical thermal expansion curves are shown in Fig. 1, and the variation of the transformation temperature,  $M_s$ , on cooling as a function of the  $\text{Yb}_2\text{O}_3$  content is shown in Fig. 2. It can be observed that the addition of  $\text{Yb}_2\text{O}_3$  lowers both the transformation temperature and the hysteresis of zirconia, and these changes are more pronounced in those samples probably lying at room temperature in the monoclinic zirconia single-phase field. Thus  $M_s$  decreased sharply up to about 1.6 mol %  $\text{Yb}_2\text{O}_3$  and then slowly diminished up to about 2.4 mol %  $\text{Yb}_2\text{O}_3$ . For higher  $\text{Yb}_2\text{O}_3$  concentrations the transformation temperature remained constant, and no transformation occurred above 5 mol %.

As it will be seen below, 1.6 mol %  $\text{Yb}_2\text{O}_3$  is approximately the solubility limit for  $\text{Yb}_2\text{O}_3$  in monoclinic zirconia at the eutectoid temperature, and 2.4 mol %  $\text{Yb}_2\text{O}_3$  is near the composition of the eutectoid point. Between 1.6 and 2.4 mol %  $\text{Yb}_2\text{O}_3$  a two-phase field, monoclinic + tetragonal zirconia solid solutions, seems to exist above the eutectoid temperature. Beyond 2.4 mol %  $\text{Yb}_2\text{O}_3$  two phases, tetragonal or monoclinic + cubic zirconia solid solutions, are coexisting above or below the eutectoid temperature, respectively. This fact and the constant transformation temperature ( $400 \pm 20^\circ \text{C}$ ) for 3 and 3.5 mol %  $\text{Yb}_2\text{O}_3$  support the idea of the existence of a eutectoid reaction, located at about 2.4 mol %  $\text{Yb}_2\text{O}_3$ , in which the tetragonal zirconia solid solution decomposes into monoclinic + cubic zirconia solid solutions. A similar reaction was reported by Stubican [12] but at 520 °C.

Since, as reported by Yashima *et al.* [13] in the case of the  $\text{ZrO}_2$ – $\text{Er}_2\text{O}_3$  system, the equilibrium temperatures between tetragonal and monoclinic zirconia solid solutions can be better represented by  $T_o^{t-m} = (A_s + M_s)/2$ , these  $T_o^{t-m}$  calculated temperatures have also been included in Fig. 2. As for the  $M_s$  variation, a curve consisting of a slanted and a horizontal line was found. Yashima *et al.* [13] found only a slanted curve, and estimated that such a curve represents the relationship between the stabilizer concentration and the  $M_s$  temperature. They did not find any transformation above room temperature in compositions containing more than 2 mol %  $\text{Er}_2\text{O}_3$ . On the assumption of the existence of a eutectoid reaction in this region of all  $\text{ZrO}_2$ – $\text{Re}_2\text{O}_3$  (Re = rare-earth element) systems [14], the reported results of Yashima *et al.* [13] could correspond to a non-equilibrium state and, therefore, they should not be considered as a true phase equilibrium diagram but like a metastable phase relationship

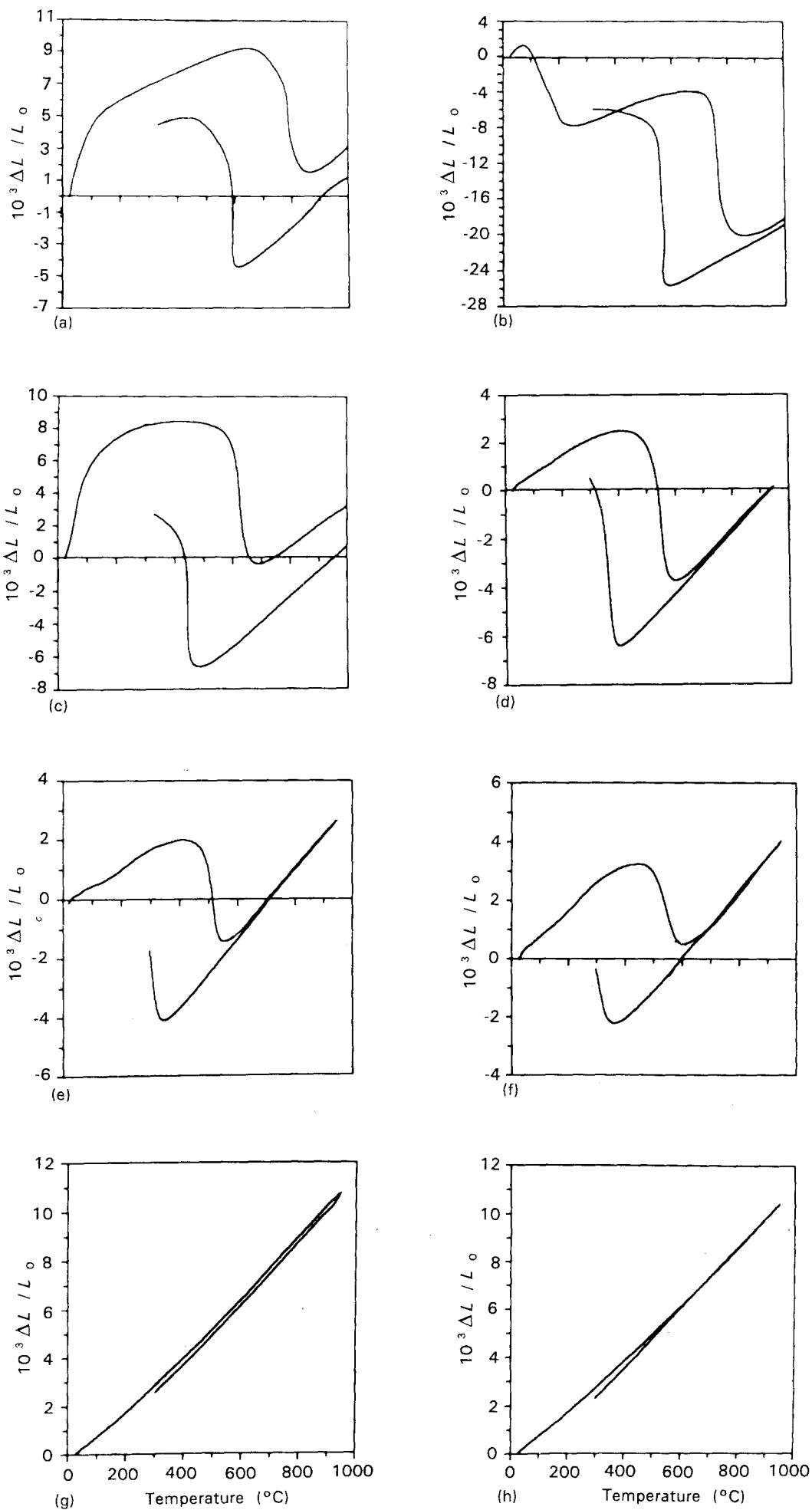


Figure 1 Thermal expansion hysteresis loops registered for several  $ZrO_2$ - $Yb_2O_3$  solid solutions: (a) 1.4 Yb-TZP, (b) 1.6 Yb-TZP, (c) 1.8 Yb-TZP, (d) 2.4 Yb-TZP, (e) 3.0 Yb-TZP, (f) 3.5 Yb-TZP, (g) 5 Yb-PSZ, (h) 7 Yb-FSZ.

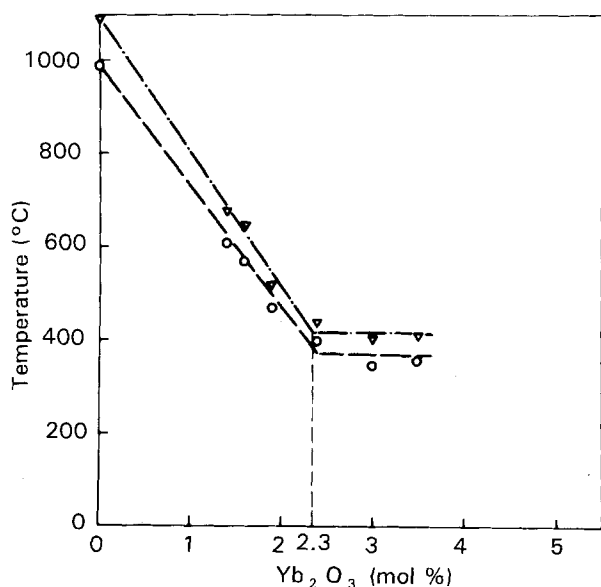


Figure 2 (○) Cooling transformation temperature ( $M_s$ ) and (▽) calculated equilibrium temperature ( $T_0^{(m)}$ ) variation with  $\text{Yb}_2\text{O}_3$  concentration.

in the system. Their melted and rapidly quenched samples could have metastably retained the tetragonal phase at room temperature and, depending on its tetragonality ( $c/a$  axial ratio) and the cooling rate, they could have failed to find any transformation in their thermal expansion experiments.

### 3.2. Zirconia solid solution domains

The room-temperature XRD patterns of the sintered furnace-cooled samples showed the presence of a unique phase, monoclinic zirconia solid solution, from 0 to about 0.8 mol % ytterbia. Beyond that ytterbia concentration, cubic zirconia solid solution appears and a mixture of these two phases exists between 0.8 and 8 mol % ytterbia. For higher ytterbia concentration a single-phase fluorite-type structure is present. Therefore, it can be established that at room temperature the solubility limit of ytterbia in monoclinic zirconia is lower than 1 mol %, and the left-hand boundary of the zirconia cubic solid solution field is at about 8 mol % ytterbia.

It must be mentioned that in both sintered air-blast quenched and plasma-melted water-quenched samples containing less than 1.6 mol % ytterbia the tetragonal zirconia phase was not retained at room temperature. This would indicate that these compositions could, on cooling, be lying in the monoclinic zirconia single-phase field. If this is so, then the solubility of ytterbia in monoclinic zirconia above room temperature could be higher than that established above. Thus the higher limit of the monoclinic zirconia phase was extended up to 1.4 mol % ytterbia at the eutectoid temperature.

Above the pure zirconia transformation temperature the annealed and rapidly quenched samples containing less than 1.6 mol % ytterbia consisted of monoclinic zirconia phase or a mixture of monoclinic and a small amount of metastably retained tetragonal zirconia. In that ytterbia concentration range, the

tetragonality ( $c/a$  axial ratio) must be too high, so that the tetragonal zirconia phase could not be retained at room temperature. Between 1.8 and 3 mol % ytterbia a clear tetragonal zirconia single phase was retained at room temperature, and an axial ratio of 1.014 for the 3 mol % ytterbia composition could be measured. Beyond that ytterbia concentration, the splitting of the tetragonal X-ray reflections evidenced the appearance of the cubic zirconia phase. The coexistence of these two phases made it difficult to determine the right-hand boundary of the tetragonal zirconia single-phase field with precision. To overcome such a problem, sintered samples containing from 1.8 to 8 mol % ytterbia were polished, thermal-etched and the microstructures observed by SEM. The polished samples were then annealed at different temperatures below 1680 °C and the microstructures were observed again. As an example, Fig. 3 shows the evolution of the microstructure from a tetragonal single-phase to a cubic one for samples annealed at 1600 °C for 24 h. In this way, the right-hand boundary of the tetragonal zirconia single-phase field was found to be 3, 2.5 and 2.3 mol % ytterbia at 1100, 1400 and 1600 °C, respectively.

As it can be seen in Fig. 4, the lower limit of the cubic zirconia single-phase field was determined quite accurately at 840, 1290, 1640 and ~1700 °C by measuring the lattice parameters of the cubic zirconia solid solution at room temperature, and it was established to be at 7, 6, 5 and 4.8 mol % ytterbia, respectively. These values are somewhat lower than those reported by Stubican [12] for ytterbia-fully stabilized zirconia at different temperatures. This was probably due to his use of incompletely reacted samples.

### 3.3. Ordering studies

Owing to the similarity with the zirconia-yttria system, only the composition of 40 mol % ytterbia was chosen to study ordering phenomena. Thus the sample sintered at 1650 °C for 2 h was a well-defined cubic zirconia solid solution with a lattice parameter of  $a = 0.5165 \pm 0.0005$  nm. After annealing at about 1000 °C for  $\geq 4$  months an ordered compound,  $\text{Zr}_3\text{Yb}_4\text{O}_{12}$ , was found. This compound is isostructural with those of the  $\text{M}_7\text{O}_{12}$  type and the measured lattice parameters were  $a = 0.9641 \pm 0.0005$  nm and  $c = 0.8978 \pm 0.0005$  nm. Its thermal stability was studied by heating the ordered phase to increasing temperatures, and it was found that at  $1630 \pm 10$  °C it decomposes in a few hours into cubic zirconia by an order-disorder reaction. This result is in closed agreement with that reported by Stubican [12],  $1637 \pm 13$  °C. No other ordered compounds, if any, were studied in this system.

### 3.4. Phase relations in the $\text{ZrO}_2$ -rich region of the zirconia-ytterbia system

According to the experiments described above, and on the basis of the results obtained, we can construct a tentative phase diagram for temperatures below about 1700 °C (see Fig. 5) as follows:

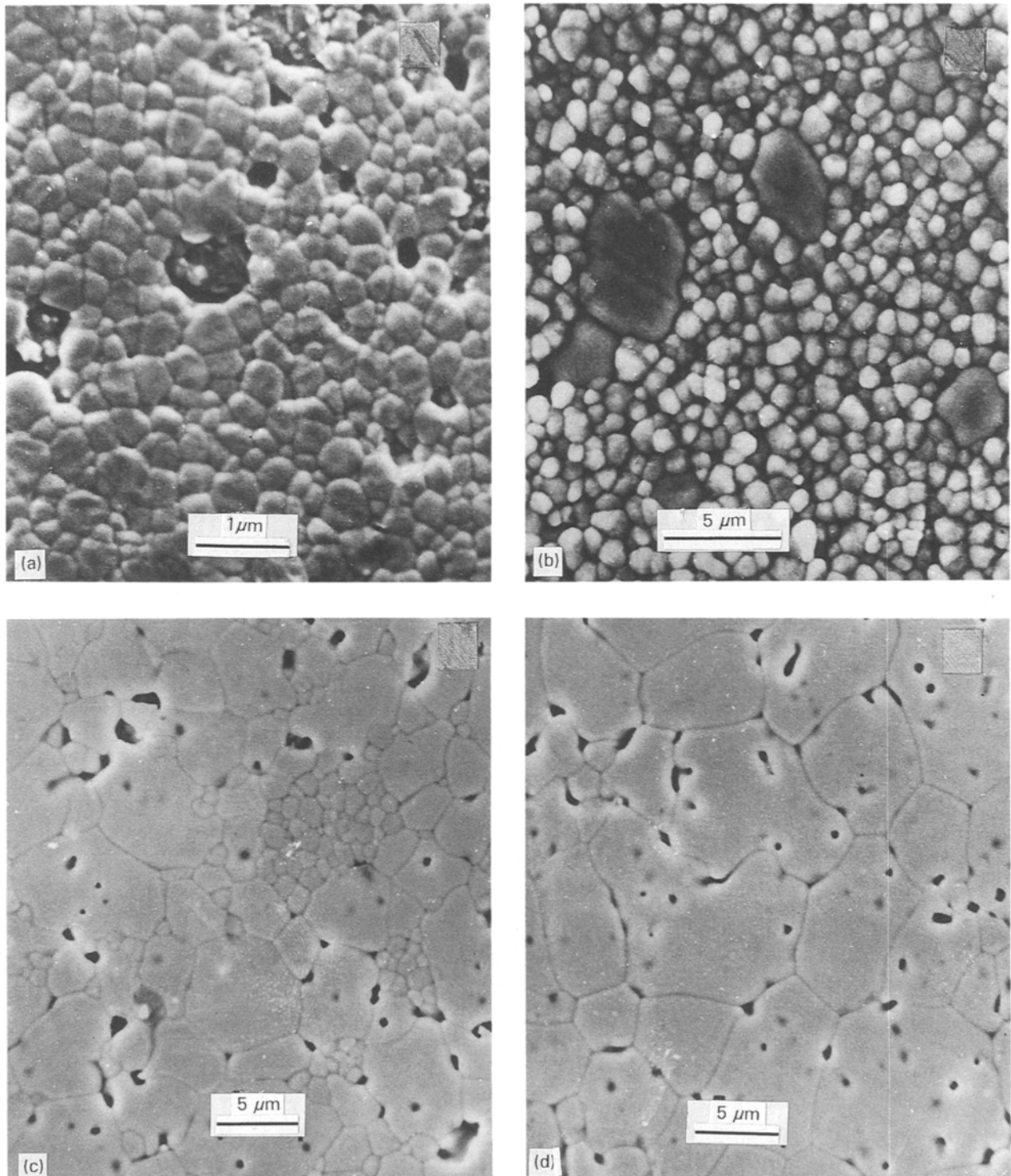


Figure 3 SEM micrographs of sintered  $ZrO_2$  doped with (a) 1.8, (b) 2.4, (c) 5 and (d) 7 mol %  $Yb_2O_3$  annealed at  $1600^\circ C$  for 24 h.

(a) At room temperature the solubility limit of ytterbia in monoclinic zirconia is less than 1 mol %, and about 8 mol % ytterbia are necessary to fully stabilize zirconia in the cubic phase.

(b) Above the pure zirconia transformation temperature a tetragonal zirconia single-phase field between 0 and 3 mol % ytterbia exists. This tetragonal zirconia solid solution transforms by a eutectoid reaction, located at  $400 \pm 20^\circ C$  and about 2.3 mol % ytterbia, into monoclinic + cubic zirconia solid solutions (Figs 1 and 2). The existence of these two phases at room temperature, between 0.8 and 8 mol % ytterbia, sup-

ports the idea of the presence of such a eutectoid reaction. The left-hand boundary of the tetragonal zirconia single-phase field was determined taking into account the tetragonal-monoclinic transformation temperatures,  $M_s$ . The right-hand boundary was defined by studying the microstructure of the annealed and quenched samples at 1100, 1400 and  $1600^\circ C$  (Fig. 3).

(c) A two-phase field exists between the tetragonal and the cubic zirconia solid solutions. This two-phase field extends from 3 to 6 mol % ytterbia at  $840^\circ C$ , and from 2 to 4.8 mol % ytterbia at about  $1700^\circ C$ .

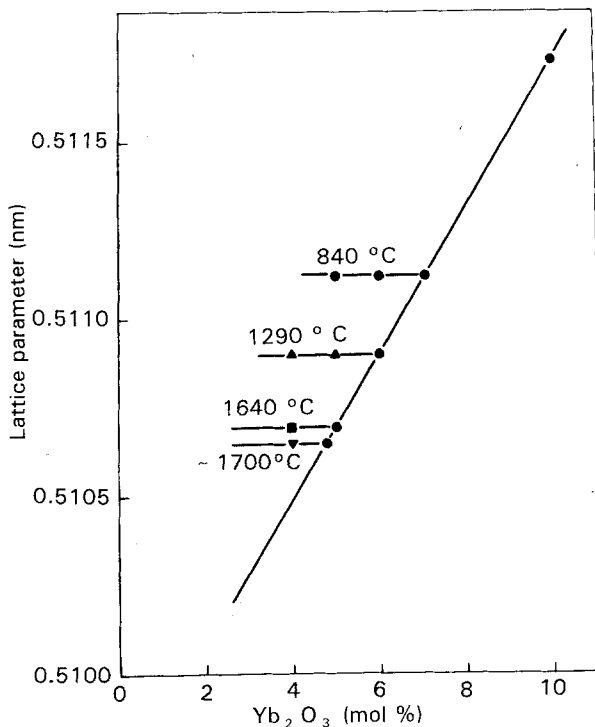


Figure 4 Variation of lattice parameters of fluorite-type zirconia structure with  $\text{Yb}_2\text{O}_3$  content at temperatures below  $1700^\circ\text{C}$ .

(d) An extensive cubic zirconia single-phase field exists beyond 8 mol % ytterbia at room temperature and 4.8 mol % ytterbia at about  $1700^\circ\text{C}$ . The left-hand boundary of this field was determined at 840, 1290, 1640 and about  $1700^\circ\text{C}$  by using the precision lattice parameter method (Fig. 4).

(e) The existence of an ordered phase,  $\text{Zr}_3\text{Yb}_4\text{O}_{12}$ , of the  $\text{M}_7\text{O}_{12}$  type has been confirmed. The formation of this compound from sintered samples is a very sluggish process but it decomposes in a few hours at  $1630 \pm 10^\circ\text{C}$  into cubic zirconia solid solution by an order-disorder reaction.

Summarizing, a complex picture of phase transformation was found in the zirconia-rich region of the zirconia-ytterbia system and a tentative phase diagram which is in agreement with the Gibbs phase rule was proposed. There are two important regions: one is that of metastable tetragonal zirconia solid solution, and the other corresponds to fully stabilized cubic zirconia, with potential technological interest for structural ceramic materials and high-performance electrolytes, respectively.

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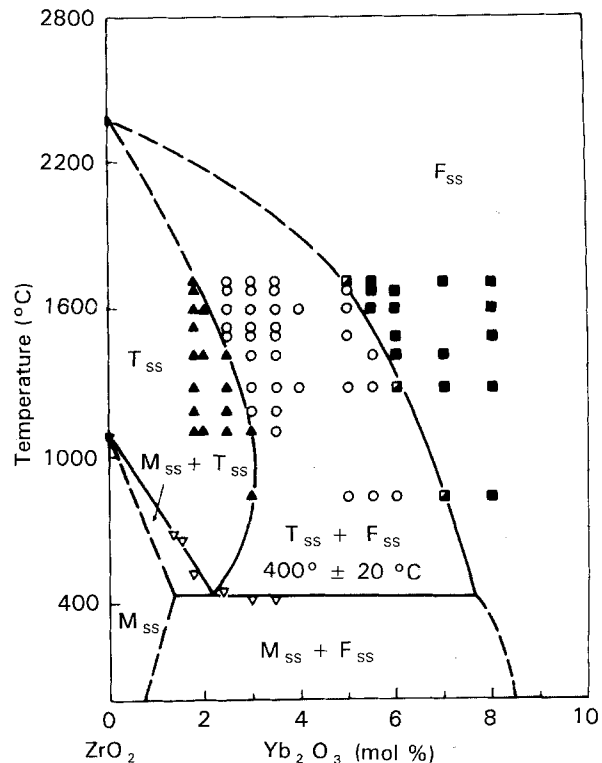


Figure 5 Proposed phase equilibrium diagram in the  $\text{ZrO}_2$ -rich region of the  $\text{ZrO}_2$ - $\text{Yb}_2\text{O}_3$  system. ( $T_{ss}$ ) tetragonal solid solution; ( $M_{ss}$ ) monoclinic solid solution; ( $F_{ss}$ ) fluorite-type cubic solid solutions

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