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Effect of Preparation Conditions on the Phase Composition of ZrO_2–Al_2O_3–CeO_2 Powders

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Abstract—Data are presented on the phase composition of ZrO_2–Al_2O_3–CeO_2 powders containing 10, 30, and 70 mol %, prepared via coprecipitation and successive precipitation. The precipitation procedure is shown to have a strong effect on the phase composition of the heat-treated powders and the state (inter- or intracrystalline) of the T-ZrO_2 phase, thereby changing its stability. At an Al_2O_3 content of 30 mol %, the M-ZrO_2 content is independent of the precipitation procedure.

INTRODUCTION

The ZrO_2–Al_2O_3 system is of immense importance in the production of structural ceramics possessing high strength and fracture toughness owing to the partial stabilization of tetragonal (T) or cubic (C) ZrO_2 via doping with rare-earth or other cations [1, 2].

ZrO_2 and Al_2O_3 do not form solid solutions. The eutectic temperature in the ZrO_2–Al_2O_3 system is in the range 2193–1983°C, but the eutectic composition has not been established with certainty and has been variously reported to be 45 [3], 30 [4], or 38 mol % ZrO_2 [5]. At the same time, according to Adylov *et al.* [6] single-phase T-ZrO_2-based materials can be obtained in the composition range 35–70 mol % ZrO_2 under certain conditions. Such materials must possess a high strength.

One advantageous method for preparing ceramic powders is the sol–gel process, which enables the preparation of materials with controlled structure and particle size [7–9]. As shown earlier using zirconium and yttrium hydroxides as an example [9], the precipitation sequence may have a significant effect on the phase composition of the reaction products since it influences the size and elastic strain of the particles.

The purpose of this work was to study the effect of the precipitation sequence in systems containing Zr, Al, and Ce cations on the phase composition of the products of subsequent calcination.

EXPERIMENTAL

Characterization techniques. The specific surface of the powders was determined by low-temperature BET measurements (Autosorb-1 instrument).

Particle-size analysis and microstructural examination were performed using a JSM-35CF scanning electron microscope (SEM) at an accelerating voltage of 20 kV and magnifications from ×1000 to ×10000.

Phase composition was determined by x-ray diffraction (XRD) analysis on a DRON-3 diffractometer (CuK_α radiation) using JCPDS Powder Diffraction File data. Quantitative phase analysis was carried out using XRD intensity data and well-crystallized calibration standards.[1]

The elemental composition of the powders was determined using a Getan energy-dispersive spectrometer equipped with Si(Li) detectors.

Synthesis of powders. T-ZrO_2 was partially stabilized by introducing CeO_2. The basic composition contained 88 mol % ZrO_2 and 12 mol % CeO_2. The Al_2O_3 content was 10, 30, or 70 mol %.

Hydroxides were precipitated by adding aqueous 1 M solutions of zirconyl chloride, cerium nitrate, and aluminum nitrate to aqueous 6 M ammonia [7, 10].

In our preparations, we used two procedures:

(1) First, zirconium and cerium hydroxides (90, 70, or 30 mol % of the total amount of reagents) were pre-

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[1] The procedure standardized at the State Institute of Glass.

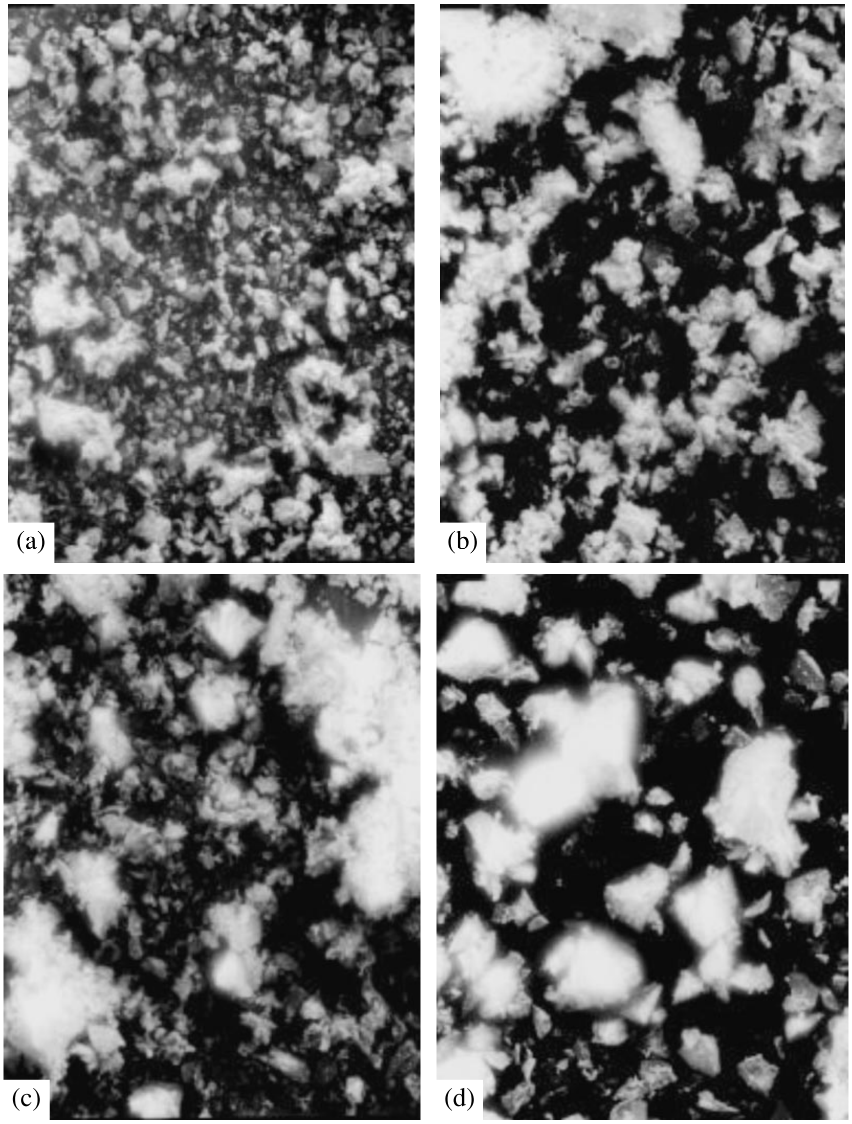

Fig. 1. SEM micrographs of powders prepared by (a, c) successive precipitation and (b, d) coprecipitation, followed by calcination at 950°C; (a, b) 10, (c, d) 70 mol % Al_2O_3.

cipitated. After 15 min, an appropriate amount of the aluminum nitrate solution was added.

(2) The three hydroxides were precipitated in parallel.

Table 1. Specific surface of powders calcined at 950°C

Sample no.	Procedure	mol % Al_2O_3	S, m^2/g
1	Coprecipitation	10	30
2		30	60
3		70	100
4	Successive precipitation	10	50
5		30	60
6		70	120

After drying, the powders were calcined at 950, 1250, 1350, and 1500°C.

RESULTS AND DISCUSSION

The specific surface of the powders was found to depend on the precipitation procedure (Table 1).

As apparent from Table 1, the specific surface of the coprecipitated powders is smaller, presumably because they contain a large amount of an amorphous phase. Typical SEM micrographs of the powders are displayed in Fig. 1.

The powders with a nearly eutectic composition (30 mol % Al_2O_3) are close in specific surface, independent of the precipitation procedure.

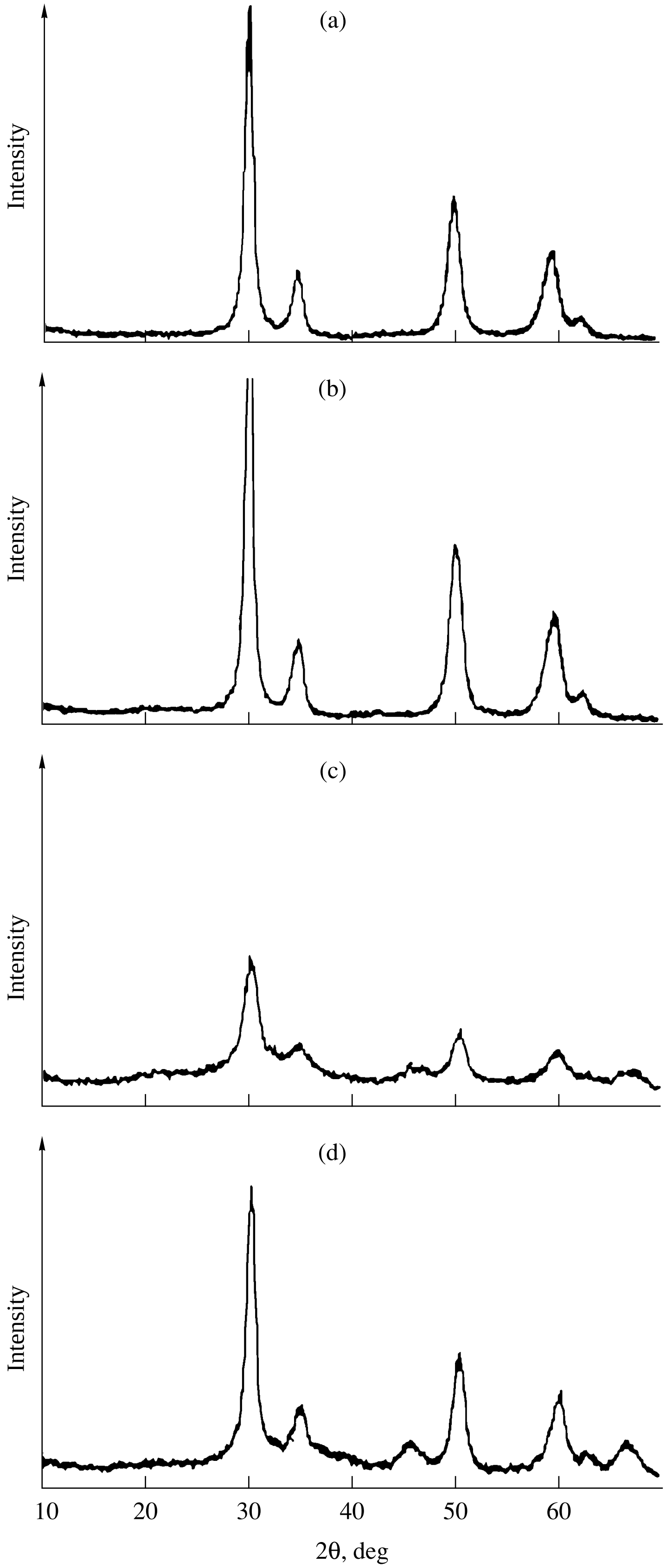

Fig. 2. XRD patterns of samples prepared by (a, c) successive precipitation and (b, d) coprecipitation, followed by calcination at 950°C; (a, b) 10, (c, d) 70 mol % Al_2O_3.

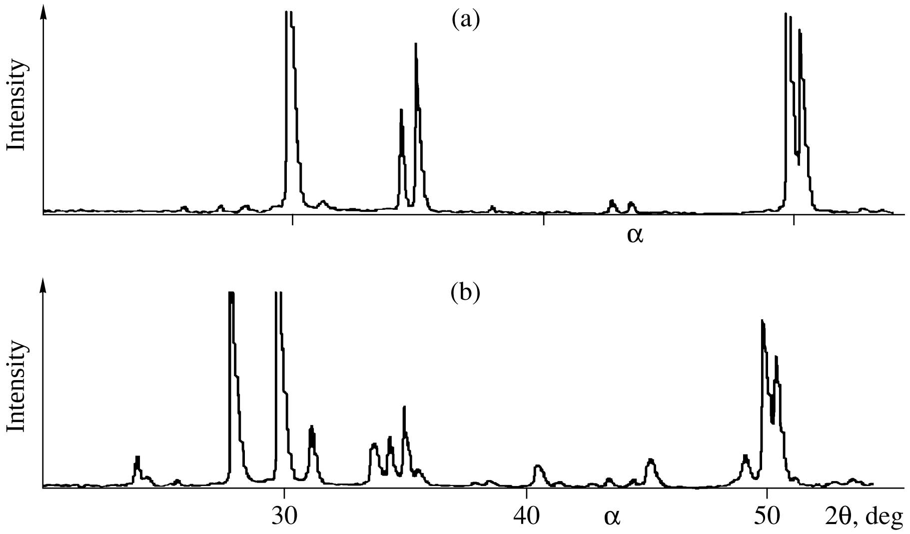

Fig. 3. XRD patterns of samples containing 10 mol % Al_2O_3, prepared by (a) coprecipitation and (b) successive precipitation, followed by calcination at 1500°C.

The phase composition of the samples was found to depend not only on their elemental composition but also on the precipitation procedure (Table 2).

The powders calcined at 950°C consisted, for the most part, of a pseudocubic ZrO_2-based solid solution, independent of the precipitation procedure. In the sample containing 70 mol % Al_2O_3, a small amount of γ-Al_2O_3 was present (Fig. 2).

Note that the fraction of crystalline phases increased nonmonotonically as the calcination temperature was raised from 950 to 1250°C. The likely reasons are that α-Al_2O_3 crystallization occurred in several steps and that this process was accompanied by partial decomposition of the already present metastable, amorphous phases $CeAlO_3$ and $Ce_2O_3 \cdot 11Al_2O_3$, which are readily formed in an oxidizing atmosphere. $CeAlO_3$ is known to undergo a reversible transformation at 980°C [3], and $Ce_2O_3 \cdot 11Al_2O_3$ decomposes in air between 1200 and 1400°C.

In the powders prepared via successive precipitation and containing 10 and 70 mol % Al_2O_3, the tetragonal phase converts rapidly into the monoclinic phase as the

Table 2. Phase composition of heat-treated powders

t_{HT}, °C	Phase composition	Weight percent					
		1*	2	3	4	5	6
950	C-ZrO_2***	75	75	45	88	77	76
1250	T-ZrO_2	75	80	80	85	80	85
	M-ZrO_2	<5	15	<5	>5	15	>5
	α-Al_2O_3	–	–	tr	–	–	tr
1350	T-ZrO_2	85	85	70	75	80	25
	M-ZrO_2	>5	10	15	15	15	35
	α-Al_2O_3	–	>5	15	<5	<10	20
1500**	T-ZrO_2	90	85	55	45	80	20
	M-ZrO_2	<5	<5	20	50	>5	45
	α-Al_2O_3	<5	>5	20	<5	10	30

* The same samples as in Table 1.

** Grinding in a planetary mill.

*** Pseudocubic ZrO_2.

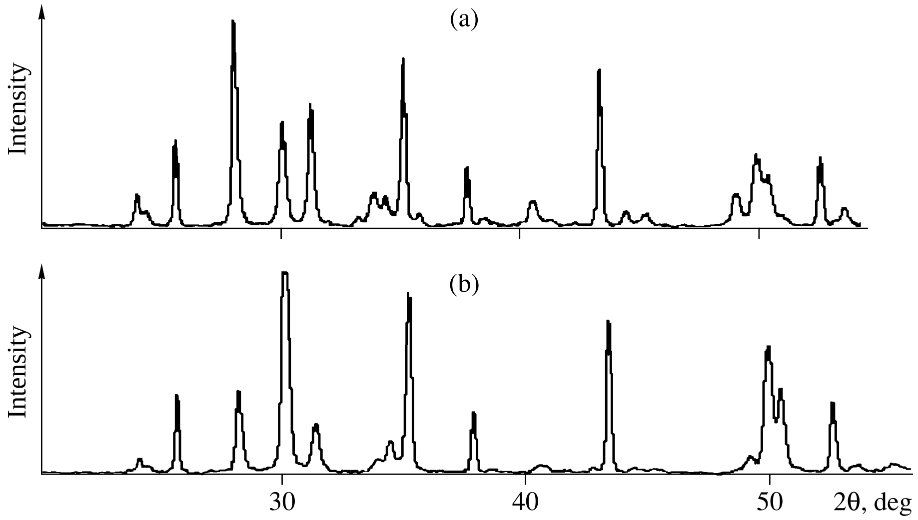

Fig. 4. XRD patterns of samples containing 70 mol % Al_2O_3, prepared by (a) successive precipitation and (b) coprecipitation, followed by calcination at 1500°C.

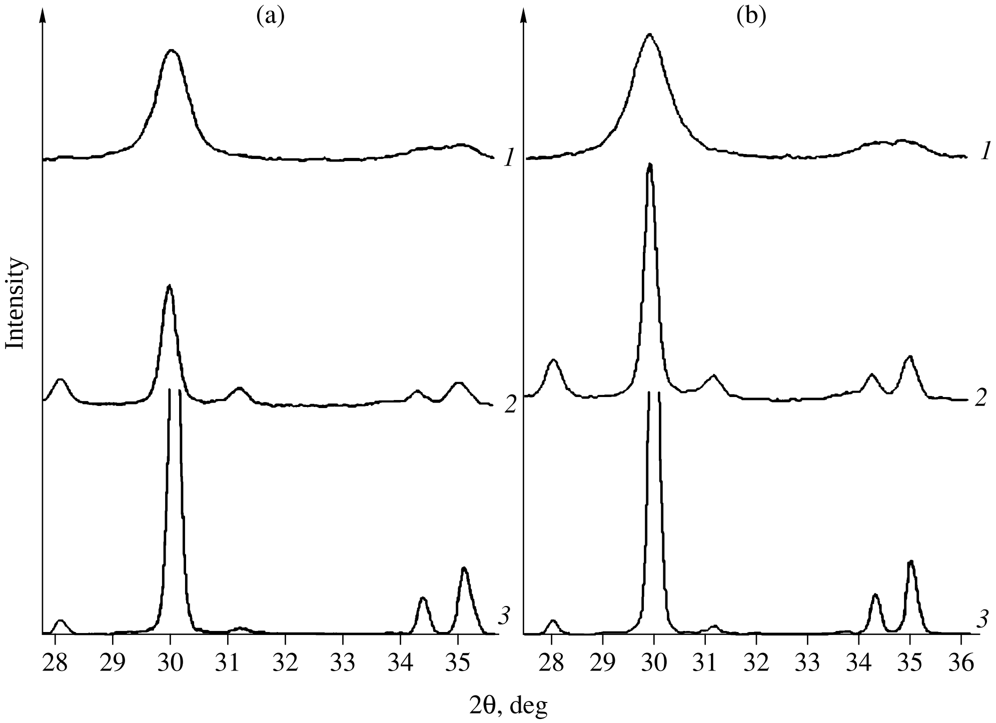

Fig. 5. XRD patterns of powders containing 30 mol % Al_2O_3, prepared by (a) successive precipitation and (b) coprecipitation, followed by calcination at (*1*) 950, (*2*) 1250, and (*3*) 1500°C.

temperature is raised to 1500°C, while the coprecipitated powders with the same compositions contain a *T*-ZrO_2-based solid solution, as evidenced by the XRD scans in the range 2θ = 26°–36° displayed in Figs. 3 and 4.

Zirconia particles may be present in the host material as an intercrystalline or intracrystalline phase [11]. In our experiments, successive precipitation and coprecipitation result in intercrystalline and intracrystalline ZrO_2, respectively. Thermodynamic calculations indicate that *T*-ZrO_2 stabilization depends on the particle size and structural perfection of the material. The thermal expansion mismatch between Al_2O_3 and *T*-ZrO_2 [$(7–8) \times 10^{-6}$ and $(9–11) \times 10^{-6}$ K^{-1}, respectively] gives rise to thermoelastic strain, which varies from 0.2 to 0.4%, depending on orientation [6]. In the coprecipi-

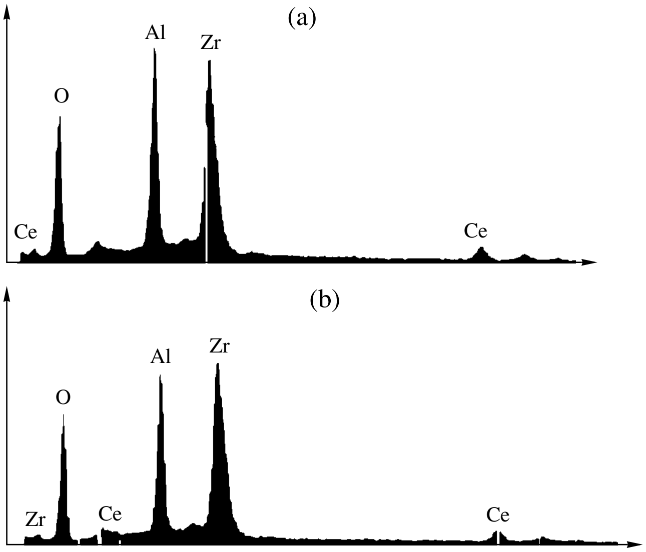

Fig. 6. Chemical composition of powders containing 30 mol % Al_2O_3, prepared by (a) successive precipitation and (b) coprecipitation, followed by calcination at 950°C.

tated powders, the particle size of ZrO_2 is smaller owing to the higher stress, which contributes to T-ZrO_2 stabilization.

These conclusions do not apply to the nearly eutectic samples (30 mol % Al_2O_3), which differ little in crystallinity (Fig. 5), in agreement with earlier reported findings [6]. The likely reason for the insignificant effect of the precipitation procedure is that the particles crystallize from an amorphous eutectic mixture.

According to analytical data, the powders containing 30 mol % Al_2O_3 differ slightly in Al and O contents (Fig. 6). This is probably due to the presence of α-Al_2O_3, which forms in larger amounts during successive precipitation.

CONCLUSION

Using different precipitation procedures in the ZrO_2–Al_2O_3–CeO_2 system, one can produce powders differing not only in particle size but also in crystallinity and, hence, phase composition. Successive precipitation results in intracrystalline T-ZrO_2, which contributes to the stabilization of this phase.

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