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Study on properties of the single-phase cubic $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution

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Abstract

Using nanoparticles of CeO_2 and ZrO_2 prepared by a chemical precipitation method as starting materials, single-phase cubic $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution (c- $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$) has been synthesized under 3.1 GPa at 1073 K for the first time. The EPR and XPS measurements show that there exists no Ce^{3+} in it and that the Ce^{4+} has not been reduced to Ce^{3+} after annealing. The transport mechanism is ionic for the c- $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. The bulk conductivity is the same as that of CeO_2 , but smaller than that of Y_2O_3 -stabilized ZrO_2 .

(Some figures in this article are in colour only in the electronic version)

1. Introduction

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 [1]. There have been few reports [2, 3] 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 [3, 4].

The crystallite size of nanoparticles is very small and there are a large number of atoms on the surface of nanoparticles. Previous studies on thermal diffusion indicate that the ratio of interface energy in nanometre materials is two times as large as that in normal polycrystalline materials, and the diffusion coefficient of the interface atoms in the former is 10^4 higher than in the latter [5]. Because it can strongly change the interatomic distance and atomic states in solid materials, pressure, like temperature and composition, can also influence the structure and properties of the solid material to a certain extent. In this work, using nanoparticles of CeO_2 and ZrO_2 prepared by a chemical precipitation method as starting materials, the high-pressure synthesis and properties of the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution are investigated for the first time.

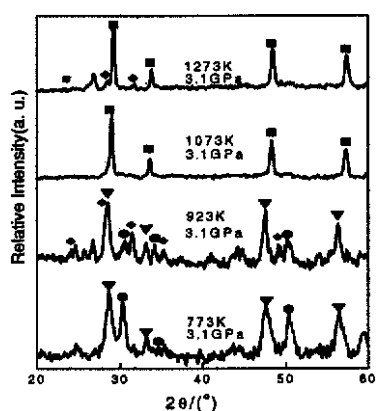


Figure 1. The XRD patterns of the samples synthesized at various temperature under the high pressure of 3.1 GPa. ■ CeZrO₂, ◆ m-ZrO₂ ▲ c-CeO₂, ● c-ZrO₂.

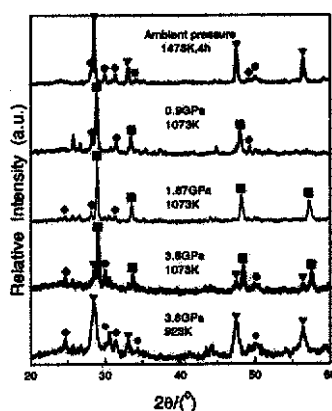


Figure 2. The XRD patterns of the samples synthesized under different pressure and temperature for half an hour.

2. Experimental procedure

The ultrafine precursor powders of ZrO₂ and CeO₂ were prepared by a precipitation method using ZrOCl₂ · 8H₂O(A.R) and Ce(NO₃)₃ · 6H₂O(A.R) as starting materials, respectively. The solid-state reaction was investigated under high pressure and high temperature by using a belt-type press with pressure range of 0–4.0 GPa. The structure and properties of the samples were measured by XRD, Raman spectra, EPR spectra, XPS spectra and alternating current impedance spectroscopy.

3. Results and discussion

3.1. The characterization of the precursor powders of ZrO₂ and CeO₂

The XRD analysis shows that after calcined at 573 K for 2 hours, the precursor powders of ZrO₂ have a disordered structure. After the calcination at 773 K for 2 hours, the diffraction peaks of the powers can be indexed by a fluorite structure and a monoclinic phase, but the proportion of the monoclinic phase is less than that of the cubic phase. The TEM micrographs show that the ZrO₂ powders heat-treated at 773 K for 2 h are uniform spherical particles with an average diameter of 10 nm. The XRD analysis shows that the precursor powders of dried CeO₂ are already composed of well-crystallized crystallites with the fluorite structure. Their TEM micrographs show that the crystallites are also uniform spherical particles, with an average diameter of 6 nm.

3.2. The high-pressure synthesis and the thermal stability of the Ce_{0.5}Zr_{0.5}O₂ solid solution

The precursor powders of ZrO₂ were heat-treated in air at 573 K for 2 h to remove absorbed impurities. With mechanical mixing of the nanopowders of heat-treated ZrO₂ with dried CeO₂ in molar ratio of 1:1 as starting material, the ceria–zirconia solid solutions were prepared. The XRD analysis shows that preparation conditions can strongly affect the crystal structure of the resulting products. The single-phase Ce_{0.5}Zr_{0.5}O₂ solid solution can be formed only under the condition of 3.1 GPa and 1073 K (figures 1 and 2). According to the standard x-ray diffraction results [6], this structure belongs to the cubic phase, with the lattice parameter $a = 0.5336$ nm.

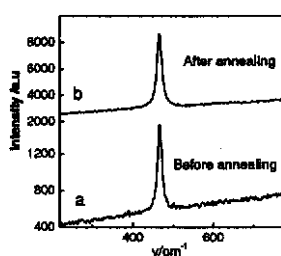


Figure 3. Raman spectra for the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solutions before and after annealing (773 K, 1 h).

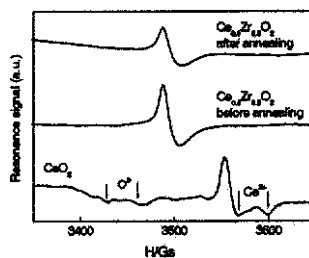


Figure 4. Room-temperature EPR spectra of the $\text{c-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ before and after annealing (773 K, 1 h) and CeO_2 nanoparticles.

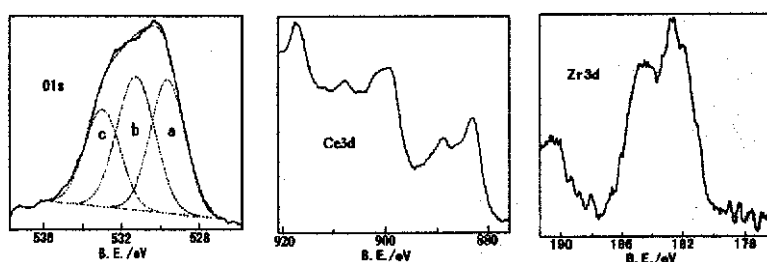


Figure 5. XPS spectra for the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution.

We distinguished the structure of the single-phase sample synthesized under 3.1 GPa and 1073 K through Raman scattering. Previous studies on Raman scattering have shown that the tetragonal phase of ZrO_2 , $\text{ZrO}_2\text{-RO}_{1.5}$ solid solutions ($R = \text{rare earths}$) have six Raman active modes, and the fluorite structure has only one Raman active mode [7]. For the present solid solution, the Raman spectrum displays only one mode at 466 cm^{-1} (see figure 3(a)), similar to that of doped ceria. This suggests that the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution synthesized under high pressure has the fluorite structure.

We have also investigated the thermal stability of the $\text{c-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ synthesized under high pressure. The XRD results show that after the solid solutions were annealed in air at 773 K for 1 h, the position and width of every diffraction peak was unchanged. For the annealed solid solution, the Raman spectrum also displays one peak at 466 cm^{-1} , but the Raman intensity increases obviously (see figure 3(b)). This confirms that the $\text{c-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solutions synthesized under high pressure can maintain stable structure below 773 K.

3.3. EPR and XPS study

The room-temperature EPR spectra of the $\text{c-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ before and after annealing at 773 K for 1 h and the precursor powders of CeO_2 are shown in figure 4. The spectrum of CeO_2 is characteristic of Ce^{3+} ions meanwhile, the O^- signal is also observed. It can be seen from figure 4 that only one resonance signal ($g = 1.990$) has been detected in the $\text{c-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. After annealing at 773 K for 1 h, the g -factor value does not change, but the relative intensity is slightly weaker. This signal cannot be attributed to Ce^{3+} ions due to the obvious variation of the g -factor value. It may be caused by some Zr^{4+} ions lying in a special crystal environment in the $\text{c-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$.

The XPS spectra of Ce 3d, Zr 3d and O 1s for the $\text{c-Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution are shown in figure 5. The O 1s XPS spectrum displays three components. The low-BE component at

529.64 eV and the middle-BE component (531.27 eV) are ascribable to oxide species adjacent to Ce^{4+} and Zr^{4+} ions, respectively, whereas the high-BE component at 533 eV is attributed to absorbent species. The main peak position for Ce 3d_{5/2} is at 882.7 eV, and the adjacent peak appears at 889.2 eV. This gives no indication of Ce^{3+} , and the peak at a high binding energy of 916 eV appearing in the Ce 3d spectrum is ascribed to Ce^{4+} [9]. In the Zr 3d spectrum, the position of the main peak and adjacent peak is similar to that for zirconia but the spectrum is not smooth and symmetrical. This result suggests that the states of Zr^{4+} in the c-Ce_{0.5}Zr_{0.5}O₂ solid solution and ZrO₂ are not quite the same.

3.4. Transport properties and microhardness of the Ce_{0.5}Zr_{0.5}O₂ solid solution

The conductivities of the c-Ce_{0.5}Zr_{0.5}O₂ have been investigated by the complex impedance method in the temperature range of 473–1123 K in air. The impedance plots for the c-Ce_{0.5}Zr_{0.5}O₂ showed only one distinct semicircle at this temperature range, which was primarily contributed by the bulk effect. The plot of $\ln(\sigma T)$ versus $1/T$ displays that the conductivity is gradually enhanced with increasing temperature ($\sigma = 1.2 \times 10^{-5} \text{ S cm}^{-1}$ at 823 K and $\sigma = 2.1 \times 10^{-3} \text{ S cm}^{-1}$ at 1123 K), which is the same as for pure CeO₂ at 823 K, but smaller than that of doped-zirconia at 1123 K. It is noteworthy that the conductivity data for the c-Ce_{0.5}Zr_{0.5}O₂ fall onto two straight lines below and above 823 K, respectively. This shows that the conductivity–temperature dependencies for the c-Ce_{0.5}Zr_{0.5}O₂ exhibit Arrhenius behaviour in a different temperature range. However, it was opposite to that reported in the literature [10, 11].

The microhardness of the samples was measured with a hardness test. The average microhardness for the Ce_{0.5}Zr_{0.5}O₂ solid solution is 572 under a load of 50 g HV⁻¹. After the sample is annealed at 773 K for 1 h, the average microhardness decreases slightly.

4. Conclusion

Nanocrystalline mixtures of CeO₂ and ZrO₂ (molar ratio of 1:1) can form the single-phase cubic Ce_{0.5}Zr_{0.5}O₂ solid solution only under the condition of 3.1 GPa and 1073 K.

The structure of the c-Ce_{0.5}Zr_{0.5}O₂ synthesized under high pressure remains stable below 773 K. The EPR and XPS measurements show that there exists no Ce^{3+} in the c-Ce_{0.5}Zr_{0.5}O₂ and the Ce^{4+} has not been reduced into Ce^{3+} after annealing at 773 K. The transport mechanism is ionic for the c-Ce_{0.5}Zr_{0.5}O₂ at 473–1123 K and the conductivities are primarily contributed by the bulk effect. The average microhardness for the Ce_{0.5}Zr_{0.5}O₂ solid solution is about 570 under a load of 50 g HV⁻¹.

Acknowledgment

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