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The influence of high pressure and high temperature on the structure of ZrO₂ nanosolids

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Abstract

Using nanoparticles of ZrO₂ (disordered structure) prepared by the method of precipitation as starting materials, ZrO₂ nanosolids have been synthesized under different pressures and at different temperatures. The x-ray diffraction results show that the crystallization temperature of the nanoparticles and the temperature at which the structural cubic–monoclinic transformation occurs are obviously reduced for the nanosolids synthesized under high pressure. X-ray photoelectron spectroscopy and EPR measurements indicate that there are some Zr³⁺ ions in nanosolids. With increasing pressure, the number of Zr³⁺ ions in the nanosolids essentially does not vary, and yet the content of oxygen ions with unsaturated bonds and dangling bonds in the interfacial region gradually decreases. The effect of synthesis pressure on the structure and interface states is mainly due to the decrease of the interatomic distance and the increasing interdiffusion of atoms in the interface phase.

1. Introduction

In recent years, much attention has been paid to research on nanosolid materials (nanosolids) because the structure and properties of this new type of material are very different from those of bulk polycrystalline materials [1, 2]. Nanosolids are usually prepared by compacting nanoparticles under high pressure and at high temperature. After nanosolids have been formed, the free surface of a nanoparticle becomes a grain interface. Because the crystallite size is very small, there is a large fraction of atoms lying in the nearly disordered interfacial region in nanosolids [3]. High pressure can substantially change the interatomic distance and atomic states in the interfacial region, and it also influences the crystal coordination environment of these atoms and their electronic and magnetic interactions with each other. Therefore, the

structure and properties of nanosolids will vary with change of the synthesis pressure to a certain extent.

The study of ZrO₂ has attracted considerable attention because of the various important applications [4, 5]. Now stabilized zirconia, which has a cubic structure, is mainly used as the electrolyte material in fuel cells and related devices [6]. Stabilization of the high-temperature cubic phase of ZrO₂ can be achieved at room temperature by the addition of a few moles of Y₂O₃, CaO, etc [7]. In recent years, there have been some reports on the formation of metastable cubic phase with small particle size without adding any stabilizers [8, 9]. In the present work, using nanoparticles of ZrO₂ prepared by the method of precipitation as starting materials, ZrO₂ nanosolids have been synthesized under different pressures and at different temperatures. The effect of synthesis pressure and temperature on the structure and interface states of ZrO₂ nanosolids has been investigated by means of XRD, XPS and EPR.

2. Experimental procedure

The ultrafine precursor powders of ZrO₂ were prepared by the precipitation method [8, 10, 11]. The XRD analysis shows that after calcining at 300 °C in the atmosphere for 2 h, the precursor powders of ZrO₂ are disordered in structure. And after calcining at 500 °C in the atmosphere for 2 h, several broad diffraction peaks appear, which can be indexed to a fluorite structure (JCPDS 30-1468) and a monoclinic phase (JCPDS 36-420), but the content of the monoclinic phase is less than that of the cubic phase as indicated by scaling up the relative intensities of their diffraction peaks. The TEM micrographs show that the ZrO₂ powders heat treated at 500 °C for 2 h are uniform spherical particles with the average diameter of 10 nm.

The precursor powders of ZrO₂ were heat treated in air at 300 °C for 2 h to remove absorbed impurities, and then were pressed into pellets 6 mm in diameter and 8 mm in height under a shaping pressure of 40 MPa. The nanosolids were synthesized under high pressure at different temperatures for 30 min with a belt-type press. The structure and composition of the nanosolids were determined by XRD with a Rigaku D/max-rA 12 kW x-ray diffractometer. EPR spectra were detected by an ER2000-SRC ESR spectrometer. XPS spectra were recorded on an ESCALAB MKII spectrometer.

3. Results and discussion

Figure 1 gives the XRD patterns of the nanosolids synthesized at 300 °C under pressures of 1.2, 3.1, 3.8 GPa. Analysis shows that the nanosolids synthesized under 1.2 GPa at 300 °C are two-phase mixtures of the cubic phase (as the major phase) and the monoclinic phase. The average crystallite size of the cubic phase is 27 nm. Upon increasing pressure up to 3.8 GPa and keeping the temperature at 300 °C, the amount of the cubic phase decreases, but the cubic phase is still the major phase in the nanosolids and the average crystallite size of the cubic phase increases to 34 nm. When the temperature is increased from 300 to 800 °C and the pressure remains under 3.1 GPa, the cubic phase transforms quickly to the monoclinic phase and the average crystallite size of the monoclinic phase increases obviously from 20 to 120 nm at the same time (see figure 2). By comparison with the crystallization and cubic–monoclinic structural transformation of the precursor powders of ZrO₂ at ambient pressure [8, 10], it is seen that high pressure reduces the crystallization temperature and promotes transformation from the cubic to the monoclinic phase. This may be explained as follows: although the high pressure can restrain the long-range diffusion of atoms, the average interatomic distance reduces and short-range diffusion of atoms accelerates in nanosolids. Therefore the crystallization temperature

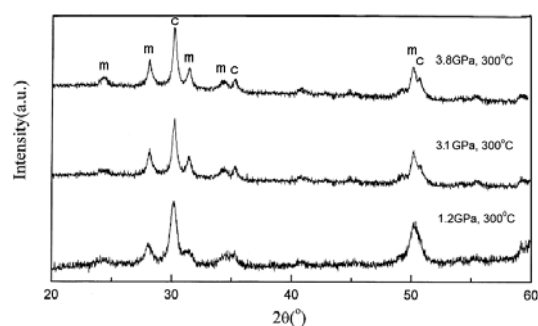


Figure 1. XRD patterns of the nanosolids synthesized at 300 °C under different pressures; c: cubic phase; m: monoclinic phase.

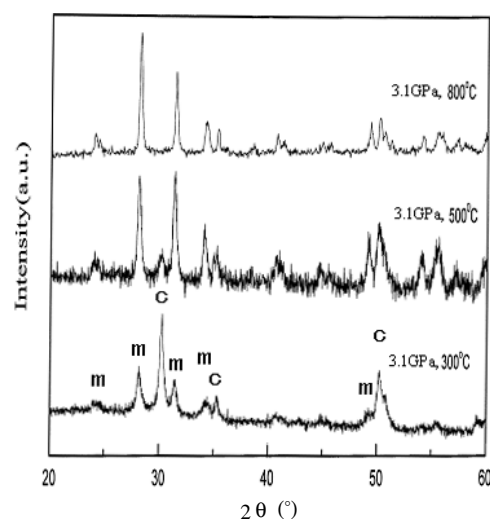


Figure 2. XRD patterns of the nanosolids synthesized under 3.1 GPa at different temperatures.

reduces under high pressure. The increase of the monoclinic form content with pressure increase is due to the martensitic tetragonal \rightarrow monoclinic phase transition [9].

The XPS investigations show that there are two components in the O 1s XPS spectrum for the nanosolids synthesized under high pressure. The low-BE component and the high-BE component are ascribable to the oxide species in the lattice inside the crystallites and the oxide species lying in the nearly disordered interfacial region, respectively [12]. With pressure increase, at the lower temperature, the content of the high-BE component decreases gradually, but the binding energy increases.

The binding energy of Zr 3d versus synthesis pressure and temperature is given in figure 3. The binding energy of Zr 3d electrons in the ZrO₂ nanosolids formed under 1.2 GPa at 300 °C is 182.4 eV, higher than that of the bulk ZrO₂ (182.2 eV) [12]. With pressure increasing up to 3.8 GPa at 300 °C, the binding energy decreases and is lower than that of the bulk ZrO₂ (about 1 eV). When temperature increases from 300 to 800 °C and the pressure is kept under 3.1 GPa, the binding energy increases. This indicates that there may exist some low-valence-state Zr ions in the ZrO₂ nanosolids formed under high pressure at lower temperature.

The room temperature EPR measurements (figures 4 and 5) show that there are two resonance signals (A and B) with *g*-factors of 2.063 and 1.989 in the EPR spectrum for the

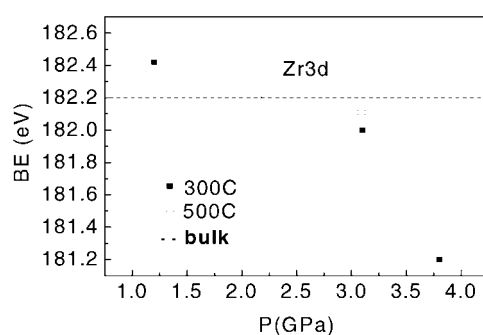


Figure 3. The relation of the binding energy (BE) of Zr 3d versus synthesis pressure and temperature.

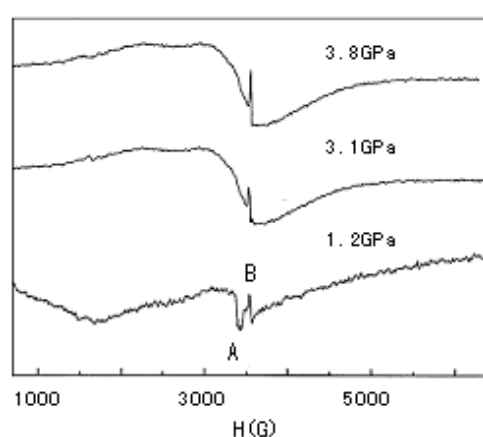


Figure 4. The room temperature EPR spectra of the ZrO_2 nanosolids synthesized at 300°C under pressures of 1.2–3.8 GPa.

ZrO_2 nanosolids synthesized under 1.2 GPa at 300°C . With the pressure increasing and the temperature kept at 300°C , signal A disappears rapidly. The intensity of signal B decreases slightly at first and then increases with further increase of pressure from 1.2 to 3.8 GPa at 300°C , but decreases rapidly with increase of temperature under 3.1 GPa. According to previous studies [13], the signals A and B result from the dipole interaction of $\text{Zr}^{3+}\text{--O}^-$ and Zr^{3+} ions, respectively. The above results show that the number of Zr^{3+} ions in the nanosolids does not vary obviously with the increase of the synthesis pressure at lower temperature 300°C , but decreases rapidly with enhancement of synthesis temperature which results in increase the crystallite size.

On increasing the pressure gradually, the atom density in the interface phase increases because of the reduction of the interparticle distance. Some ions of O and Zr with unsaturated bonds and dangling bonds lying in the nearly disordered interfacial region become take on saturation coordination through the ordering arrangement. So the high-BE component decreases gradually and its binding energy increases, and signal A disappears rapidly. It has been observed that Zr^{3+} ions locate only at the surfaces of polycrystalline grains [9]. The present experimental results (figures 3 and 4) suggest that Zr^{3+} ions locate not only at the surface but also inside the crystallites of nanosolids when the size of particles is very small.

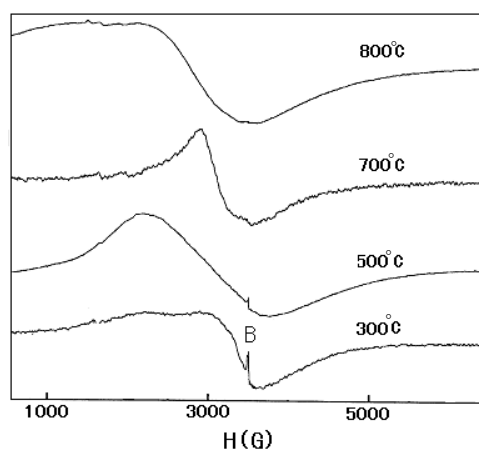


Figure 5. The room temperature EPR spectra of the ZrO₂ nanosolids synthesized under 3.1 GPa at temperatures of 300–800 °C.

4. Conclusions

Using nanoparticles of ZrO₂ (disordered structure) prepared by the method of precipitation as starting materials, ZrO₂ nanosolids have been synthesized under different pressures and at different temperatures. The crystallization temperature of ZrO₂ nanoparticles and the structural cubic–monoclinic transformation temperature reduce obviously for the nanosolids synthesized under high pressure. There are some Zr³⁺ ions in the nanosolids. With pressure increasing, the number of Zr³⁺ ions in the nanosolid does not vary substantially, yet the content of oxygen ions with unsaturated bonds and dangling bonds in the interfacial region decreases gradually. The effect of synthesis pressure on the structure and interface states is mainly due to the reduction of the interatomic distance in the interface phase and the increasing interdiffusion of atoms.

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References

- [1] Tschope A and Birringer R 1993 *Acta Metall. Mater.* **41** 2791–5
- [2] Dickenscheid W *et al* 1991 *Solid State Commun.* **79** 683–7
- [3] Mitsuyasu H *et al* 1998 *Solid State Ion.* **113–15** 279–84
- [4] Garvie R C, Hannink R H and Pascoe R T 1975 *Nature* **258** 703–4
- [5] Enzo S *et al* 1999 *Nanostruct. Mater.* **12** 6
- [6] Chiodelli G *et al* 1996 *Solid State Ion.* **91** 109–21
- [7] Lucchini E *et al* 1997 *Key Engineering Materials* vol 132–6 (Zurich: Trans. Tech.) pp 1353–6
- [8] Benedetti A *et al* 1990 *J. Mater. Sci.* **25** 1473
- [9] Chatterjee A *et al* 1994 *J. Mater. Res.* **9** 263
- [10] Zheng F L *et al* 1997 *J. Electrochem. Soc.* **97** 1213–22
- [11] Senguttuvan G *et al* 1999 *J. Mater. Synth. Process.* **7** 175–85
- [12] Yashuma M *et al* 1993 *Science and Technology of Zirconia* (Lancaster, PA: Technomic)
- [13] Azzoni C B *et al* 1993 *J. Mater. Sci.* **28** 3951