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Low temperature phase equilibria and ordering in the ZrO_2-rich region of the system ZrO_2–CaO

P. DURAN, P. RECIO, J. M. RODRIGUEZ
Instituto de Cerámica y Vidrio (CSIC), Departamento de Materiales Cerámicos Especiales, Arganda del Rey, Madrid, Spain

From co-precipitated powder samples, the solid state reactions occurring between room temperature and 1500° C in the ZrO_2–CaO system have been studied. At low temperatures, compositions containing < 25 mol % CaO show a complex picture of phase transformation and ordering in the system. From the obtained results the following singular reactions have been established. (i) Tetragonal zirconia solid solution decomposes eutectoidally at 7 mol % CaO and 1048 ± 4° C into monoclinic zirconia solid solution and calcium zirconate (CZ). (ii) Cubic zirconia solid solution undergoes a eutectoidal decomposition at 17.5 mol % Cao and 1080 ± 20° C into tetragonal solid solution + calcium zirconate. (iii) The monoclinic ordered phase, $CaZr_4O_9$ (Φ_1), undergoes an order–disorder transformation into cubic zirconia solid solution at 1232 ± 5° C. (iv) Cubic zirconia solid solution undergoes a eutectoidal decomposition into two ordered phases, $\Phi_1 + \Phi_2$ at 21 mol % CaO and 1200 ± 10° C. (v) Hexagonal ordered phase $Ca_6Zr_{19}O_{44}$ (Φ_2) decomposes peritectoidally into cubic zirconia solid solution + calcium zirconate at 1360 ± 10° C. The two ordered phases Φ_1 and Φ_2 seem to be unstable below ~1100° C. By using DTA, X-ray diffraction and SEM techniques, the extent of the tetragonal and cubic zirconia solid solution fields have been established. From the above experimental results a new tentative phase diagram is given for the ZrO_2-rich region of the system, ZrO_2–CaO.

1. Introduction

Since the first major contribution to the study of the zirconia–calcia system [1] many papers have attempted to establish the phase equilibria distribution in the more relevant zones of the system [2–6]. All have made use of different raw materials and methods of investigation and thus the possibility of reaching an agreement on the range of existence of the different zirconia solid solutions has become more difficult. Garvie [7] claimed that by using the lattice parameter method and well crystallized pure oxides as reagents, the reliability of the experimental results could be assured. Nevertheless, his claim for an enlarged cubic zirconia solid solution field when $CaCO_3$ was used as reagent and, on the other hand, the fact that there is no well established eutectoid point for the system imply that other phenomena could be present which do not permit us to establish without ambiguity the definitive phase equilibrium diagram in the zirconia-rich part of this binary system.

The last major contributions on this system are those of Stubican *et al.* [8–11]. They used reactive gels fired at 2000° C and precision X-ray lattice parameter measurements to study the phases present. In this way they established in a first study [8] that an ordered compound, $CaZr_4O_9$ (Φ_1), and a eutectoid point at 750° C and 14.5 mol % CaO exist in the system. Further [10], a new phase distribution was established for the system, and a new ordered phase, $Ca_6Zr_{19}O_{44}$ (Φ_2), at 24 mol % CaO was reported, the eutectoid point being located at 1140 ± 40° C and 17.0 ± 0.5 mol % CaO. By using TEM and SAD techniques they also studied the early stages of ordering on two compositions, hypoeutectoid and hypereutectoid, quenched from 2000° C and annealed. Their results, similar to those obtained by Hudson *et al.* [12] and Schoenlein *et al.* [13] enabled them to establish both the extent of the cubic zirconia solid solution field and the ordering in the ZrO_2–CaO system.

Better techniques for samples preparation and characterization have been used [8–11] and the phenomena occurring in these samples could be better evidenced. Nevertheless it is true that the variations in composition taking place during sintering at very high temperatures (> 2000° C) or during the elaboration of the single crystals could lead to a confused interpretation of such phenomena. The present paper was undertaken to achieve, from a solid state reactions study, a better knowledge of the phase equilibrium diagram on co-precipitated powder samples with a very fine particle size, controlled grain size, and no previous manipulation. In this way it was believed that neither composition variations nor transformation phenomena in such working conditions could be expected, and more reliable results and, therefore, a better equilibrium phase diagram for the ZrO_2–CaO system could be established.

2. Experimental procedure

2.1. Materials

In all cases zirconium tetrabutoxide and hydrated calcium nitrate were used as the starting raw materials.

2.2. Sample preparation

The different sample compositions were prepared by mixing alcoholic solutions of zirconium tetrabutoxide and hydrated calcium nitrate by sitrring. The addition of an ammonia aqueous solution produced the co-precipitation of the hydroxides, and the pH was carefully controlled in order to achieve completion. After washing and drying the co-precipitated powders were ball milled with isopropanol for several hours, dried and calcined at 900° C until all the CaO was reacted with zirconia. After that a part of the powder (particle size $< 0.1\,\mu$m) previously isopressed at 250 MPa was heat-treated at 1720° C for 8 h; these samples will be referred to as high temperature quenched samples. After quenching the samples were isothermically heat-treated at different temperatures between 1050 and 1700° C for several hours and quickly air quenched. The other part of the isopressed powder was heated from 950 to 1450° C for several hours and quenched by air blasting. These samples will be referred to as low temperature reacted samples. In both cases the equilibrium was considered to be achieved when no variation occurred in the lattice parameters of the present phases with time. In view of the metastability of both tetragonal and cubic solid solutions, only the low temperature experiments were taken into account for measuring the lattice parameters. Where this was not possible the phase disappearance method was used. The influence of CaO additions on tetragonal–monoclinic transformation temperature was studied on high temperature quenched samples by using the DTA technique. For phase identification and lattice parameter measurements a Philips model 1040 diffractometer and Cu$K\alpha$ radiation were used. To calculate the lattice parameters with precision (± 0.00005 nm) only high angle peaks ($2\theta > 60°$) were used, obtained by using the $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ Riley and Nelson function.

Ordering phenomena in the ZrO_2–CaO system were studied on co-precipitated powder samples containing 20, 22.22 and 24 mol % CaO. After calcining, the isopressed samples were sintered at 1720° C for 8 h and air-quenched. The quenched samples were annealed for a long time ($\geqslant 2400$ h) between 950 and 1400° C. In an attempt to synthesize the ordered phases by solid state reaction, the same compositions were reacted at low temperature (between 950 and 1200° C) for different periods of time. From time to time the samples were air-quenched and the present phases were studied by X-ray diffraction. Then the samples were reground, pressed and heat-treated again at the desired temperature. In this manner the formation of ordered phases in the system could be studied in two different ways, (i) from the high temperature disordered fluorite phase; and (ii) from the low temperature tetragonal or fluorite precursor phases.

In addition, to establish without ambiguity the invariant eutectoid point in which the decomposition of the cubic zirconia solid solution takes place, co-precipitated powders containing from 8.4 to 19 mol % CaO were heated below 1400° C at an adequate temperature and time to avoid the tetragonal transformation on cooling, then polished, thermal etched, and annealed at a lower temperature, between 1150 and 1050° C, for a long time. After this heat-treatment the microstructure of the samples was observed by SEM.

3. Results and discussion

3.1. Region of the system involving the tetragonal–monoclinic transformation

DTA data obtained during heating up ($8°\,C\,min^{-1}$) in the 1, 2, 4, 6, 8 and 10 mol % CaO compositions show that small additions of calcium oxide to zirconia strongly decreases the monoclinic–tetragonal transformation temperature from 1190 to 1100° C for 1 mol % CaO, 1070° C for 2 mol % CaO, 1060° C for 4 mol % CaO, 1052° C for 6 mol % CaO, and 1048° C for 7 mol % CaO. Beyond that CaO concentration, the transformation temperature remains constant (see Fig. 1). Below 1048° C a two phase field, monoclinic zirconia + calcium zirconate, was present between 1 and 10 mol % CaO. These results lead to the assumption that a eutectoid reaction, tetragonal zirconia solid solution → monoclinic zirconia solid solution + calcium zirconate, takes place at about 1048° C and 7 mol % CaO. Above this temperature a tetragonal zirconia solid solution from 0 to 7 mol % CaO is present in the system. It must be mentioned that the solubility of CaO in tetragonal zirconia is very low at higher temperatures.

3.2. The cubic zirconia solid solution field

Between 1150 and 1700° C the present phases in the zirconia-rich region were determined from room temperature X-ray diffraction studies of quenched samples. The left boundary of the cubic solid solution field was established by both the disappearance of the 1 1 1 and 1 1 $\bar{1}$ monoclinic zirconia solid solution peaks, and by the precise lattice parameter measurements. The

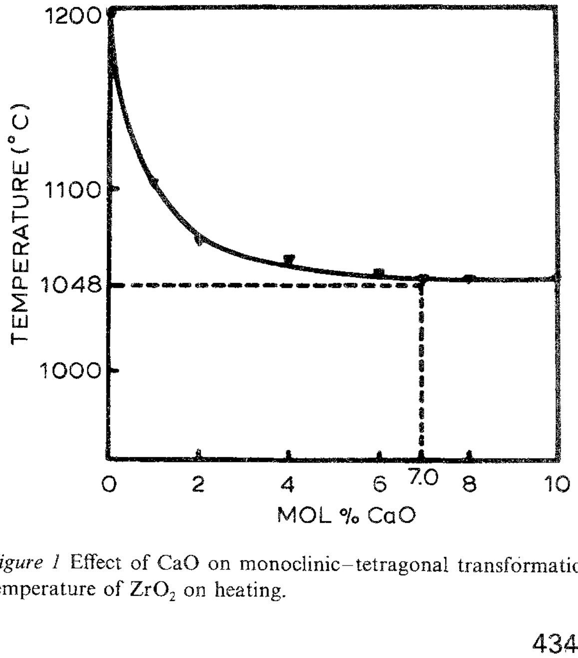

Figure 1 Effect of CaO on monoclinic–tetragonal transformation temperature of ZrO_2 on heating.

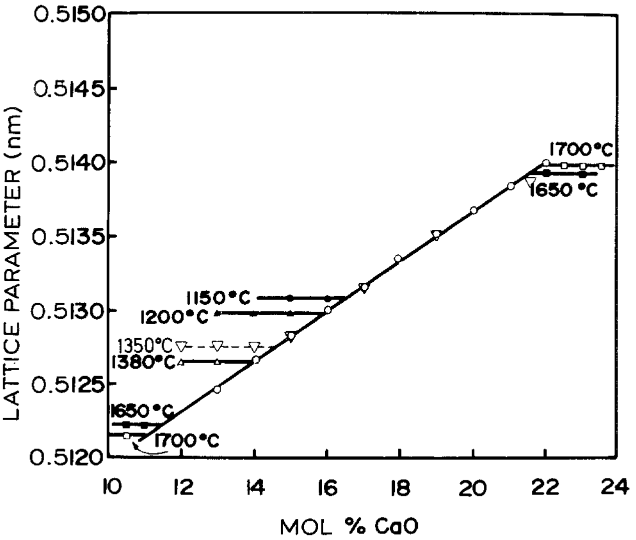

Figure 2 Room temperature lattice parameters of ZrO_2–CaO compositions quenched from different temperatures. (□) 1700; (■) 1650; (△) 1380; (▽) 1350; (▲) 1200; (●) 1150.

accuracy between the two methods was quite good (± 0.1 mol % CaO), and the boundary was defined as 11 mol % CaO at 1700° C, 11.4 mol % CaO at 1650° C, 14.0 mol % CaO at 1380° C, 14.7 mol % CaO at 1290° C, 15.8 mol % CaO at 1250° C, 15.9 mol % CaO at 1200° C, and 16.5 mol % CaO at 1150° C. The solubility limits of calcia in zirconia at the right of the cubic solid solution field have been established as 21.5 mol % CaO at 1650° C and 21.9 mol % CaO at 1700° C. Beyond these limits a two phase field, fluorite + calcium zirconate (CZ), exists. Fig. 2 shows the relation between lattice parameters and composition for the cubic zirconia solid solution at different temperatures.

Below 1100° C, and for compositions containing less than 20 mol % CaO, a two phase field tetragonal or monoclinic zirconia solid solution + calcium zirconate was present. These results show that a eutectoid reaction, cubic zirconia solid solution → tetragonal zirconia solid solution + calcium zirconate, must exist in this area of the system. Nevertheless the exact location of such an invariant point is at present in controversy. From the above precise lattice parameter measurements, and with the help of the phase disappearance method, it seems clear that a eutectoid reaction could be located between 1050 and 1100° C for a composition near 17.5 ± 0.1 mol % CaO. Hellmann *et al.* [10] located the eutectoid reaction at a higher temperature and lower CaO concentration. On the other hand, Marder *et al.* [14] suggested a still lower eutectoid temperature and CaO concentration. The discrepancy could be explained if both the method for sample preparation and the characterization technique used in those cases is taken into account.

During the elaboration of the single crystals as well as in the sintering above 2000° C, a CaO evaporation could take place according to the following reaction:

$$yZrO_{2-x} \cdot xCaO \rightarrow yZrO_{2-x} + xCa + x/2O_2$$

leading to a different CaO concentration in both the original surface and the interior of the sample. The quenched samples could probably be formed in this way, in the simpler case, by a sequence of phases which, depending on the evaporated CaO amount, would fluctuate from a transformable low CaO tetragonal solid solution + low CaO cubic zirconia solid solution to a non-transformable CaO rich tetragonal zirconia solid solution + CaO-rich cubic zirconia solid solution. If this is so, the first case could take place on cooling the following reactions: low CaO tetragonal solid solution would directly decompose to monoclinic zirconia solid solution, while low CaO cubic zirconia solid solution would decompose to tetragonal or monoclinic zirconia solid solution + calcium zirconate. In the second case, CaO-rich tetragonal zirconia solid solution could retain, depending on the precipitate size, its tetragonal structure constrained by the cubic matrix, while CaO-rich cubic zirconia solid solution would decompose eutectoidally to tetragonal or monoclinic zirconia solid solution + calcium zirconate. Furthermore, it is well known that some tetragonal–monoclinic transformation could take place during the foil preparation by ion-beam thinning to be observed in the TEM and therefore that is another factor leading to a final confused interpretation of the phenomena. Evidently all of these phenomena, arising from a probable non-equilibrium situation, are more clearly evidenced by using a very sensitive transmission electron microscope. The conclusions obtained from such evidence will be in agreement with the phase distribution present in such a sample, but they cannot be transplanted to a phase equilibrium diagram. On the contrary, it could lead to a greater confusion in establishing such a diagram.

It is true that the metastability phenomenon present in this area of the system is the main problem in reaching a successful statement. In an attempt to establish without ambiguity both the temperature and composition of the eutectoid point, as well as the phase assemblages in this region of the system, low temperature reacted compositions containing 8.4, 16.1, 16.4, 17.0, 17.5, 18.0, 20.0, 22.22 and 24.0 mol % CaO were heated at 1350° C until equilibrium was attained. It was considered to be achieved when the lattice parameters were the same for both the samples quenched from 1720° C and annealed at 1350° C, and the samples heated at 1350° C for several hours. On the other hand, taking into account that tetragonal zirconia solid solution could more easily transform on cooling into monoclinic phase when the grain size is greater than a critical size, then the low temperature reacted

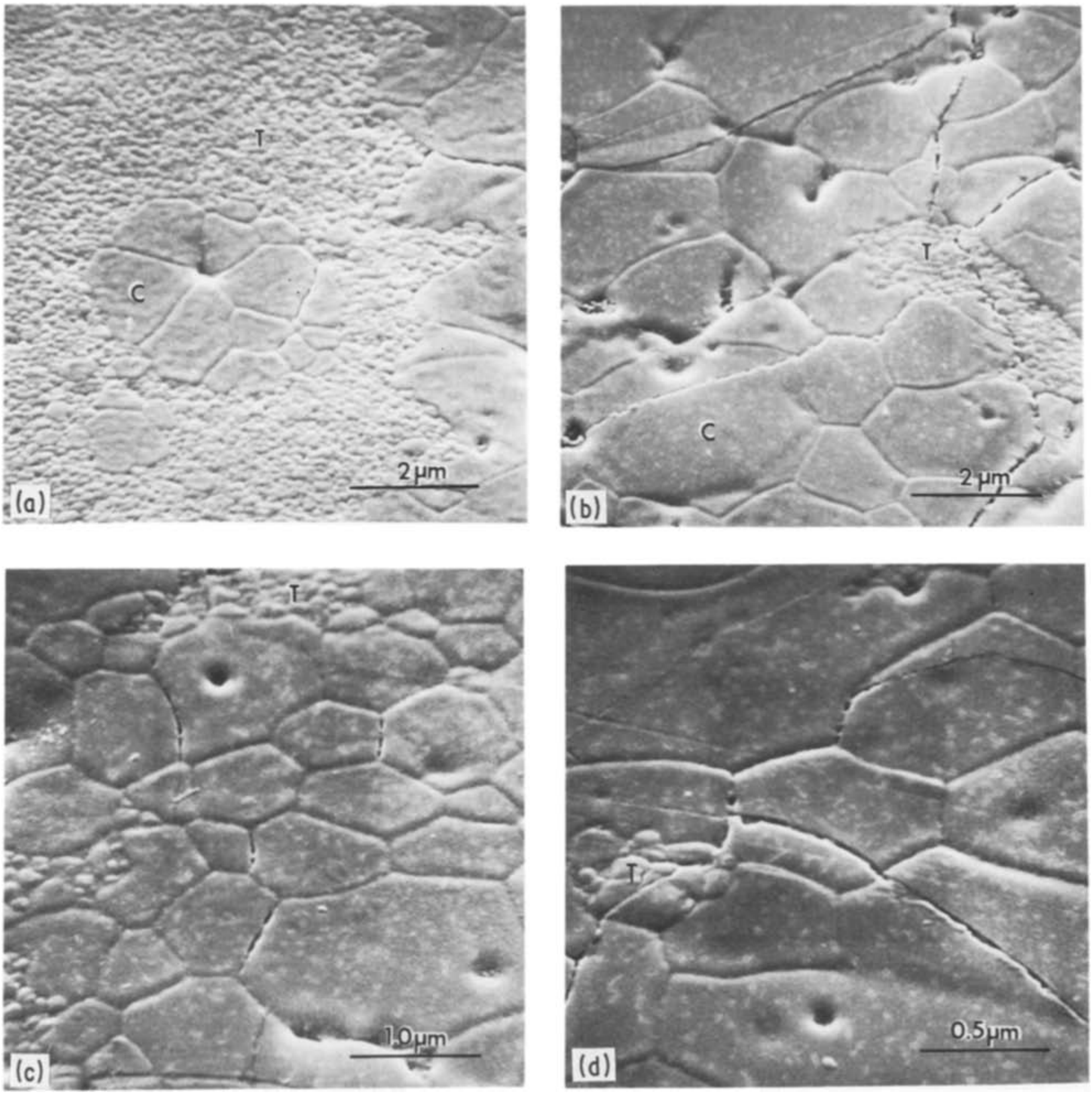

Figure 3 Microstructural development of low temperature reacted ZrO_2–CaO compositions annealed at 1150° C for 50 days: (a) 8.4; (b) 16.1; (c) 17.0 and (d) 17.5 mol % CaO.

samples were never heated for a time greater than that necessary to reach the critical grain size. In this way it was found that the tetragonal structure can be retained in a constrained matrix up to a grain size $\lesssim 190$ nm, beyond which the tetragonal phase transforms to the stable monoclinic structure during cooling to room temperature. This is a lower value than that found by Gupta *et al.* [15] in the case of the Y-tetragonal zirconia for which a critical grain size of 320 nm was reported. Nevertheless Hannink *et al.* [16] and Marder *et al.* [14] pointed out that Ca-tetragonal precipitated larger than 90 nm lost coherency and transformed to the stable monoclinic phase. It must be noted that the tetragonal precipitates in a cubic matrix are probably more weakly constrained than in a microstructure of tetragonal grains, in which the constraint is imposed on one another by neighbouring grains with a higher anisotropy and, in that case, the tetragonal structure could be retained in grains larger than the critical size. In such conditions the present phases in heated low temperature reacted and quenched samples from 1350° C could be more clearly studied. By measuring the lattice parameters and comparing them with those measured on high temperature quenched and annealed samples, the lower limits for both tetragonal and cubic zirconia solid solution fields were established. In Fig. 2 the lattice parameters were shown as a temperature function in which they correspond to those measured on high temperature quenched and annealed samples, except for the cases of the isothermal treatments at and below 1350° C, in which the lattice parameters were measured on low temperature reacted samples in the heating. The close concordance obtained indicates that equilibrium was attained.

By decreasing the temperature quickly from 1350 to 1150° C and maintaining the samples at that thermal level for several days the lattice parameters of the tetragonal phase shifted towards a lower tetragonality, from 1.020 at 1350° C to 1.018 at 1150° C. This means that the CaO solubility in tetragonal zirconia is

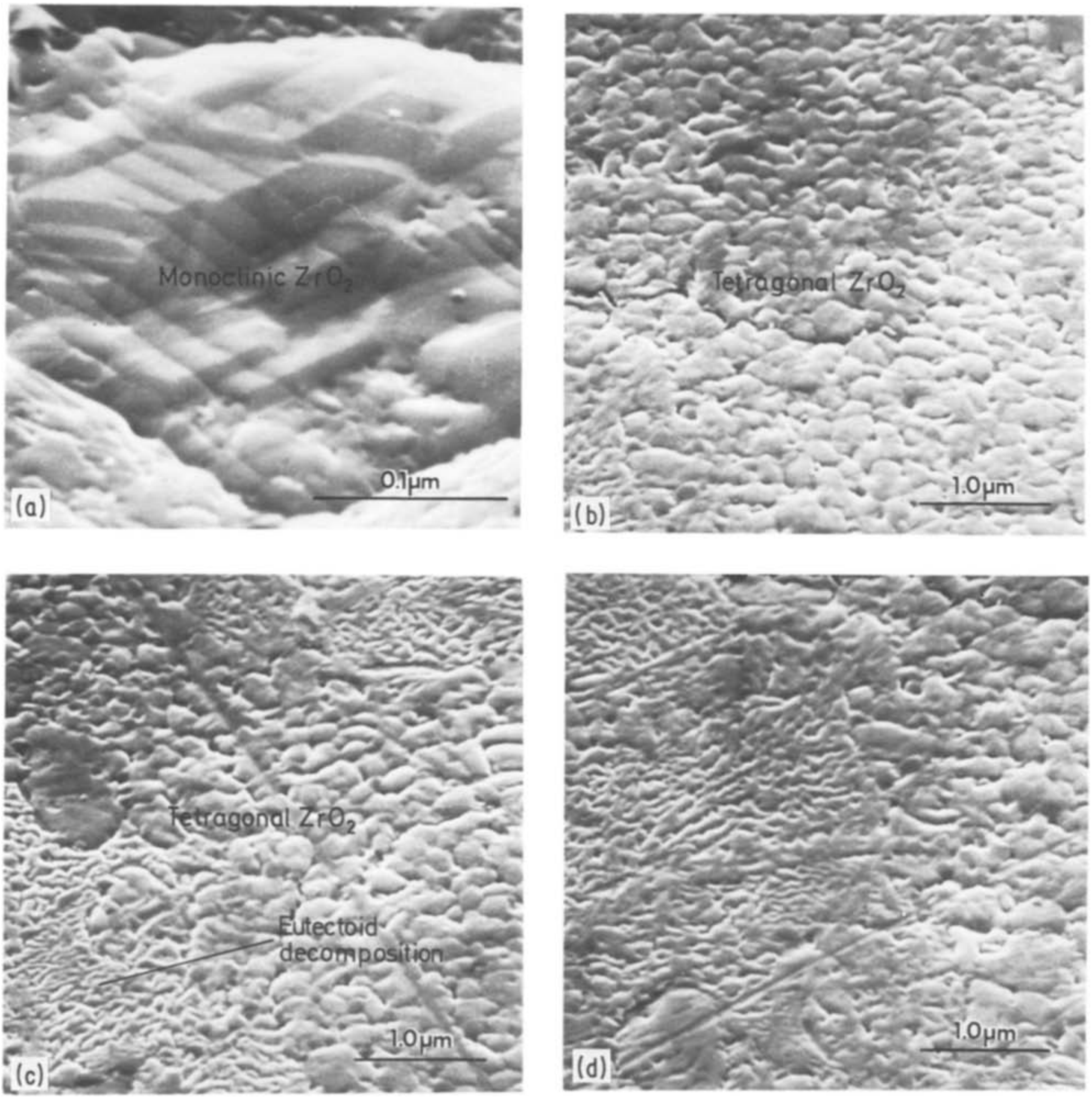

Figure 4 Microstructural development of low temperature reacted ZrO_2–CaO compositions annealed at 1050° C for 50 days: (a) 8.4; (b) 16.1; (c) 17.0 and (d) 17.5 mol % CaO.

greater at that temperature. Samples previously polished and thermal etched at 1350° C were heat-treated in the same way and observed by SEM. Fig. 3 shows an impressive evolution of the microstructure as a composition function in annealed samples at 1150° C. It can be seen that the coexistence of the tetragonal zirconia grains (D = 190 nm) and the cubic zirconia grains (D = 3 μm) is stable in all the composition ranges, and no precipitation on the cubic zirconia surface grains was observed. At 17.5 mol % CaO the presence of few tetragonal grains was still detected, and beyond 17.5 mol % CaO only cubic zirconia grains were present. This means that the eutectoid composition is probably located at or higher than 17.5 mol % CaO. By quenching the samples from 1150 to 1050° C and annealing for several days the precipitation phenomenon on the surface of the cubic zirconia grains as consequence of the eutectoidal decomposition could be observed. Fig. 4 shows that most of the tetragonal grains remained at that thermal level and only a few grains transformed to the monoclinic phase. It could be that the tetragonal nuclei could have been present before and do not precipitate until the critical size was reached. If this is the case, the eutectoid temperature would be located just above 1050° C; however no precipitation phenomena was observed, at least by the SEM technique, above that temperature. Below 1050° C a two phase field, monoclinic zirconia solid solution + calcium zirconate, was present. Despite these results, in view of the strong metastability phenomena existing at this region of the system, the temperature for the eutectoid point has been established at 1080 ± 20° C and 17.5 ± 0.1 mol % CaO. Table I shows the phase assemblages for the ZrO_2–CaO system, and Fig. 5 shows the equilibrium phase diagram drawn according to the above-described results.

TABLE I Phase assemblages in low temperature reacted samples*

Compositions (mol % CaO)	Phases present at		
	1350° C	1150° C	1050° C
8.4	$T_{ss} + F_{ss}$	$T_{ss} + F_{ss}$	$T_{ss} + CZ\uparrow$
16.1	F_{ss}	$T_{ss} + F_{ss}$	$\downarrow T_{ss} + CZ\uparrow$
16.5	F_{ss}	$T_{ss} + F_{ss}$	$\downarrow T_{ss} + CZ\uparrow$
17.0	F_{ss}	F_{ss}	$\downarrow T_{ss} + CZ\uparrow$
17.5	F_{ss}	F_{ss}	$\downarrow T_{ss} + CZ\uparrow$
18.0	F_{ss}	F_{ss}	$\downarrow T_{ss} + CZ\uparrow$
20.0	F_{ss}	Φ_1	$\downarrow T_{ss} + CZ\uparrow$
22.2	$F_{ss} + \Phi_2$	$\Phi_1 + \Phi_2$	$\downarrow T_{ss} + CZ\uparrow$
24.0	Φ_2	Φ_2	$\downarrow T_{ss} + CZ\uparrow$

*All the samples containing less than 20 mol % CaO were heated at 1350° C annealed for 50 days, and successively quickly cooled at 1150 or 1050° C and annealed for 50 days.

3.3. Ordering

Below 1500° C, one of the goals of the present work was to define the composition, existence domain and estability of the different ordered phases existing in the ZrO_2–CaO system. To do that two kinds of samples, both low temperature reacted and high temperature quenched, containing from 20 to 24 mol % CaO were annealed for long periods of time in the temperature range 950 to 1400° C. After 30 days at 950° C, no ordering was detected, but the following phases sequence in the low temperature reacted samples was observed: monoclinic + calcium zirconate phases at 20 mol % CaO, and cubic or tetragonal + CZ phases at 22.22 and 24 mol % CaO. After 40 days at 1100° C the three compositions presented a mixture of two phases, cubic or tetragonal zirconia + calcium zirconate, and a certain ordering began to be detected. After two months calcium zirconate disappeared and Φ_1 and Φ_2 phases were clearly observed. No ordering was observed in the high temperature quenched samples, which indicates that probably the grain size and the nature of the grain boundary could be influencing the rate of the ordering processes. Since the ordering process is too sluggish, the temperature was increased up to 1195° C and, at that thermal level, a perfect ordering was observed in the low temperature reacted samples, and no ordering was detected in the high temperature quenched samples. If it is assumed that the ordered vacancy phases form quickly [17], then such sluggish ordering in the ZrO_2–CaO system suggest that ordering of the metal atoms is probably required during the ordering process. After 100 days at 1195° C ordering was detected in high temperature quenched samples, and it was completed beyond four months of heat-treatment at that temperature. The above results imply that the solid state reactions in the Φ_1 and Φ_2 formation proceeds, as a first step, with the formation of the two stable phases at room temperature monoclinic zirconia solid solution + calcium zirconate. Both phases react at high temperature (> 1050° C) to form, in a second step, tetragonal zirconia solid solution + calcium zirconate. In the final step (above 1100° C) these two phases react to give the ordered phases Φ_1 and Φ_2. It seems probable that the formation of the ordered phases from a tetragonal symmetry was more favoured than that from the high temperature disordered fluorite structure.

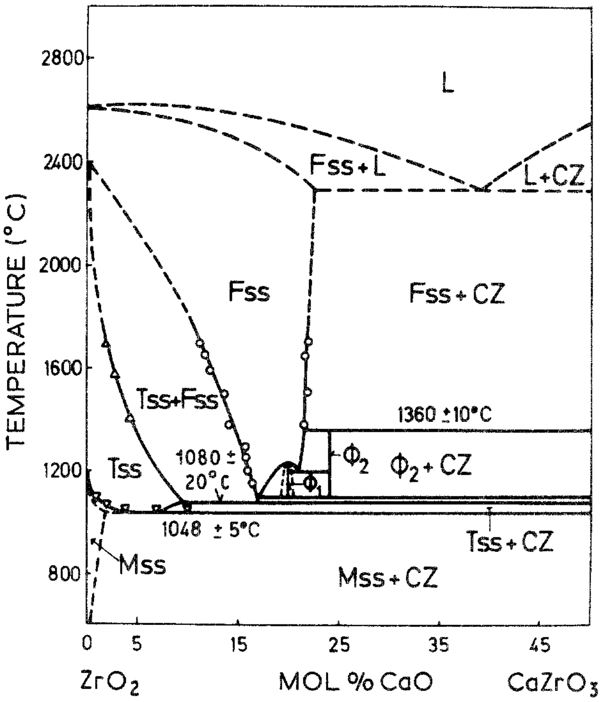

Figure 5 Phase equilibrium diagram for the ZrO_2-rich region of the ZrO_2–CaO system showing a complex picture of phase transformations and ordering; results obtained by (▽) DTA; (△) phase disappearance method. (○) precise lattice parameters measurements.

In all cases the ordered phases found corresponded to $CaZr_4O_9$ (Φ_1) (20 mol % CaO) and $Ca_6Zr_{19}O_{44}$ (Φ_2) (24 mol % CaO). The 22.2 mol % CaO sample was always, after that heat-treatment, a mixture of the two phases Φ_1 and Φ_2. In agreement with Alpress *et al.* [18] the ordered phase $CaZr_4O_9$ can be indexed on the basis of a monoclinic unit cell. Fig. 6 shows the X-ray powder diagram for that phase, and Table II shows

TABLE II Indexing of the $CaZr_4O_9$ compound*

d (nm)			
Observed	Calculated	*hkl*	Intensity
0.5980	0.5962	021	W
0.5257	0.5231	002	W
0.4856	0.4855	310	W
0.3863	0.3864	400	M
0.3743	0.3745	$13\bar{2}$	M
0.3743	0.3745	$33\bar{1}$	M
0.3674	0.3679	$42\bar{2}$	M
0.3510	0.3503	$22\bar{3}$	M
0.3342	0.3339	$24\bar{1}$	M
0.2055	0.3044	$33\bar{3}$	W
0.2055	0.3045	331	W
0.2961	0.2958	$20\bar{4}$	VS
0.2961	0.2958	$60\bar{2}$	VS
0.2961	0.2961	241	VS
0.2647	0.2644	440	VW
0.2561	0.2563	402	VS
0.2561	0.2563	$44\bar{3}$	VS
0.2185	0.2183	710	VW
0.2105	0.2104	$46\bar{2}$	VW

*Monoclinic cell $a = 1.7550$, $b = 1.4527$, $c = 1.2029$ nm and $\beta = 119.46$, $V = 2.6702$ nm^3.
Intensity: VW = Very weak; W = weak; M = medium; S = strong; VS = very strong.

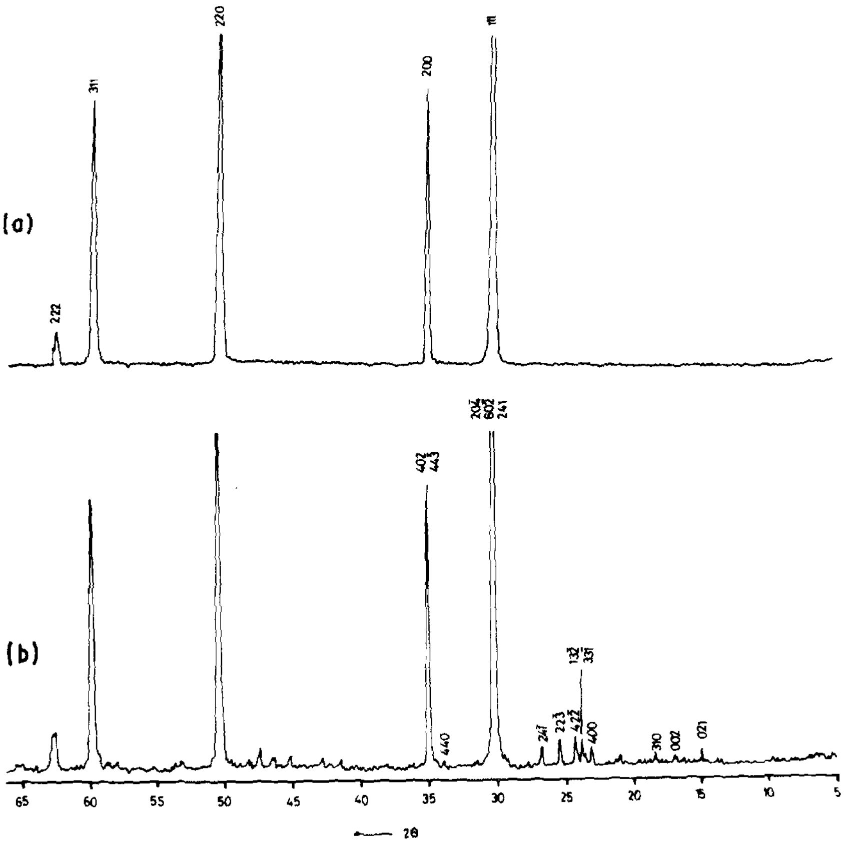

Figure 6 X-ray diffraction patterns of disordered and ordered phases, (a) fluorite (> 1235° C) and (b) $CaZr_4O_9$ (1195° C) compounds.

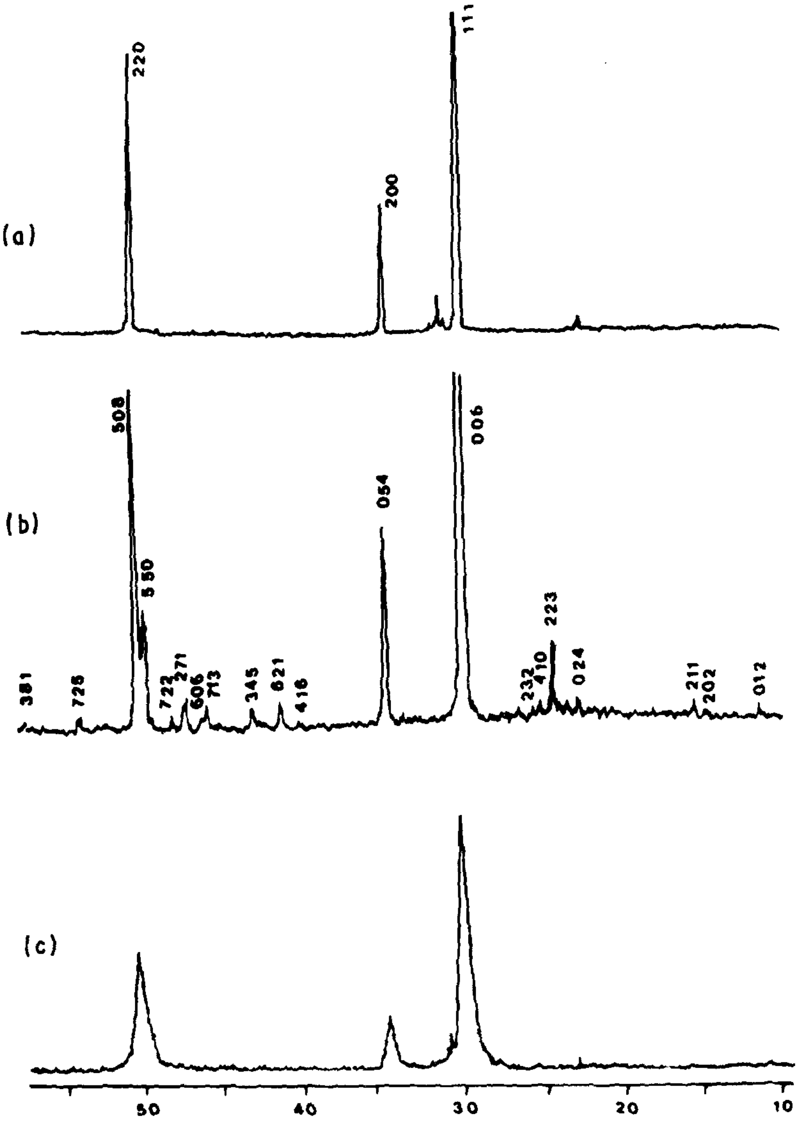

Figure 7 X-ray diffraction patterns of disordered fluorite + CZ and $Ca_6Zr_{19}O_{44}$. (a) F + CZ (> 1365° C), (b) ϕ_2 (1195° C), (c) T(F) + CZ (< 1100° C).

TABLE III Indexing of $Ca_6Zr_{19}O_{44}$ compound*

d (nm)			
Observed	Calculated	*hkl*	Intensity
0.7688	0.7738	0 1 2	W
0.5901	0.5905	2 0 2	VW
0.5622	0.5668	2 1 1	MW
0.4237	0.4261	1 3 1	VW
0.3839	0.3869	0 2 4	MW
0.3601	0.3615	2 2 3	M
0.3504	0.3454	4 1 0	W
0.3342	0.3360	2 3 2	W
0.2962	0.2981	5 0 2	VS
0.2650	0.2709	3 3 3	W
0.2576	0.2577	0 5 4	S
0.2239	0.2246	4 1 6	VW
0.2184	0.2178	6 2 1	MW
0.2097	0.2080	1 2 8	W
0.1975	0.1976	7 1 3	MW
0.1963	0.1968	6 0 6	W
0.1925	0.1922	2 7 1	MW
0.1890	0.1889	7 2 2	W
0.1829	0.1827	5 5 0	S
0.1814	0.1816	5 0 8	VS
0.1697	0.1698	7 2 5	W
0.1603	0.1600	3 8 1	W

*Rhombohedric cell $a = 1.8274$, $c = 1.7742$ nm.
Intensity: VW = Very weak; W = weak; M = medium; S = strong; VS = very strong.

the indexing of the $CaZr_4O_9$. The lattice parameters for this phase were $a = 1.7550 \pm 0.0005$ nm, $b = 1.4527 \pm 0.0005$ nm, $c = 1.2029 \pm 0.0005$ nm, and $\beta = 119.46°$. These values are in agreement with those reported by Hellmann *et al.* [10], although these are slightly lower. By heating small samples of the $CaZr_4O_9$ phase to successively higher temperatures the transition to a disordered fluorite solid solution has been found to occur at 1232 ± 5° C. This feature disagrees with that of Hellmann *et al.* [10] in which a peritectoidal decomposition $CaZr_4O_9 \rightarrow$ fluorite solid solution + $Ca_6Zr_{19}O_{44}$ was established. In the present work, as will be later seen, such peritectoidal decomposition was not detected either in the heating or in the cooling. It should be noted that the disordering of the $CaZr_4O_9$ phase was very rapid at 1235° C, and only a few hours were necessary to reach completion. Therefore the order–disorder transition temperature must be somewhat lower than that reported by Hellmann *et al.* [10].

At both sides of the considered ideal $CaZr_4O_9$ composition, the lattice parameters of the ordered phase varied with the composition, and the monoclinic unit cell volume was 2.6607 nm^3 for 19.5 mol % CaO composition, 2.6702 nm^3 for $CaZr_4O_9$ in the pure state, and 2.687 nm^3 for the 20.5 mol % CaO composition. It suggests that the $CaZr_4O_9$ compound could not be a line in the system, and that a very narrow homogeneity range must exist for this phase. If this is so, then an ideal formula for this monoclinic phase probably does not exist. In this way Hellmann *et al.* [10] found that this phase, after a prolonged heat-treatment, rejected some zirconia, and no variation in the unit cell was detected. At the present time this discrepancy is not well understood. Below approximately 1100° C, Φ_1 is not stable.

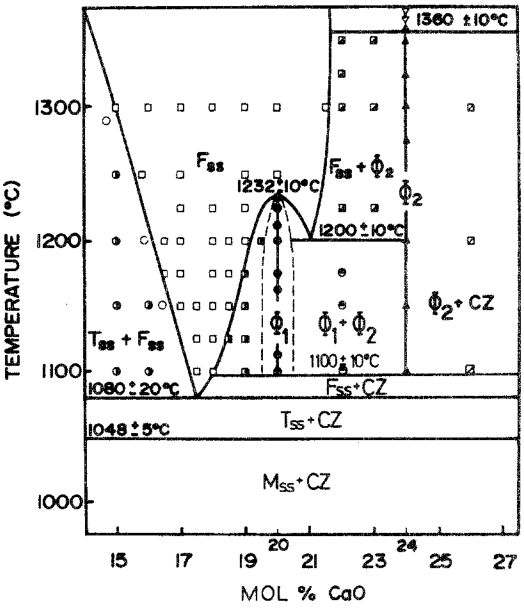

Figure 8 Scanning electron microscopy results and precise cell dimension measurements obtained on low temperature reacted samples.

The hexagonal compound $Ca_6Zr_{19}O_{44}$ was found to be stable between approximately 1100 and 1360 ± 10° C. Below that temperature a mixture of two phases, fluorite or tetragonal zirconia + CZ was found. As described above it seems probable that the tetragonal zirconia is a precursor of the $Ca_6Zr_{19}O_{44}$ phase formation. Fig. 7 shows the X-ray diffraction powder diagram for the $Ca_6Zr_{19}O_{44}$ ordered phase, and Table III shows the calculated and observed *d* (nm) values and their relative intensities. The lattice parameters measured for this phase are $a_H = 1.8274$ nm and $c_H = 1.7742 \pm 0.0005$ nm. The constancy of the same at both sides of the ideal composition, 76 mol % ZrO_2–24 mol % CaO, suggests that the hexagonal compound $Ca_6Zr_{19}O_{44}$ is a line in the system. Above 1360° C it decomposes peritectoidally into two phases, fluorite solid solution + CZ, in close agreement with the results reported by Hellmann *et al.* [10]. The fact that tetragonal zirconia + CZ below 1100° C was also found in the case of the 20 mol % CaO composition enables one to establish the phase equilibrium diagram for this zone of the ZrO_2–CaO system as shown in Fig. 8, in which there are some differences from that reported by Hellmann *et al.* [10]. The complete phase equilibrium diagram for this system will need more investigation, if the complex metastability phenomena present are taken into account; however from the experimental results described above a new tentative phase equilibrium for the ZrO_2–CaO system can be proposed, as shown in Fig. 5.

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