High-pressure synthesis and properties of CeO$_2$-ZrO$_2$ solid solution

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Abstract Using nanoparticles of CeO$_2$ and ZrO$_2$ prepared by the chemical precipitation method as starting materials, the single-phase cubic Ce$_{0.5}$Zr$_{0.5}$O$_2$ solid solution (c-Ce$_{0.5}$Zr$_{0.5}$O$_2$) has been synthesized under 3.1 GPa at 1073 K for the first time. The structure of the c-Ce$_{0.5}$Zr$_{0.5}$O$_2$ has not been changed before and after annealing at 773 K for 1 h. Only an unknown EPR signal (g ~ 1.990) has been observed in the c-Ce$_{0.5}$Zr$_{0.5}$O$_2$ and not varied after annealing at 773 K for 1 h, which exhibited that there exists no Ce$^{3+}$ in the c-Ce$_{0.5}$Zr$_{0.5}$O$_2$ and the Ce$^{4+}$ has not been reduced into Ce$^{3+}$ after annealing. The transport mechanism is ionic for the c-Ce$_{0.5}$Zr$_{0.5}$O$_2$. The bulk conductivity ($\sigma = 1.2 \times 10^{-9}$ S/cm at 823 K, $\sigma = 2.1 \times 10^{-3}$ S/cm at 1123 K) is the same as that of CeO$_2$, but smaller than that of Y$_2$O$_3$-stabilized ZrO$_2$. A marked curvature at $T = 823$ K has been observed in the Arrhenius plot of the bulk conductivity. The activation energy below 823 K is lower than that above 823 K, and the reason has been discussed.

Keywords: CeO$_2$-ZrO$_2$, nanocrystalline, high-pressure and -temperature, solid-state reaction, solid solution.

Since Garvie et al. published the seminal paper$^{[1]}$ on ceramic steel, the formation and properties of ceramic materials and oxide composite materials have been widely investigated and great development has been achieved for their applications. As known, CeO$_2$ and ZrO$_2$ are two kinds of oxide-ion conductors with various important applications. Cerium is a rare-earth element with valence variation, which can have compounds with two oxidation states, Ce$^{4+}$ and Ce$^{3+}$. Compounds containing cerium ions always exhibit novel structures and properties. Zirconia with stable monoclinic structure at room temperature shows various phase transformations with temperature increasing. CeO$_2$-ZrO$_2$ alloys can be formed in any composition, but the formation region of the stable phase is usually restricted by the solubility described in the temperature-composition equilibrium phase diagram$^{[2]}$. There are only few reports$^{[3-5]}$ published on the properties of CeO$_2$-ZrO$_2$ solid solutions so far because the preparation of single-phase solid solutions is more difficult. But it has been affirmed that some phases of CeO$_2$-ZrO$_2$ solid solutions exhibit novel properties, such as tetragonal zirconia-ceria solid solution exhibiting the excellent mechanical properties$^{[6-8]}$, which appears to be feasible as structural materials for cryogenic application. Therefore, the study on the formation and properties of CeO$_2$-ZrO$_2$ solid solutions has attracted considerable attention, and several techniques have been used to produce CeO$_2$-ZrO$_2$ solid solutions$^{[6-8]}$. The melt-quenching technique$^{[9]}$ often yields composition inhomogeneities in CeO$_2$-ZrO$_2$ system due to the evaporation and/or the segregation of CeO$_2$. The non-equilibrium cooling method$^{[10]}$, which was first utilized to prepare CeO$_2$-ZrO$_2$ solid solutions from mechanically mixed oxide powders, requires a high temperature treatment for some hours to homogenize the ceria composition. Excellent precursor has been required to prepare homogeneous solid solutions at lower temperatures and/or for shorter annealing time. Wet-chemical method$^{[5]}$, hydrothermal method$^{[11]}$ and mechanical milling method$^{[12]}$ have widely been utilized to obtain homogeneous precursor in recent years.

The crystallite size of nanoparticles is very small and there are a large number of atoms on the surface of nanoparticles. After forming nanosolids, the free surface of nanoparticles changes into the interface of grains. The previous studies on thermal diffusion indicated that the ratio interface energy in nanometer materials is two times as large as that in normal polycrystalline materials, and diffusion coefficient of interface atoms in the former is 10$^4$ higher than that in the latter$^{[13, 14]}$. Because it can strongly change the interatomic distance and atomic states in solid materials, the pressure, which is similar to temperature and composition, would also influence the structure and properties of solid materials to a certain extent. Therefore, it will be very interesting to study the formation of solid solution and the solid-state reaction mechanism using nanocrystalline mixtures as starting materials under high pressure. There has so far been no report on the formation of CeO$_2$-ZrO$_2$ solid solutions under high pressure and high temperature. In this work, using nanoparticles of CeO$_2$ and ZrO$_2$ prepared by the chemical precipitation method as starting materials, the high-pressure synthesis and properties of the Ce$_{1-x}$Zr$_x$O$_2$ solid solutions have been investigated for the first time.

1 Experimental procedure

The ultrafine precursor powders of ZrO$_2$ were prepared by the precipitation method. The ZrOCl$_2$ · 8H$_2$O (A,R) was dissolved into distilled water (0.075 mol/L). The solution was first dropped slowly into the NaOH solution with pH value of 9 at 333 K, while another NaOH solution (0.1 mol/L) was also dropped slowly into the mixed solution in order to keep the pH value constant, with magnetic stirring until the precipitation completely. Then the precipitate was washed with hot de-ionized water and alcohol in a centrifugal drier time after time until the filter liquor was neutral. Finally the precipitate was
dried under infrared lamp, and the untrafine precursor powders of ZrO\textsubscript{2} were obtained. Using Ce (NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (A.R) as starting materials, the untrafine powders of CeO\textsubscript{2} were prepared by the same method as that of ZrO\textsubscript{2}, but the pH value of the mixed solution was 11.

The solid-state reaction under high pressure and high temperature was investigated by using a belt-type press of the pressure range of 0—4.0 GPa. Firstly the precursor powders of CeO\textsubscript{2} and ZrO\textsubscript{2} were mixed in a certain ratio, and then were pressed into pellets of 6 mm in diameter and 8 mm in height under a pressure of 40 MPa. Finally, the pellets were treated under different pressures and temperatures. The compacting process was described as follows. The pressure was first loaded to a certain value, and then the temperature was gradually increased to the appointed value in rate of 200 K/min. After being kept under this pressure and temperature for 30 min, the specimens were quenched to room temperature in a rate of about 100 K/s under this pressure, and finally the pressure was released.

The structure and composition of the samples were determined by XRD with a Rigaku D/max-5A 12 kW X-ray diffractometer. The thermal stability analysis measurements (TG-DTA) were carried out with a Rigaku ME800 type thermogravimetry and differential-thermal analysis instrument. The EPR spectra of samples were detected by an ER2000-SRC ESR spectrometer. The ionic conductivity measurements for samples were performed by Hewlett-Packard HP4192-LF type alternating current impedance spectroscopy with a frequency between 5 Hz and 13 MHz at an amplitude of 5 mV, using silver electrode.

### 2 Results and discussion

(i) The characterization of the precursor powders of ZrO\textsubscript{2} and CeO\textsubscript{2}. The TG-DTA measurements for the precursor powders of ZrO\textsubscript{2} show that there exist a broad endothermic peak and an apparent weight loss about 25% between 300 and 573 K, and a sharp exothermic peak without weight loss at 750 K. The XRD analysis shows that after being calcined at 573 K for 2 h, the precursor powders of ZrO\textsubscript{2} are disorder structure, and after the calcination at 773 K for 2 h, several broad diffraction peaks appear, which can be indexed by a fluorite structure [JCPDS 30-1468] and a monoclinic phase [JCPDS 36-420], but the proportion of the monoclinic phase is less than that of the cubic phase by scaling up the relative intensities of their diffraction peaks. These results indicate that the broad endothermic peak and the obvious weight loss at 300—573 K in TG-DTA curves of the precursor powders of ZrO\textsubscript{2} are caused by the escape of many kinds of impurities absorbed in the sample, and the sharp exothermic peak at 750 K results from the structural transformation of ZrO\textsubscript{2} from disorder structure to the cubic and monoclinic phase accompanying the exothermic reaction. The TEM micrographs show that the ZrO\textsubscript{2} heat-treated at 773 K for 2 h are uniform spherical particles with the average diameter of 12 nm, but being the obvious agglomeration in the sample. The XRD analysis exhibits that the precursor powders of CeO\textsubscript{2} dried are already composed of well-crystallized crystallites with the fluorite structure [JCPDS4-0606 and 4-0593]. Their TEM micrographs display that the crystallites are also uniform spherical particles with the average diameter of 6 nm.

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<thead>
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(ii) The high-pressure synthesis and the thermal stability of the Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} solid solution. The precursor powders of ZrO\textsubscript{2} were heat-treated in air at 573 K for 2 h to remove absorbed impurities. Mechanically mixing the nanopowders of ZrO\textsubscript{2} heat-treated with CeO\textsubscript{2} dried in molar ratio of 1 : 1 as starting materials, the ceria-zirconia solid solutions were prepared either under high pressure and high temperature or by calcination in air. The preparation conditions are presented in table 1. The XRD analysis exhibits that preparation conditions can strongly affect the crystal structure of resulting products. Fig.1 gives the XRD patterns of the samples synthesized at various temperatures under the high pressure of 3.1 GPa. It can be found from fig.1 that the sample prepared at 773 K under 3.1 GPa is the mixtures of cubic CeO\textsubscript{2} and cubic ZrO\textsubscript{2} by comparison with the standard CeO\textsubscript{2} and ZrO\textsubscript{2}. With increasing synthesis temperature up to 923 K, the sample is still the mixtures of CeO\textsubscript{2} and ZrO\textsubscript{2}. But the diffraction peaks of monoclinic phase of ZrO\textsubscript{2} appear, and these peaks are stronger than those of cubic phase of ZrO\textsubscript{2}. In addition, all the diffraction peaks of the sample prepared at 973 K are sharper than that of one prepared at 773 K. It is clear that there exists the phase transformation of ZrO\textsubscript{2} from cubic to monoclinic, and the crystallite size increases at 923 K under 3.1 GPa. In the XRD pattern of the sample prepared at 1073 K under 3.1 GPa, only four diffraction peaks corresponding to a fluorite structure have been detected below 2\(\theta\) = 60° (see fig. 1). The least square fitting was used to obtain the lattice parameter of this phase. According to standard X-ray diffraction results, this structure belongs to the cubic phase with the lattice parameter \(a = 0.5336\) nm. It is evident that the solid-state reaction between CeO\textsubscript{2} and ZrO\textsubscript{2} occurs and the single-phase cubic Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} solid solution (c-Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}) has been synthesized under the pressure of 3.1 GPa and temperature of 1073 K. With temperature increasing up to 1273 K at 3.1 GPa, the two-phase mixtures of a cubic phase as the major phase and the monoclinic ZrO\textsubscript{2} have been formed. As compared with the c-Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} synthesized at 1073 K under 3.1 GPa, all diffraction peaks of this cubic phase...