JOURNAL OF MATERIALS SCIENCE 31 (1996) 4945–4949

Solid solutions of metastable tetragonal ZrO_2 and Ce_3ZrO_8 in the system ZrO_2–CeO_2

AKIO KAWABATA, SHINGO HIRANO, MASARU YOSHINAKA, KEN HIROTA, OSAMU YAMAGUCHI*
Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyoto Tanabe 610-03, Japan

In the system ZrO_2–CeO_2, metastable t-ZrO_2 solid solutions containing up to 30 mol % CeO_2 crystallize at temperatures of 385–430 °C from amorphous materials prepared by the hydrazine method. Crystalline Ce_3ZrO_8 solid solutions are formed in as-prepared powders between 30–75 mol % CeO_2. The variation of the lattice parameters of both solid solutions is determined as a function of CeO_2 content. The value of the lattice parameter of pure Ce_3ZrO_8 (cubic) is $a = 0.5342$ nm. Detailed characterization of the Ce_3ZrO_8 powder has been performed. Crystallite size and particle size are strongly dependent on the heating temperature. Specific surface areas do not drop below 40 $m^2 g^{-1}$ until the heating temperature is above 1000 °C.

1. Introduction

Since the solid solutions in the system ZrO_2–CeO_2 are important for electrode materials, fuel cells, and toughened ceramics, many studies have been undertaken on the phase relationships in this system [1]. Two compounds are known to exist in this system: $Ce_2Zr_3O_{10}$ (tetragonal) [2–4] and $Ce_{0.75}Zr_{0.25}O_2$ (Ce_3ZrO_8, cubic) [5]. During the course of the preparation of the phase diagram, Longo and co-workers [2–4] showed the presence of a new binary phase which was intimated by measurements of electrical conductivity as a function of temperature. X-ray diffraction studies [4] identified the phase as being $Ce_2Zr_3O_{10}$, which is stable at temperatures below 870 °C. However, Tani *et al.* [6] reported that no presence of this compound could be found in the phase diagram attained by hydrothermal techniques. However, little detailed attention has been paid to the formation of Ce_3ZrO_8. The only report dealing with the subject was published by Smith and McCarthy [5]; the compound was formed by heating for 48 h at 1400 °C using coprecipitated powders from cerium and zirconium nitrates.

The present authors have developed a new powder preparation method using hydrazine monohydrate [7–9]. In this study, solid solutions of metastable t-ZrO_2 and Ce_3ZrO_8 were found to form up to 30 mol % CeO_2 and between 30–75 mol % CeO_2, respectively, by the hydrazine method. In addition, well-crystallized Ce_3ZrO_8 was formed near room temperature. The present paper deals with the formation of both solid solutions and the characterization of Ce_3ZrO_8.

2. Experimental procedure

Zirconium oxynitrate ($ZrO(NO_3)_2 \cdot 2H_2O$, 99.9% pure), cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.9% pure), and hydrazine monohydrate ($(NH_2)_2 \cdot H_2O$, 80%) were used as the starting materials. The former two materials were adjusted to 0.5 mol/L aqueous solutions by dissolving in distilled water. The mixed aqueous solution (pH = 2) was stirred with a magnetic stirrer for 30 min at room temperature, and then hydrazine monohydrate was dripped into the mixed solution at 60 °C, with stirring, until the resulting suspension reached pH = 8. Then, the suspension was heated for 1 h at the same temperature. The products of the various compositions, shown in Table I[‡], were separated from the suspensions by centrifugation, washed more than five times in hot water to remove adsorbed hydrazine and nitride ions, and then dried at 120 °C under a reduced pressure. The powders obtained are termed "starting powders A through P".

The starting powders and specimens, obtained from the differential thermal analysis (DTA) runs after cooling, were examined by X-ray diffraction (XRD) using Ni-filtered CuK_α radiation. Electron microscopic examination of the powders was carried out using transmission electron microscopy (TEM).

---

* To whom all correspondence should be addressed.

[‡] Each product from $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ prepared by the present method consisted of crystalline CeO_2 and an amorphous material. As will be described, t-ZrO_2 crystallized at 385–430 °C. Therefore, the starting powders were described by the oxide composition.

TABLE I Chemical composition of the starting powders

Starting powder	Composition (mol %)	
	ZrO_2	CeO_2
A	100	0
B	95	5
C	90	10
D	85	15
E	80	20
F	75	25
G	70	30
H	65	35
I	60	40
J	55	45
K	50	50
L	45	55
M	40	60
N	35	65
O	30	70
P	25	75

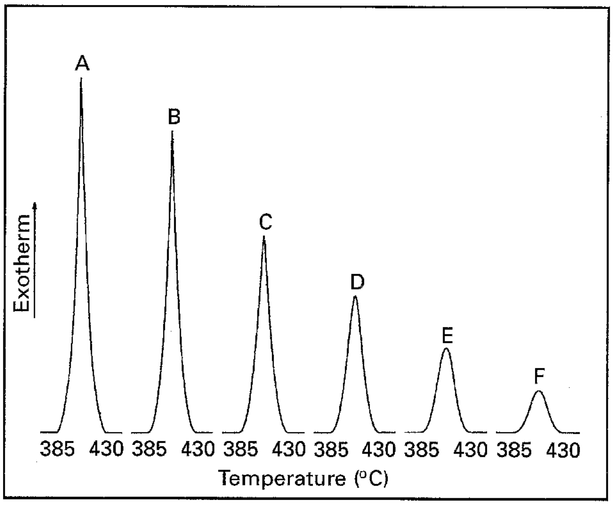

Figure 1 DTA curves for starting powders A through F.

The crystallite size was determined from X-ray line broadening [10]. The specific surface areas of heated specimens were measured by the Brunauer-Emmett-Teller (BET) method of nitrogen adsorption performed on powders that had been dried at 250 °C in vacuum.

3. Results and discussion

3.1. Crystallization of pure ZrO_2

The starting powder A is amorphous. Fig. 1A shows a DTA curve of this powder; it reveals a sharp exothermic peak resulting from the crystallization of t-ZrO_2 at 385–430 °C. The formation of t- or c-ZrO_2 at low temperatures has been reported by many investigators, see for example reference [11]. In the present study, t-ZrO_2 heating continued to be crystallized as the only observed phase at temperatures up to 700 °C. Interplanar spacings were measured via XRD techniques with the aid of an internal standard of high-purity silicon, and unit-cell values were determined by a least-squares refinement. The value of the lattice parameter of t-ZrO_2 prepared by heating for 1 h at 600 °C was $a = 0.5087$ nm and $c = 0.5167$ nm. These values agree with data ($a = 0.509$ nm and $c = 0.518$ nm) for the tetragonal form obtained by the hydrothermal treatment of amorphous hydrated ZrO_2 precipitated from zirconyl oxychloride solution with ammonia [12]. ZrO_2 powders heated at 720–1050 °C were mixtures of t- and m-ZrO_2, the amount of the latter form increasing with increasing temperature. Single-phase m-ZrO_2 was produced after heating at 1070 °C.

3.2. Crystallization of the t-ZrO_2 solid solution

The starting powders B through F showed exothermic peaks in the same temperature range (385–430 °C) as in A. However, with increased CeO_2 content they decreased successively in height from B to F (Fig. 1). As described below, these peaks resulted from the crystallization of t-ZrO_2 solid solutions. No significant changes in the amorphous structure for the powders B through F, were observed up to the temperatures of the exothermic peaks. The specimens heated at higher temperatures showed single phase t-ZrO_2 in XRD patterns. The XRD peaks of the m-ZrO_2 phase began to appear for the B powder at 1100 °C and the intensity increased with increasing temperature in inverse proportion to that of the m-ZrO_2 phase. Finally, the m-ZrO_2 phase for B and t-ZrO_2 phases for C through F were produced when heated at 1300 °C. These results suggest that metastable ZrO_2 solid solutions were formed up to 30 mol % CeO_2 contents.

Compositional changes result in a significant variation in the cell dimensions. Fig. 2 shows the variation of lattice parameters of t-ZrO_2 phases prepared by heating at 1000 °C (1 h) for B and 1200 °C (1 h) for C through F; with increased CeO_2 content. The values

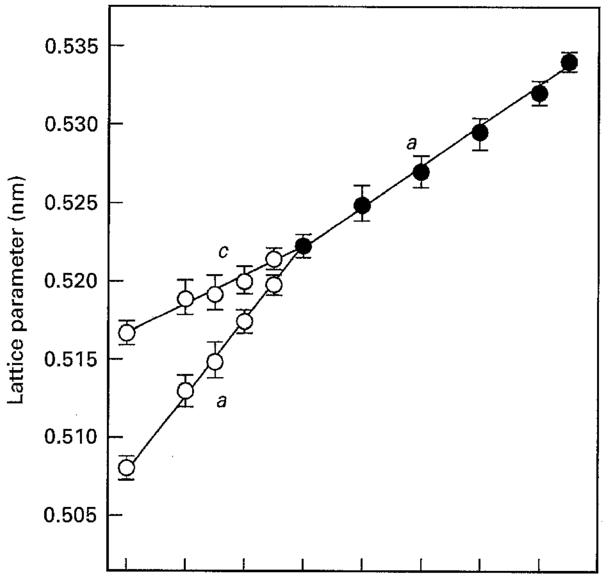

Figure 2 Lattice parameters for (○) t-ZrO_2 phase and (●) Ce_3ZrO_8 phase as a function of composition.

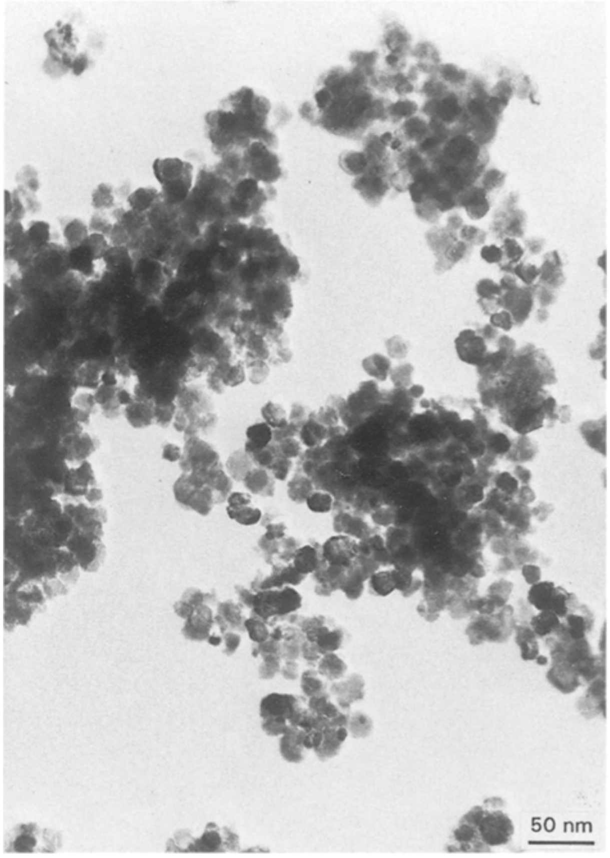

Figure 3 Transmission electron micrograph of starting powder P.

changed linearly with a and c increasing from 0.5087 to 0.5224 nm and from 0.5167 to 0.5224 nm, respectively.

3.3. Crystallization of the Ce_3ZrO_8 solid solution

The XRD analysis of powders G through O revealed the existence of crystalline Ce_3ZrO_8 [5]; with increased CeO_2 content, the diffraction peaks were shifted to a lower diffraction angle and increased in intensity. No peaks due to the crystallization of the t-ZrO_2 solid solution occurred in the DTA curves. The evidence thus obtained supports the view that Ce_3ZrO_8 solid solutions containing ZrO_2 were formed between 30–75 mol % CeO_2. The XRD peaks of t-ZrO_2 resulting from the decomposition of Ce_3ZrO_8 solid solutions appeared at 1050 °C. The specimens heated at 1200 °C were mixtures of Ce_3ZrO_8 and t-ZrO_2. The lattice parameters of the solid solutions are shown in Fig. 2. The lattice parameter, a, increased linearly from 0.5224–0.5317 nm with increased CeO_2 content. No formation of $Ce_2Zr_3O_{10}$ described by Longo and co-workers [2–4] was observed in the present study.

3.4. Characterization of Ce_3ZrO_8

The starting powder P, consisting of primary particles of size ≈15 nm (Fig. 3), produced an XRD pattern consistent with well-crystallized Ce_3ZrO_8. Table II contains this XRD data. All diffraction peaks could be indexed as a cubic unit cell with $a = 0.5403$ nm. In the DTA curve an endothermic peak resulting from the release of absorbed water occurred at 90–180 °C. The lattice parameter of Ce_3ZrO_8 heated for 1 h at 400 °C after dehydration was $a = 0.5342$ nm, agreeing with the value ($a = 0.5349$ nm) reported in reference [5] (Table II, Fig. 2).

Ce_3ZrO_8 powders heated to various temperatures at a heating rate of 10 °C per min were fully characterized. Fig. 4 shows the electron micrographs of the powders. The average particle size in the powders for temperatures up to 900 °C was almost the same as that of powder P. Particles of ≈20 nm size were observed in the powder at 1000 °C. They grew to ≈50 nm and ≈80 nm at 1100 °C and 1200 °C, respectively and attained ≈150 nm at 1300 °C. The crystallite size was calculated using the (111) diffraction peak by application of the Scherrer formula [10], $D = 0.9\lambda/\beta\cos\theta$, where D is the crystallite size, λ is the wavelength (CuK_α), β is the corrected halfwidth obtained using the (111) line of high-purity silicon as the standard and the Warren formula [10] and θ is the diffraction angle. The variation of crystallite size with increasing

TABLE II X-ray diffraction data for Ce_3ZrO_8

As-prepared powder$^{(a)}$				Sample heated for 1 h at 400 °C$^{(b)}$				Data of Reference [1]$^{(c)}$	
d_{obs} (nm)	d_{calc} (nm)	I/I_0	hkl	d_{obs} (nm)	d_{calc} (nm)	I/I_0	hkl	d (nm)	I/I_0
0.312	0.312	100	1 1 1	0.308	0.308	100	111	0.3090	100
0.270	0.270	30	2 0 0	0.267	0.267	30	200	0.2675	35
0.191	0.191	50	2 2 0	0.189	0.189	45	220	0.1892	60
0.1631	0.1630	35	3 1 1	0.1611	0.1611	30	311	0.1614	50
0.1559	0.1560	10	2 2 2	0.1542	0.1542	15	222	0.1544	12
0.1352	0.1351	5	4 0 0	0.1336	0.1336	5	400	0.1337	10
0.1240	0.1240	10	3 3 1	0.1226	0.1226	10	331	0.1228	20
0.1210	0.1208	10	4 2 0	0.1195	0.1195	10	420	0.1197	14
0.1104	0.1103	10	4 2 2	0.1091	0.1091	10	422	0.10921	18
0.1040	0.1040	10	5 1 1	0.1028	0.1028	10	511	0.10296	16
0.0955	0.0955	< 5	4 4 0	0.0945	0.0945	< 5	440	0.09456	6
0.0913	0.0913	10	5 3 1	0.0903	0.0903	10	531	0.09042	16
0.0900	0.0900	< 5	6 0 0	0.0891	0.0891	< 5	600	0.08915	8

$^{(a)}$ cubic; $a = 0.5403$ (nm). $^{(b)}$ cubic; $a = 0.5342$ (nm). $^{(c)}$ cubic; $a = 0.5349$ (nm).

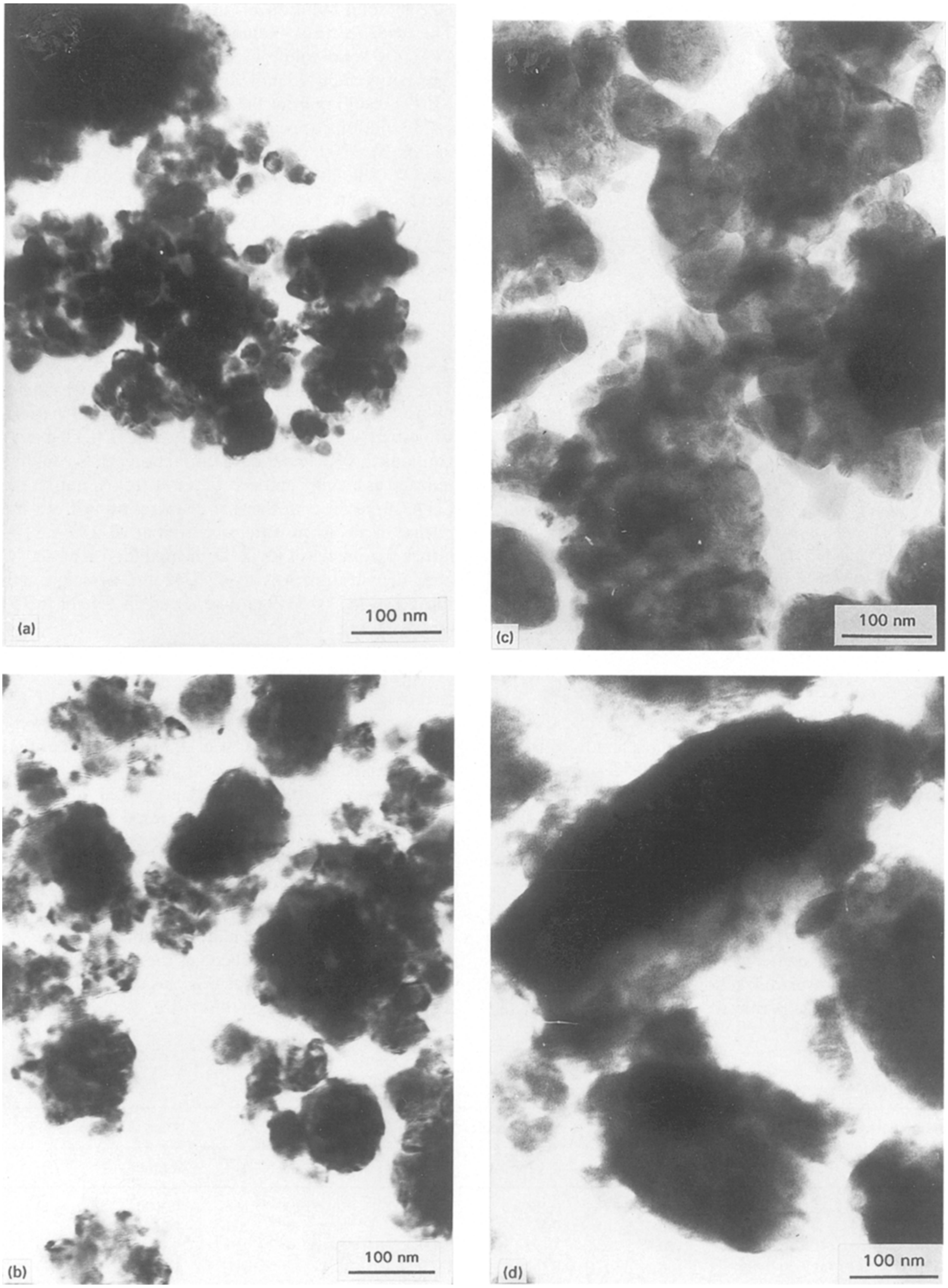

Figure 4 Transmission electron micrographs of Ce_3ZrO_8 powders heated at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

temperature is shown in Fig. 5. A marked increase in crystallite growth occurred above 1100 °C. This result agrees with the observations made by electron microscopy. A decrease in specific surface area with increasing temperatures is shown in Fig. 5. Surface areas at low temperatures were very high, although they decreased rapidly between 800–1100 °C, the value at 1000 °C was still 40 $m^2 g^{-1}$.

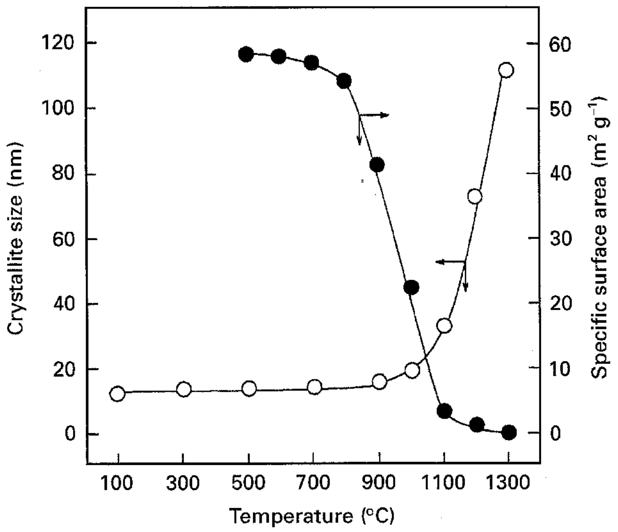

Figure 5 Crystallite size and specific surface area of Ce_3ZrO_8 powders heated at various temperatures.

4. Conclusions

Little detailed attention has been paid to the formation of Ce_3ZrO_8 (cubic). The hydrazine method has been applied to the preparation of the compounds in the system ZrO_2–CeO_2. Solid solutions of metastable t-ZrO_2 and Ce_3ZrO_8 are formed up to 30 mol % CeO_2 and between 30–75 mol % CeO_2, respectively. Well-crystallized Ce_3ZrO_8, consisting of ultra fine particles ($\approx$ 15 nm), is formed in the as-prepared powder. Crystallite size and particle size of the Ce_3ZrO_8 powder are strongly dependent on the heating temperature. Surface areas at low temperatures are very high; the value at 1000 °C is still 40 $m^2 g^{-1}$.

References

1. V. S. STUBICAN and J. R. HELLMANN, in "Advances in Ceramics Vol. 3, Science and Technology of Zirconia", edited by A. H. Heuer and L. W. Hobbs (American Ceramic Society, Columbus, OH, 1981) pp. 25–36.
2. V. LONGO and S. ROITTI, *Ceramurgia Int.* **1** (1971) 4.
3. S. ROITTI and V. LONGO, *ibid.* **2** (1972) 97.
4. V. LONGO and D. MINICHELLI, *J. Amer. Ceram. Soc.* **56** (1973) 600.
5. Powder Diffraction File, Card No. 28–271. (Joint Committe on Powder Diffraction Standards, Swarthmore, PA, 1986).
6. E. TANI, M. YOSHIMURA and S. SŌMIYA, *J. Amer. Ceram. Soc.* **66** (1983) 506.
7. K. ISHIDA, K. HIROTA, O. YAMAGUCHI, H. KUME, S. INAMURA and H. MIYAMOTO, *ibid.* **77** (1994) 1391.
8. S. KIMOTO, K. HIROTA, O. YAMAGUCHI, H. KUME, S. INAMURA and H. MIYAMOTO, *ibid.* **77** (1994) 1694.
9. M. FUKUYA, K. HIROTA, O. YAMAGUCHI, H. KUME, S. INAMURA and H. MIYAMOTO, *Mater. Res. Bull.* **29** (1994) 619.
10. M. I. OSENDI, J. S. MOYA, C. J. SERNA and J. SORIA, *J. Amer. Ceram. Soc.* **68** (1985) 135.
11. T. MITSUHASHI, M. ICHIHARA and V. TATSUKE, *ibid.* **57** (1974) 97.
12. H. NISHIZAWA, N. YAMASAKI, K. MATSUOKA and H. MITSUSHIO, *ibid.* **65** (1982) 343.

Received 2 August 1994
and accepted 13 February 1996