STUDY ON THE STRUCTURAL TRANSFORMATION AND THE MECHANISM OF CUBIC STABILITY IN NANO-PARTICLES OF (ZrO$_2$)$_{1-y}$(Y$_2$O$_3$)$_y$

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ABSTRACT

In this paper, (ZrO$_2$)$_{1-y}$(Y$_2$O$_3$)$_y$ nano-particles were prepared by the coprecipitation method. A sequence of structural transformations with variation of nano-particle size has been studied and the hyperfine structure of $^{91}$Zru with unsaturated coordination in electron spin resonance (EPR) spectra of ZrO$_2$ nano-particles has been found. A mechanism of cubic stability in the nano-particles is discussed.

INTRODUCTION

In general, the size of nanocrystallites is within the range of 1-100 nm. As the grain size drops to several nanometers such as 5 nm, the number of surface atoms will form up to 30% of total atoms of the crystallite. There are a large number of unsaturation bonds and dangling bonds on the surface of the grain. This leads to a lot of differences in physical and chemical properties between nanocrystalline and polycrystalline materials. For example, the EPR signal was found in nanocrystalline SnO$_2$ but not in polycrystalline SnO$_2$. This was related to interface component in nanosized grain \textsuperscript{(1)}. In a perfect single crystal ZrO$_2$, no paramagnetic resonance center exists, so no EPR signal appears. In single crystal ZrO$_2$ - Y$_2$O$_3$ (YSZ), because some oxygen deficiencies created by replacing Zr$^{4+}$ with Y$^{3+}$ lead to the formation of paramagnetic resonance center, an EPR signal could be observed \textsuperscript{(2)}. The EPR signal obtained in polycrystalline YSZ is attributed to the ionic deficiency inside the crystallite and to the presence of Y$_2$O$_3$ aggregates\textsuperscript{(3,4)}. Considering
many important technological applications of YSZ solid electrolyte material in fuel cells, oxygen sensors and oxygen pumps, $(\text{ZrO}_2)_{0.88}(\text{Y}_2\text{O}_3)_{0.12}$ (YSZ₁₂) and ZrO₂ nanopowders have been synthesized by chemical precipitation technique, and the EPR spectra of these samples have been investigated. The changes of the EPR spectra with decreasing nanocrystallite size and the differences in EPR spectra between nanocrystalline ZrO₂ and ZrO₂-Y₂O₃ are analyzed in detail.

EXPERIMENTAL

ZrOCl₂ and Y(NO₃)₃ solution were mixed in a certain ratio, and then the solution was added dropwise to aqueous ammonia until the precipitation of Zr(OH)₄ was complete. The PH value of the solution was approximately 9. The precipitate was washed many times with hot di-ionized water and alcohol in a centrifugal drier until Cl could not be found in the solution, then the precipitate was dried at 330K in a vacuum drying oven. Finally the YSZ₁₂ samples of A₁, A₂, A₃, A₄ and the ZrO₂ samples of B₁, B₂, B₃ treated at different heating and annealing temperatures have been obtained respectively. The structure of the samples were determined by XRD with a Rigaku D/max-rA 12kw x-ray diffractometer, and their morphology was observed by JEM-2000 ES transmission electron microscope (TEM). The EPR spectra of samples were measured with an ES 200D-SRC ESR spectrometer operating at X-band frequency (=9.776GHz) with 100kHz magnetic field modulation at room temperature. Reference signals of Mn²⁺ ions in MgO were used as the standards for the linewidth and effective g-factor value.

RESULTS AND DISCUSSION

The x-ray patterns of each sample are given in Fig. 1 respectively, the average grain size D of different samples is calculated from the halfwidth β of their XRD patterns. According to the Scherrer formula $D = 0.89\lambda/\beta\cos\theta$, here λ is the wavelength of X-ray and θ is the diffraction angle, β is obtained by deducting the effect of geometrical broadening caused by instrument and microstrain inside nano-particles. The results are listed in Table 1. From Fig. 1 and Table 1, it can be seen that at room temperature, the crystal structure of YSZ₁₂ nano-particles remains cubic with decreasing grain size, while the ZrO₂ nano-particles show the structural transformation of monoclinic-tetragonal-cubic with decreasing grain size from 40nm to 4nm. A. Chatterjee has reported similar result in Ref. (7). This shows a strong size-effect on the structure in ZrO₂ nano-particles. However, for the normal bulk polycrystalline ZrO₂, the structure is monoclinic at room temperature, tetragonal above 1440 K and cubic above 2640 K. The TEM morphology of sample B₃ is...
shown in Fig. 2, it could be seen objectively that the grain size is almost within the range of 4nm to 6nm, the distribution of grain size is uniform.

EPR technique is a usual analysis method for researching the state of paramagnetic ions in their crystal environment. EPR is very sensitive to the unpaired electron, therefore the formation and state of dangling bonds and unsaturation bonds in solid can be studied by EPR measurement.

It is well known that there is not paramagnetic center in perfect ZrO₂ single crystal (without unpaired electron), and EPR signal cannot be detected. However, EPR signal could be observed as grain size reduced to nanometer magnitude or ZrO₂ was doped (2,3,4). Fig. 3 shows EPR spectra of YSZ₁₂ and ZrO₂ nano-particles. The EPR spectrum of YSZ₁₂ sample is the same as reported in Ref. (3). Three types of signals could be identified, marked as A, B, C, respectively.

A signal, g=4.30, the shape and position of signal are typical for ions with spin S=5/2 and orbital angular moment L=0 such as Fe³⁺ ion (4), this kind of weak signal appears in every EPR spectrum. Impurity with Fe³⁺ ion which was introduced in the process of synthesis, is responsible for this EPR signal. ZrO₂ is often contaminated by Fe₂O₃.

B signal, g=2.38 .Because this signal has a broad linewidth and intensive peak ,it might be a superposition signal. Up to now, this kind signal could not be exactly identified (1)

C signal, g=2.063gₑ (g factor of free electron) (1) and is a sharp resonance peak. Accompanied with reduction of grain size, its effective g factor does not alter, but the intensity of the resonance peak becomes weak. The C signal possibly comes from several causes. The first one is that the signal results from O²⁻ or O₂²⁻ adsorbed on the surface of grain. Since O₂²⁻ is unstable, it cannot produce stable EPR signal. The C signal, however is stable during our experiment. The O₂²⁻ ion can produce an EPR signal, but its g factor should be slightly lower than gₑ and its intensity would increase with the reduction of grain size. According to the above analysis, C signal is not originated from O₂⁻ or O₂²⁻ ion adsorbed on the surface of the grain. The second cause can be the oxygen deficiencies and Zr³⁺ ions inside grains. But it is impossible for YSZ₁₂ sample to have Zr³⁺ ion because of the presence of Y³⁺ ion. If Zr³⁺ ion exists, its concentration and intensity of EPR signal would increase with the reduction of grain size, this is not in accord with our result. So the C signal cannot be produced by Zr³⁺ ion. We think that the C signal is caused by oxygen deficiencies in the YSZ₁₂ grains, formed by substituting low valance Y³⁺ for Zr⁴⁺ ion. Lattice distortion occurs near the oxygen deficiencies, and an electron could be

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trapped, thus forming a paramagnetic center. This kind of paramagnetic center is related with the bulk of the grain. Therefore the intensity of this EPR signal increases with increasing grain size and is closely related to that of F centers in polycrystalline materials.

The EPR spectra of ZrO₂ nano-particles are shown in Fig. 3(b). In addition to the A, B, C resonance peaks that are the same as the EPR signals in YSZ₁₂ samples, there are another EPR signals in ZrO₂ nano-particles marked as P, L, M₁₋₆.

The signal P has a narrow linewidth, its g factor and linewidth are the same as that of the EPR signal of an F center forming on the surface of the ZrO₂ grain. Oxygen deficiencies on the surface of ZrO₂ grain could trap an electron and forms an F center with paramagnetic behavior, thus causing an EPR signal appears. With the decrease of the grain size, the intensity of the signal P increases, because the number of F centers increases.

The intensity of the signal L increases with the reduction of the grain size, and its g factor is smaller than gₑ. This signal is caused by O₂⁻ adsorbed on the grain surface. With the reduction of grain size, the specific surface increases, the number of O₂⁻ ions adsorbed on the grain surface increases as well. Specially, as the grain size reduces to several nanometers, such as 5 nm, the ratio of Zr to O is seriously out of the normal proportion, such as 1:1.57. This leads to a large number of oxygen deficiencies on the surface of the grains. O₂⁻ ion is easily adsorbed on the surface of the grain keeping the charge balanced. An O₂⁻ ion adsorbed on the surface of the grain is a paramagnetic center, and could produce an EPR signal. The intensity of this EPR signal rises with the increase of adsorption.

The EPR signals of M₁₋₆ consist of six sharp peak with the same intensity and space. This kind of signals does not appear in the EPR spectra of YSZ samples, ZrO₂ single crystal and ZrO₂ polycrystalline. Up to now, this kind of EPR signals in YSZ or ZrO₂ sample has not been reported in literature.

The signal M₁₋₆ appears until the grain size is reduced to nanometer magnitude. The peak space is about 80Gs, The intensity of signal M₁₋₆ increases with the reduction of grain size. This kind of signals of M₁₋₆ is a hyperfine structure spectrum. According to the paramagnetic resonance theory, the spin of an atomic nucleus which could produce this kind of hyperfine structure should be I=5/2. Al or Ti ions with I=5/2 are possibly doped to YSZ₁₂ and ZrO₂ nano-particles during the synthetic reaction, but their hyperfine
structure constants do not meet with our result obtained in the experimental spectra, otherwise, these \( M_{1-6} \) signals do not appear in the EPR spectra of YSZ\(_{12}\) samples with the same grain size and synthetic method, so Al or Ti ions could not give rise to this EPR signal. The spin of the \( ^{17}\)O nucleus is \( I=5/2 \) as well, but its abundance is very small (0.036%), and its hyperfine structure constant (40Gs) is smaller than our result (80Gs), therefore these \( M_{1-6} \) signals can not be attributed to the \( ^{17}\)O nucleus.

\( ^{91}\)Zr is an isotope of \( ^{92}\)Zr. When the grain size reduces to several nanometers, the ratio of Zr to O is seriously out of the normal proportion. This gives rise to lattice distortion round oxygen deficiencies and makes Zr ion in unsaturated state. Some Zr\(^{3+}\) have formed on the surface of the grain or inside the grain, the unpaired spin is a 5S electron of the Zr\(^{3+}\) ion, it could display an EPR signal. The Fermi interaction between 5S electron and \( ^{91}\)Zr nucleus makes EPR signal split into six lines, and hyperfine structure line could be observed. The concentration of the paramagnetic center and the number of Zr\(^{3+}\) ions being in the unsaturated state will increase with the reduction of grain size. This leads to an increase in the intensity of the EPR signals. The above analysis basically concurs with our experimental result. So it is concluded that the signals of \( M_{1-6} \) are caused by \( ^{91}\)Zr\(^{3+}\) with unsaturated state on the surface of ZrO\(_2\) nano-particles.

According to the result of EPR and XRD spectra of ZrO\(_2\) nano-particles, the changes in EPR spectra seem to relate with the crystal structure. The signals of \( M_{1-6} \) do not appear if the monoclinic phase is over 60%. The intensity of \( M_{1-6} \) signals is also quite weak, even if that monoclinic phase has dropped to 20%. The intensity of \( M_{1-6} \) signals significantly increases when the monoclinic phase is only 5%. The intensity of the \( M_{1-6} \) signals gets to maximum as the crystal structure of ZrO\(_2\) is perfectly transformed to the cubic phase. The EPR signal is very sensitive to the coordination state of paramagnetic ion and changes of environment surrounding the paramagnetic ion in crystal. The structure transformation of ZrO\(_2\) nano-particles probably results in the change of the coordination environment around Zr\(^{3+}\) ion. This surely causes the variation of EPR signal. At room temperature, there exists the monoclinic structure in the ZrO\(_2\) polycrystalline and the cubic structure in the YSZ polycrystalline due to the oxygen deficiency. The cubic phase of ZrO\(_2\) nanocrystallite is stable at room temperature. This may also be related to the oxygen deficiency and the existence of Zr\(^{3+}\) on the surface of the grains. With decreasing particle size, the number of oxygen deficiencies and unsaturated Zr\(^{3+}\) gradually increases and the sequence of structure transformation occurs in the order of monoclinic phase -tetragonal phase-cubic phase. So we suggest that the changes of crystal structure and EPR spectra in nano-particles are surely caused by the oxygen deficiency and unsaturated state of Zr\(^{3+}\) formed on grain surface. However why could the signal of \( M_{1-6} \) not be found in EPR spectra of YSZ\(_{12}\) with the same size as the ZrO\(_2\) nanoparticles? Considering that the
number of Zr\textsuperscript{3+} ions on the surface of the grains rapidly decreases after Y\textsuperscript{3+} ions are partially substituted for Zr\textsuperscript{3+} with unsaturated coordination, and those Zr\textsuperscript{3+} ions which are not replaced by Y\textsuperscript{3+} might simultaneously localize at some cation sites round the same oxygen deficiency together with the Y\textsuperscript{3+} ion, the Zr\textsuperscript{3+}-Y\textsuperscript{3+} pairs can be formed, affecting the unsaturated state of the Zr\textsuperscript{3+} ion and make 5S electron of the Zr\textsuperscript{3+} pull to the Y\textsuperscript{3+} ion, therefore, the interaction between the 5S electron and \( ^{91}\text{Zr}\)\textsuperscript{3+} nuclear becomes quite weak, so that the hyperfine structure would be difficult to detect. The Zr\textsuperscript{3+}-Y\textsuperscript{3+} pairs make the trivalent Zr\textsuperscript{3+} and oxygen deficiency more stable, and make a contribution to the stability of the cubic phase in YSZ\textsubscript{12}.

CONCLUSION

With the changes of grain size from 40 nm to 4 nm, the sequence of structural transformations in ZrO\textsubscript{2} nanoparticles is as follows, monoclinic phase $\rightarrow$ tetragonal phase $\rightarrow$ cubic phase. The hyperfine EPR spectrum resulting from \( ^{91}\text{Zr}\)\textsuperscript{3+} is observed in ZrO\textsubscript{2} nanoparticles. Its intensity increases with decreasing grain size. The presence of Zr\textsuperscript{3+} shows that there exist a large number of unsaturated coordination states in ZrO\textsubscript{2} nanoparticles. The crystal structure of YSZ\textsubscript{12} nanoparticles keeps a cubic phase during the process of changing of grain size. The state under nanometer size is favorable for the stability of cubic phase in YSZ\textsubscript{12} sample.

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Table 1. Heating conditions and XRD data of YSZ and ZrO2 nanoparticles

| samples parameters | A_1 | A_2 | A_3 | A_4 | B_1 | B_2 | B_3 | B_4 |
|--------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| T(k)               | 723 | 753 | 873 | 1273| 723 | 773 | 873 | 1073|
| t(h)               | 2   | 2   | 2   | 2   | 2   | 2   | 2   | 10  |
| D(nm)              | 4   | 6   | 16  | 40  | 6   | 11  | 20  | 40  |
| Cry. structure     | C   | C   | C   | C   | T   | T+M | M   |
| I_m(%)             | 0   | 0   | 0   | 0   | 5   | 20  | 95  |
Fig. 1 The x-ray patterns of YSZ₁₂ (a) and ZrO₂ (b) nanoparticles
Fig. 2 Transmission electron microscopy morphology of sample B₁.
Fig. 3 EPR spectra of nanosized YSZ_{12} (a) and ZrO_{2} (b) nanoparticles.