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Contribution to phase equilibria in the Ce_2O_3 rich part of the Ce_2O_3–SiO_2–ZrO_2 system

S. Zec[a,*], S. Bošković[a], M. Hrovat[b], M. Kosec[b]

[a] Institute of Nuclear Science Vinča, 11001 Belgrade, P.O.B. 522, Serbia and Montenegro
[b] Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Abstract

Four ternary compositions in the Ce_2O_3 rich part of the Ce_2O_3–SiO_2–ZrO_2 system were investigated. The corresponding mixtures of CeO_2, SiO_2 and ZrO_2 were fired at 1400 °C in an Ar + 7% H_2 atmosphere until the phase equilibria were attained. The samples were characterized by XRD, SEM and EDS analysis. The thermal effects and the mass changes of the fired compositions were monitored by DTA/TG analyses. The oxyapatite phase, $Ce_{4.67}(SiO_4)_3O$, and the fcc phases identified as the solid solutions $(CeZr)O_{2-y}$, $(Ce_zZr_{1-z})O_{2-x}$ and $Ce_2Zr_2O_{7+2\delta}$ were observed in this part of the Ce_2O_3–SiO_2–ZrO_2 system. The DTA/TGA analyses indicated the presence of the Ce^{+4} ions in the fired compositions, while the lowest melting temperature was noticed at 1627 °C.

Keywords: CeO_2; SiO_2; ZrO_2; Firing; Phase equilibria

1. Introduction

Although the information enclosed in the phase diagrams are needed in the materials processing and properties evaluation, the ternary system Ce_2O_3–SiO_2–ZrO_2 from which very good additives for liquid-phase sintering of the covalent Si_3N_4 can be obtained,[1,2] has been to the best of our knowledge, not yet published. The knowledge about the phase relations in this system could be used also in other fields of technology,[3] such as catalysis, environmental protection, microelectronics, fuel cells, etc. That is why its study has started with intention to get information on the phase equilibria.

The properties of the cerium oxides have contributed to the complex phase relations in the Ce_2O_3–SiO_2–ZrO_2 ternary system. Namely, CeO_2 transforms at the elevated temperature depending on the oxygen partial pressure into defect oxides[4] with anion vacancies, CeO_{2-y} $(0 < y < 0.5)$, due to oxygen loss and corresponding reduction of the Ce^{+4} ions to the Ce^{+3} ions. Over the composition range $1.72 < 2 - y < 2$, reduced ceria retains the fcc (face-centered-cubic) fluorite structure at the temperatures higher than 1200 °C. In the range of $0.5 < 2 - y < 1.68$, Ce_2O_3 sesquioxides[5] with the bcc (body-centered-cubic) structure are formed, but at high temperatures they transform into a hexagonal structure.

The related binary phase diagrams of the Ce_2O_3–SiO_2–ZrO_2 ternary system are not completed at the time being and the data published so far are inconsistent. According to the SiO_2–ZrO_2 phase diagram,[6] the binary compound zircon, $ZrSiO_4$, exists in the system. In the Ce_2O_3–ZrO_2 system, however, cerium zirconate,[7] $Ce_2Zr_2O_7$, is formed with the cubic pyrochlore-type structure, which forms the solid solutions in the composition range from 26 to 40 mol% Ce_2O_3. The solid solutions based on Ce_2O_3 or ZrO_2 exist in this system in the narrow composition region, while in the range from 40 to 97 mol% Ce_2O_3 the metastable cubic solid solutions[7] are formed. One of the eutectic reactions[8] in this system is predicted to occur at 2100 °C. It should also, be pointed out, that the nonstoichiometric, $Ce_zZr_{1-z}O_{2-x}$ solid solutions[9] can be formed depending on the stage of CeO_2 reduction and ZrO_2 concentration. Tas and Akinc[10] have found three silicates of the trivalent cerium in the Ce_2O_3–SiO_2 binary system which melt congruently: $Ce_2Si_2O_7$, $Ce_{4.67}(SiO_4)_3O$ and the least stable one, Ce_2SiO_5. The lowest melting eutectic point occurred at 1664 °C between Ce_2O_3 and Ce_2SiO_5. Kaufman et al.[11] have calculated the phase diagram

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[*] Corresponding author at: INN Vinča, 11001 Belgrade, M. Petrovica-Alasa 12-14, P.O.B. 522, Serbia and Montenegro. Tel.: +381 11 2439 454; fax: +381 11 2439 454.
E-mail address: zec@vin.bg.ac.yu (S. Zec).

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of this system and got different results regarding the temperature of the lowest eutectic reaction (1607 °C) as well as Ce_2SiO_5 decomposition through a peritectic reaction at 1647 °C.

In the present paper the approach to phase equilibria in the Ce_2O_3 rich part of the ternary Ce_2O_3–SiO_2–ZrO_2 system after long firing at 1400 °C in an Ar + 7% H_2 atmosphere was studied.

2. Experimental procedure

The powders of CeO_2 (Aldrich, 99.9%, particle size <5 μm), ZrO_2 (magnesium electron) and amorphous SiO_2 (TU1, 99.98%, particle size <10 μm) were used as starting materials for preparing the samples. The mixtures of powders (10 g) were homogenized in a vibratory ball mill, for 2 h in isopropanol and dried at 70 °C. The mixtures were pressed uniaxially into pellets (diameter — 8 mm) under 100 MPa. Heat treatment was performed in a tubular laboratory furnace in a flowing, slightly reducing Ar + 7% H_2 atmosphere with the heating and cooling rate of 5 °C/min. The pellets were placed on molybdenum foils during firing. The samples were fired three times for 6 h at 1400 °C with intermediate grinding.

X-ray powder diffraction (XRD) analysis was carried out by a Siemens D 4 diffractometer in the range from 5 to 100° 2θ with Cu Kα radiation and the scanning speed of 0.04° 2θ/s. XRD was performed after 6 h firing and also after the full firing time. The phase identification was done according to the powder diffraction files (PDF), while the lattice parameters were refined by software WINCELL. Scanning electron microscopy (SEM) and energy-dispersive X-ray analyses (EDS), by JEOL 5800, equipped with an energy-dispersive X-ray analyzer ISIS 300, were used for the microstructure and composition analyses. The microphotographs were taken either by backscattered electrons (BEI) or secondary electrons (SEI) imaging. Differential thermal analysis (DTA) and thermogravimetry (TG) were done simultaneously by Netzsch STA 429 thermal analyzer. The sample in powdered form, previously fired 18 h at 1400 °C, was placed in a Pt crucible and heated at the heating rate of 10 °C/min from room temperature up to 1700 °C under Ar + 7% H_2.

3. Results and discussions

Four ternary compositions (A, B, D and T), pure CeO_2 (C), as well as, two binary compositions P and M (corresponding to the Ce_2SiO_5 stoichiometry), examined in this work are marked in the Ce_2O_3–SiO_2–ZrO_2 composition triangle (Fig. 1). The regions of the solid solutions (s.s.) and the eutectic points (E_1, E_2 and E_3) concerning the binary systems, which are important for these investigations are also marked in the composition triangle.

XRD patterns (Fig. 2) of the composition T fired for 6 and 18 h are the illustration of the minor changes regarding the quantity of the phases formed in the ternary compositions under our experimental conditions. According to the XRD patterns, not only in the ternary compositions fired at 1400 °C but also in the binary composition M, instead of the expected Ce_2SiO_5 phase, the oxyapatite phase $Ce_{4.67}(SiO_4)_3O$ was identified in accordance to the PDF card 43-0441. In all compositions the values of the lattice parameters of the hexagonal unit cell of the oxyapatite phase were $a = 0.9650(3)$ and $c = 0.7109(3)$ nm. Besides, it can be accepted that SiO_2 reacted completely while its diffraction lines have not been observed on the XRD patterns. This indicates that Ce_2SiO_5 is being formed via intermediate reaction stages in subsolidus range.

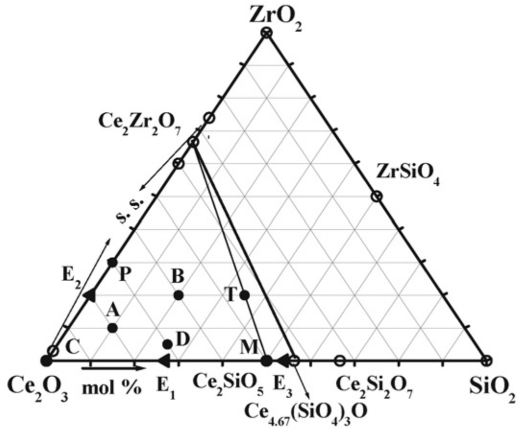

Fig. 1. The concentration triangle of the Ce_2O_3–SiO_2–ZrO_2 system.

Reactions between ceria and zirconia, which concentrations were calculated (Table 1) without reacted ceria in the oxyapatite phase, lead to the formation of the fcc cubic phases. These phases can be identified according to the values of lattice parameter (a) (Table 1). CeO_2 did not exhibit a significant loss of oxygen at the end of firing. In the compositions A and D with the low zirconia concentrations, strong diffractions of the $(CeZr)O_{2-y}$ solid solution and hardly visible diffractions of the $(Ce_zZr_{1-z})O_{2-x}$ solid solution with the higher content of zirconia were observed. In the compositions B, P and T besides these phases, the solid solution of the pyrochlore phase, $Ce_2Zr_2O_{7+2\delta}$, was observed. The presence of the weak $(1\,1\,1)_p$ diffraction in the XRD patterns, characteristic of the pyrochlore structure, confirms the pyrochlore phase formation. However, the smaller lattice parameter values of the pyrochlore phase than the value of 1.07 nm for

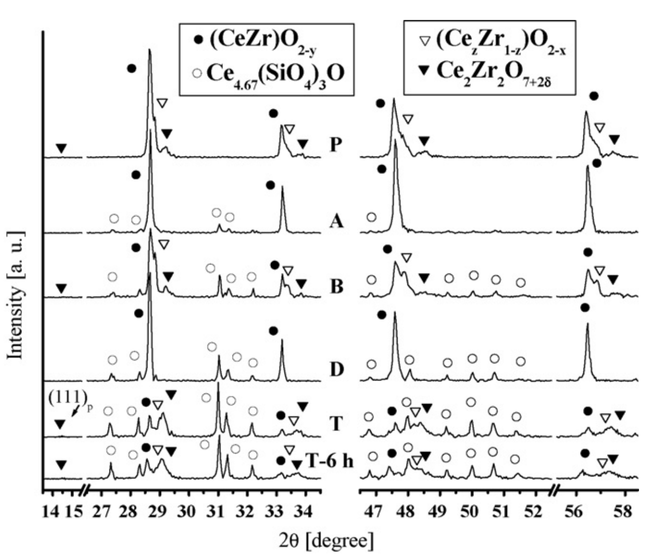

Fig. 2. XRD patterns of the compositions fired at 1400 °C; T for 6 h and T, D, B, A, P for 18 h.

Table 1
Phases formed between ceria and zirconia at 1400 °C, fired 18 h

Sign	Concentration (mol%)		Lattice parameter *a* (nm)		
	Ce_2O_3	ZrO_2	$(CeZr)O_{2-y}$	$Ce_2Zr_2O_{7+2\delta}$	$(Ce_zZr_{1-z})O_{2-x}$
C	100	0	0.5411(2)	–	–
P	70	30	0.5412(2)	1.0634(6)	0.5386(3)
A	88	12	0.5408(2)	–	0.5362(2)
D	91	9	0.5403(1)	–	0.5362(2)
B	69	31	0.5407(3)	1.0610(3)	0.5376(1)
T	47	53	0.5406(2)	1.0631(9)	0.5336(7)

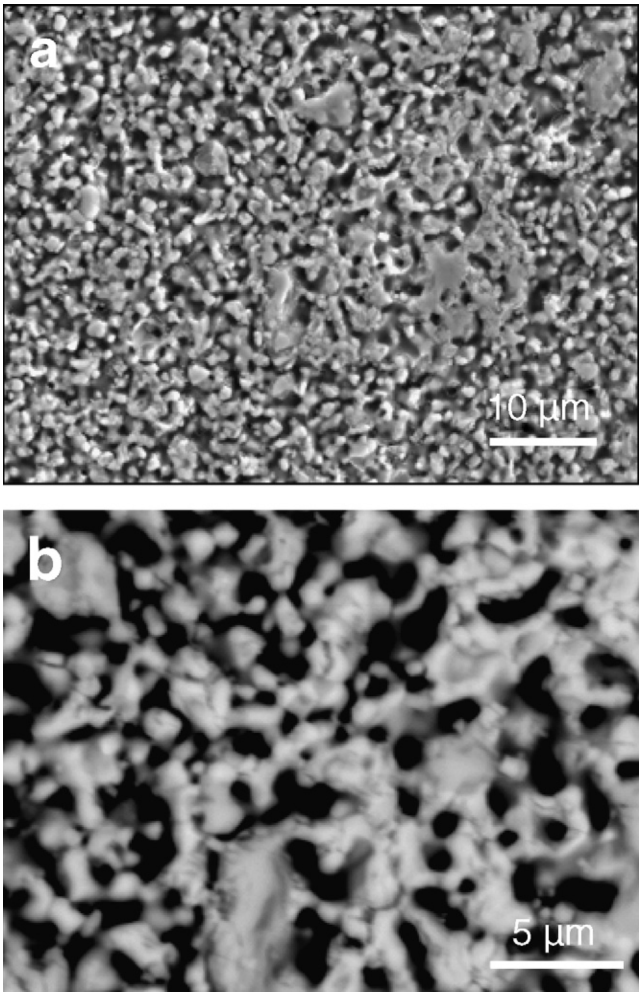

Fig. 3. SEM microphotographs of the composition B, (a) SEI and (b) BEI imaging.

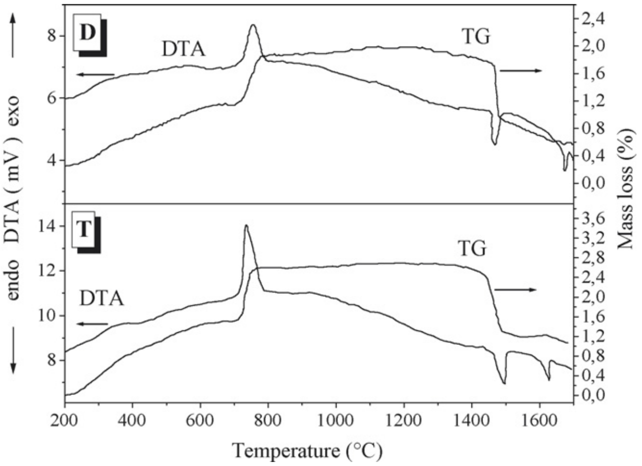

Fig. 4. DTA and TG curves.

the $Ce_2Zr_2O_7$ (PDF 8–221), could be due to the transformation of the pyrochlore phase into κ-$CeZrO_4$[12] during the slow cooling process. This phase retained the ordered distribution of the cations as it is in pyrochlore structure while the oxygen distribution is disturbed. The measured lattice parameters of the $(Ce_zZr_{1-z})O_{2-x}$ solid solutions[13] correspond $z > 0.6$.

The microstructure and composition analysis were performed for T and B samples fired for 18 h. On the SEI and BEI microphotographs of the composition B two micro-constituents, light and dark gray (Fig. 3) are visible. The EDS microanalysis was performed either in a "point" or "over the window". The concentrations of oxides obtained "over the window" are in a good agreement with T and B nominal compositions (Table 2). The concentration of oxides in the dark gray phase corresponds the composition of $Ce_{4.67}(SiO_4)_3O$, while the light gray fields are composed of the phases formed between ceria and zirconia.

On the DTA/TG curves of the T and D compositions (Fig. 4) an exothermic peak due to oxidation[13] of the Ce^{+3} ions appeared at 730 °C with the simultaneous mass increase of 1.2% for

Table 2
The EDS microanalyses

Composition	"Over the window"			Dark gray phase			Light gray fields		
	Ce_2O_3–SiO_2–ZrO_2 (mol%)			Ce_2O_3–SiO_2–ZrO_2 (mol%)			Ce_2O_3–SiO_2–ZrO_2 (mol%)		
T	48	33	20	46	54	0	64	2	34
B	63	19	18	48	52	0	76	1	23

T and 0.7% for D composition, respectively. The oxidation affected mainly the fcc phases formed between ceria and zirconia and partly the cerium silicate phase. At the temperature of about 1500 °C the endothermic reactions take place due to intensive reduction of the Ce^{+4} ions followed by something higher mass loss compared to mass increase in the process of the oxidation. This also indicates the presence of the Ce^{+4} ions in the fired compositions. It is assumed that the reaction of Ce_2SiO_5 forming, takes place at this temperature. The endothermic peaks at 1627 °C (composition T) and 1673 °C (composition D) designated the melting processes of these compositions.

4. Conclusions

The phase equilibria in the Ce_2O_3 rich part of the Ce_2O_3–SiO_2–ZrO_2 system was studied in subsolidus range at 1400 °C in an Ar + 7% H_2 atmosphere. The XRD phase analysis and the EDS microanalysis showed that the hexagonal oxyapatite phase, $Ce_{4.67}(SiO_4)_3O$, as well as the fcc phases composed of ceria and zirconia were formed in the ternary compositions during the firing of 18 h. The fcc phases are identified according to the lattice parameters as the solid solutions $(CeZr)O_{2-y}$, $(Ce_zZr_{1-z})O_{2-x}$ and $Ce_2Zr_2O_{7+2\delta}$. The DTA/TGA analyses indicate the presence of the Ce^{+4} ions in the fired compositions. The lowest melting temperature was noticed at 1627 °C, in composition T. Based on the obtained results, it is obvious that the complex phase relations exist in the Ce_2O_3 rich part of the Ce_2O_3–SiO_2–ZrO_2 system, influenced mainly by the ceria ability to form nonstoichiometric solid solutions depending on the oxygen partial pressure, temperature and the zirconia content.

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