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Crystallization process of cubic ZrO_2 in calcium acetate solution

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Ultrafine powders of cubic ZrO_2 were obtained at about 270° C by heating hydrated amorphous ZrO_2 in greater than 0.2 molal calcium acetate solutions. Ca^{2+} ions played a role as nucleii for crystallization and were introduced into distinct sites of the crystalline phases, that is, substituted for Zr^{4+} ions. Mn^{2+} ions produced almost the same effects on the crystallization of ZrO_2. EPR spectra for powder samples containing Mn^{2+} ions apparently showed two types as follows: for tetragonal ZrO_2 with a trace of monoclinic ZrO_2, the central fine structure transitions ($M = +1/2 \leftrightarrow -1/2$) showed a well-resolved hyperfine structure. In addition to the $\Delta m = 0$ transition, forbidden $\Delta m = \pm 1$ transitions were observed. For cubic ZrO_2, the broad underlying response was observed as well as the hyperfine structure composed of six main peaks.

1. Introduction

With recently developed oxygen sensors and high temperature engineering materials, the preparation of high purity, ultrafine powders of ZrO_2 has been investigated [1, 2]. There are three well-defined polymorphs; monoclinic, tetragonal and cubic forms, which are stable at higher temperatures in that order. However, it frequently happens that the tetragonal or cubic form appears during crystallization at low temperatures, at which the monoclinic form is thermodynamically stable [1–6]. Indeed, these metastable forms irreversibly transform to the stable monoclinic form after heating at relatively low temperatures or after mechanical treatment such as grinding.

Recently Nishizawa *et al.* [6] observed the crystallization process of ZrO_2 while heating hydrated amorphous ZrO_2 up to 350° C in NaOH aqueous solution at a constant rate. Cubic ZrO_2 with very small crystallite size crystallized at about 120° C with the uptake of Na^+ ions. These fine cubic ZrO_2 particles abruptly changed into needle-like monoclinic ZrO_2 single crystals at 300° C with the exclusion of Na^+ ions from solid phase. Na^+ ions were presumed to play an important part in crystallization and phase transformation. The crystallization of ZrO_2 at low temperatures is found to be easily affected by surface conditions and impurities. The crystallization process is such heterogeneous phases is very complicated and is not fully understood, but it is very important to know the interactions between the solid and the liquid phases during crystallization and whether trace products of solids form homogeneous or inhomogeneous mixtures. Through the use of electron paramagnetic resonance (EPR) techniques, precise information concerning these phenomena are attainable [7]. The use of EPR lines to study the distribution of transition element impurities in solid substances should be a very helpful approach to the problem.

In the present work, the crystallization and the transformation of ZrO_2 in calcium and/or manganous acetate aqueous solutions were investigated. Besides X-ray powder diffraction (XRD) and X-ray fluorescence spectra measurements, EPR techniques were used to study the relationship between the choice of polymorphs in crystalline phases and the uptake of ions during the crystallization of ZrO_2.

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2. Experimental

2.1. Hydrothermal reaction

Amorphous hydrated zirconium oxide as starting material was prepared according to previous work [6]. This sample was characterized by X-ray powder diffraction pattern without reflections. The water content of this sample was determined by thermogravimetric analysis which showed loss of weight (about 38% of the initial sample weight) up to 500° C. $5\,cm^3$ of an aqueous solution of calcium and/or manganese (II) acetate (guaranteed reagents, Wako Pure Chem. Ind., Ltd, Japan) and 250 mg of starting material were put in a micro-autoclave (lined with Hasteloy-C) with capacity of $8\,cm^3$, which was used as a reaction vessel. The vessel was heated by means of a well-insulated tabular furnace; the heating rate was controlled at $6^\circ\,C\,min^{-1}$ from 50 to 350° C. The reaction temperatures are probably higher than the actual values because they are measured at the outer wall of the micro-autoclave, but they are useful as a basis for comparing the data. The reaction pressure gradually increased with increasing temperature as $5\,cm^3$ of solution was sealed in the reaction vessel. The autogeneous pressure was monitored in some runs by a Heise gauge connected to the reaction vessel. The pressure increased in almost the same manner for all runs using $5\,cm^3$ solution; 6 and 16 MPa at 250 and 350° C, respectively. After the desired temperature was reached, the vessel was quenched rapidly to room temperature by immersing it in iced water. The powder products and the solution in the reaction vessel were completely recovered. They were filtered off, washed several times with distilled water, and oven dried at 60° C.

2.2. Analysis of Mn^{2+} and Ca^{2+} ions

To determine the Ca^{2+} and Mn^{2+} content of the products: (i) the filtrate was titrated with EDTA and the difference in concentration of the solutions between after and before the reaction was calculated; and (ii) the powder products were semiquantitatively analysed by scanning the X-ray fluorescence spectra in the $L\alpha$ and $L\beta$ regions of calcium and manganese with Benth–Albee correc-

EPR spectra of the powder products which occurred during the hydrothermal reactions in solutions containing manganous acetate were obtained on a Varian E-104 (X-band) spectrometer at room temperature. To allow comparison the measuring conditions for all samples were almost the same.

2.3. X-ray powder diffraction analysis

The powder diffraction patterns were obtained for all of the powder products by using a Rigaku X-ray diffractometer with Cu$K\alpha$ radiation. Only three forms of zirconia, that is, monoclinic, tetragonal and cubic forms, were detected and no carbonate compounds were formed by the decomposition of acetate ions in the present runs. The identification, quantitative analysis of these three forms, and the determination of particle size of the cubic form, were carried out according to previous works [6, 9, 10].

3. Results and discussion

3.1. X-ray powder diffraction and chemical analysis

X-ray powder diffraction patterns (Fig. 1) show the crystallization behaviour during heating of hydrated amorphous ZrO_2 in 0.2 molal calcium acetate solution compared with that in pure water. Cubic ZrO_2 begins to crystallite at about 270° C. The crystallization proceeds up to 350° C and results in only cubic ZrO_2 with lattice constant $a = 0.5137$ nm. Fig. 2 is an electron micrograph of the cubic ZrO_2 particles. The average particle size was approximately 10 nm, in fair agreement with the calculated effective crystallite size (Table I). The crystallization temperature is higher than in pure water (240° C) and in NaOH solution (130° C), but much lower than in air (430° C).

TABLE I The powder samples obtained at 350° C for several initial concentrations of calcium acetate solutions

Initial concentration molal	Crystallization temperature (° C)	Ca uptake (Ca mol %/ZrO_2)	Crystalline phase (lattice constant in nm)	Effective crystallite size (nm)
0.01	250	1.52	tetragonal ≫ monoclinic	
0.05	270	5.85	cubic ≫ tetragonal	
0.2	270	8.97	cubic (0.5137)	10.8
0.5	270	10.65	cubic (0.5142)	9.8
0.7	270	11.22	cubic (0.5145)	9.0
1.0	270	11.84	cubic (0.5147)	8.7

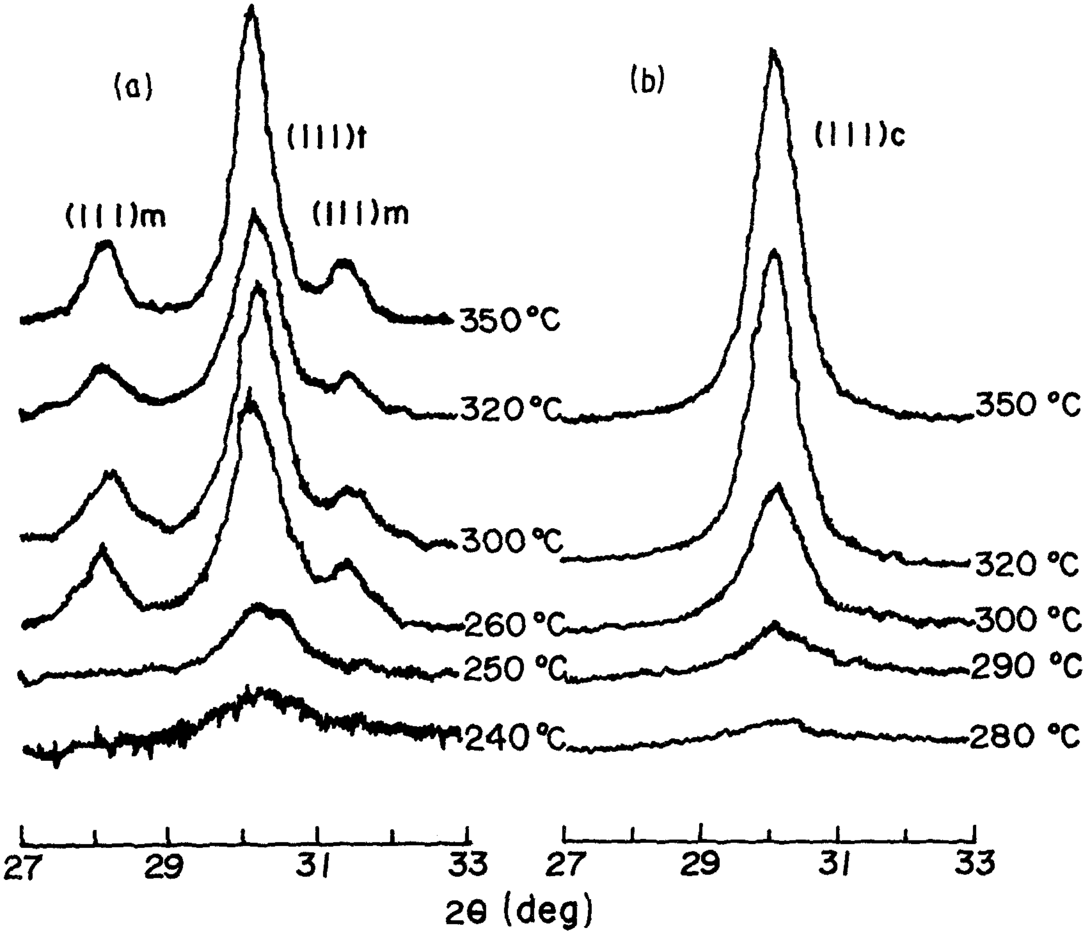

Figure 1 X-ray diffraction patterns of samples hydrothermally treated in (a) pure water and (b) 0.2 molal calcium acetate solution up to temperatures indicated.

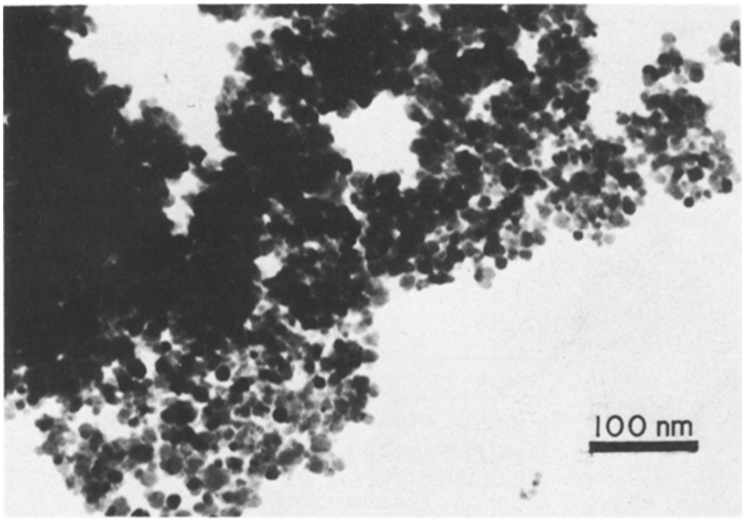

Figure 2 Transmission electron micrograph of sample hydrothermally treated in 0.2 molal calcium acetate solution up to 350° C.

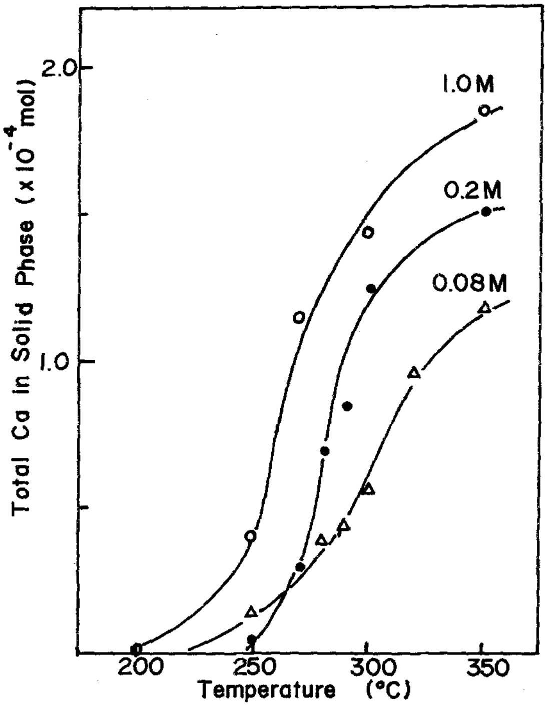

Figure 3 Total calcium uptake by the solid phase hydrothermally treated in calcium acetate solution with initial concentration indicated plotted against heat-treatment temperature.

Fig. 3 shows the calcium uptake by the solid phase during heating of the hydrated amorphous ZrO_2 powder in calcium acetate solutions of different initial concentrations. In 0.2 molal calcium acetate solution, neither calcium uptake nor crystallization occurred below 200° C but thereafter there was a rapid calcium uptake which was followed by the crystallization of cubic ZrO_2. Calcium uptake and crystallization were found to cease almost at the same time. It can be considered that Ca^{2+} ions are introduced into the noncrystalline phase only for crystallization. It was confirmed by the results that there was no calcium uptake when completely crystallized monoclinic ZrO_2 powder was heated to 350° C in the calcium acetate solution. Ca^{2+} ions may play a role as nucleii for crystallization of ZrO_2. This can explain the fact that the effective crystallite size of cubic ZrO_2 obtained decreased with increasing initial concentration of calcium acetate solution (Table I). Such a calcium uptake process seems to shift to a higher region with decreasing initial concentration, although the crystallization temperature is hardly changed. Total calcium uptake at 350° C increased linearly with the initial concentration. In solutions of concentration greater than 0.2 molal, the lattice constants of cubic ZrO_2 obtained at 350° C increased with the total calcium uptake (Table I). This indicates true solid solution formation in analogy with that at high temperatures [11], although such solid solution is thermodynamically unstable at such low temperatures. In fact, it partially decomposed to the monoclinic form after heating at 1300° C for 5h. In solutions below 0.05 molal, tetragonal ZrO_2 crystallized with traces of monoclinic ZrO_2. These tetragonal ZrO_2 crystals may be stabilized by a size effect, as indicated by Garvie, who assumed that the tetragonal phase has a lower surface energy than the monoclinic phase. It is interesting that there is a decided lower limit of calcium content required to stabilize the cubic form as in high temperature reactions [11].

3.2. EPR spectra

Fig. 4 shows the EPR spectra of samples obtained while heating hydrated amorphous ZrO_2 up to several given temperatures in 5×10^{-4} molal manganous acetate solution. No resonance lines were observed for the samples treated below 200° C, but a faint resonance line with a hyperfine structure began to appear at 250° C, at which calcium uptake commences (Fig. 3). The spectra became clearer with increasing temperature and also gave extra lines between the hyperfine struc-

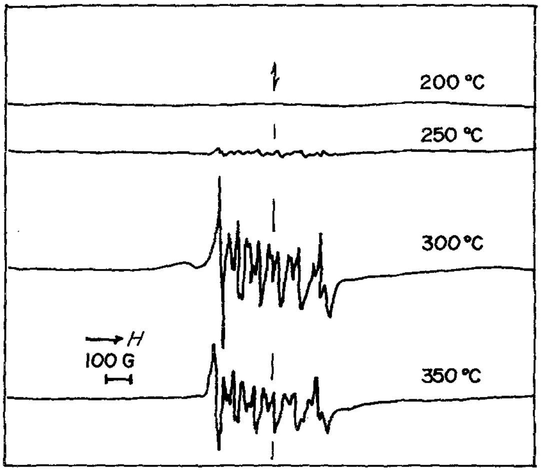

Figure 4 Room temperature EPR spectra for powder samples hydrothermally treated in 5×10^{-4} molal manganous acetate solution up to the temperature indicated. The vertical lines represent the resonance position of a standard pitch sample ($g = 2.0028$).

ture lines. The intensity of the spectra showed an almost linear increase with temperature in the range between 250 and 300° C. Thus the intensity seems to be comparable to the manganese concentration introduced into the solid phase. Qualitatively these spectra appear similar in that they can be considered to consist of six "main" lines which are centred about a g-value of 2.00 ± 0.005; the five splitting range being between 75 and 96 G. There are also other resolved lines which consist of five doublets, each doublet occurring between two "main" lines. These five doublets have been observed by several workers in single crystals [12], polycrystalline materials [13–15] and glasses [16–18] containing manganous ions, and have been attributed to forbidden $\Delta m = \pm 1$ transitions (m is the nuclear magnetic quantum number), the "main" lines, of course, being the allowed $\Delta m = 0$ transitions. The overall intensity of these signals and also the feature of the hyperfine structure remained almost unchanged at temperatures above 300° C. The crystalline phases obtained in these runs were effectively independent of Mn^{3+} ions introduced from manganous solution and the crystallization proceeded in a similar manner to Fig. 1a; in pure water. The reproducibility and sharpness of the spectra indicates that the primary Mn^{2+} sites are probably not interstitial because in that case a broad range of local environments would be expected to broaden the observed EPR spectra. It is also unlikely that the Mn^{2+} goes in as a microphase such as $MnCO_3$ or MnO because at a few per cent manganese the exchange interaction destroys the hyperfine structure completely, leaving only a broad symmetrical signal. It has been reported that the randomly distributed trace Mn^{2+} (0.01%) shows a well-resolved hyperfine structure with forbidden transitions from the EPR study of $MnCO_3$–$CaCO_3$ and MnO–CaO solid solutions [13]. It seems that Mn^{2+} ions are primarily located at well-defined sites, perhaps in the tetragonal ZrO_2 crystal.

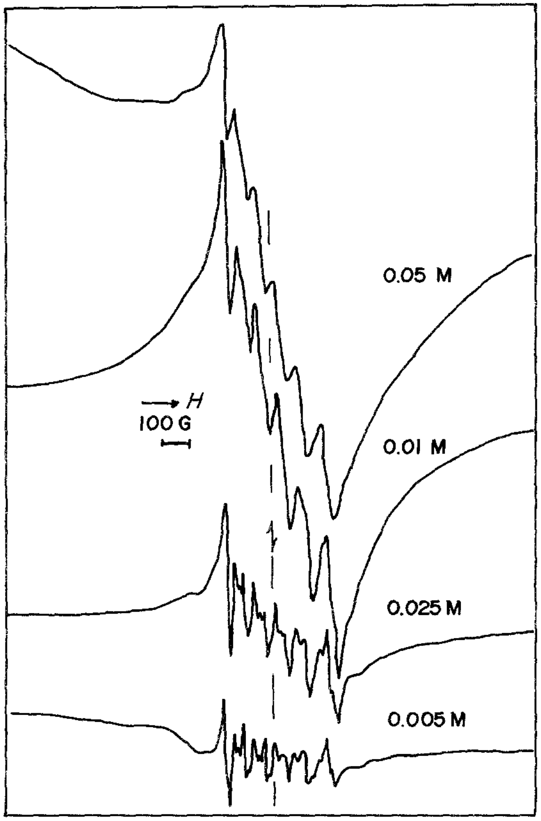

Figure 5 Room temperature EPR spectra for powder samples hydrothermally treated in manganous acetate solution with initial concentration (molal) indicated up to 350° C.

Fig. 5 shows the effect of a changing initial concentration of manganous acetate solution. The total quantity of Mn^{2+} ions introduced into the solid phase increased with increasing initial concentration and only cubic ZrO_2 was obtained at above 0.05 molal of manganous acetate solution, as for calcium acetate solution. The EPR spectra showed an obvious change at that concentration. Thus besides the hyperfine structure composed of six main peaks the broad underlying response was observed. The line width of the EPR spectrum is principally determined by the magnetic dipolar interactions of Mn^{2+} ions. The state of Mn^{2+} ions which exhibit hyperfine structure may be defined as free ions [7]. Spectra which shows superposition of hyperfine structure and a single broad line could then be interpreted either as a mixture of free and coagulated Mn^{2+} ions or in terms of the broadening of the components of hyperfine structure. In the latter case, the character of the hyperfine structure of the six main peaks is maintained until each component is smeared out by broadening as the Mn^{2+} ion concentration is increased. As the concentration of manganous acetate solution is increased, simultaneously with the quantity of manganous uptake, the overall intensity of the hyperfine structure increased at first up to 0.025 molal, and thereafter decreases and the five doublets lose their resolution. But the line widths of each component of the hyperfine spectrum observed in this experiment were

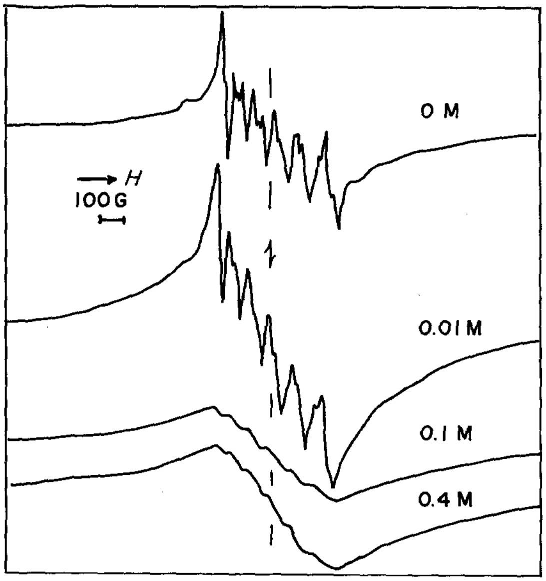

Figure 6 Room temperature EPR spectra for powder samples hydrothermally treated in mixed solution of calcium and manganous acetate with initial concentration (molal) indicated and 0.025 molal, respectively, up to 350° C.

almost identical (60 to 90G). The hyperfine structure is independent of a broad line and the features of the spectra depend on the appearance of the crystalline phase. Thus the former interpretation seems to be more reasonable. It can therefore be considered that Mn^{2+} ions in the tetragonal ZrO_2 crystal lattice show a well-resolved hyperfine structure and those in the cubic lattice show the superposition of six main peaks and a single broad line. The EPR spectra for fully crystallized samples obtained at 350° C in mixed solutions of manganous and calcium acetate, in which the Ca^{2+} ion concentration was varied from 0 to 0.4 molal while the Mn^{2+} ion concentration was kept at 0.025 molal, were observed (Fig. 6). As with the results of X-ray analysis, the appearance of the crystalline phase was almost the same as in only calcium acetate solution (Table I). At above 0.1 molal calcium acetate solution, only the cubic phase was present and the hyperfine structure was almost completely smeared out by the absorption lines. Such a superposition of six main peaks and a single broad line must be characteristic of Mn^{2+} ions in cubic ZrO_2 crystal. A higher substitution of Ca^{2+} and Mn^{2+} for Zr^{4+} ions in cubic ZrO_2 may cause coagulation of Mn^{2+} ions according to inhomogeneous statistical probability of distribution. Spectra for the samples obtained during crystallization in the mixed solution manganese and calcium acetate, 0.025 and 0.5 molal, respectively, showed only such a broad line, except that the intensities increased with temperature. It suggests that cubic ZrO_2 was not gradually stabilized through the diffusion of ions but consistently crystallized with a given amount of substitution, at which only a trace of Mn^{2+} and Ca^{2+} ions were introduced into the solid phase. This is borne out by the fact that the total quantity of calcium and manganese uptake corresponds to the crystallinity.

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