

HYDROTHERMAL PROCESSING OF ZIRCON

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Zircon was prepared hydrothermally from zirconium oxychloride, tetraethoxysilane or tetramethoxysilane, water and/or alcohol by heating in teflon-lined hydrothermal vessels at 150°C for 6 hr or at 200°C for 4 hr. The effects of starting materials, temperature, heating time and catalysts on the crystallization of zircon were studied.

The simultaneous hydrolysis of Si alkoxide and $ZrOCl_2$ leading to the formation of a single phase gel of intimately mixed Si and Zr atoms was found to be the most important process which controlled the formation of zircon. Insufficient amount of water led to a segregation of the components during the hydrothermal treatment as evidenced by the formation of monoclinic zirconia. Increased heating duration at a constant temperature of treatment led to softer powder compared to a smaller heating duration which resulted in hard agglomerates. Transmission electron microscopy revealed doughnut-like or red blood cell-like morphology for the particles which are dense at the edge and thin at the core. The individual particles may be assemblies of small crystals with the same crystallographic orientation rather than single crystals.

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Introduction

Zircon has a very high thermal shock resistance because of its low thermal expansion coefficient. Zircon single crystals are used in jewelry and zircon powder is used in glazes (1). However, the preparation of zircon needs a heat treatment of 1450°-1500°C in air by the solid state method and usually transition metal oxides are used as additives (2-4). Frondel and Collette (5) have prepared zircon hydrothermally from gelatinous ZrO_2 and SiO_2 with water in steel bombs. Single phase zircon has been obtained by heating at 325°C for 240 hrs (5). The addition of a trace amount of ZrF_2 decreased the crystallization temperature to 150°C, but heating for 500 hrs was needed.

In this study, pure zircon was prepared hydrothermally from zirconium oxychloride, Si alkoxides, water and/or alcohol.

Experimental

Zircon was prepared from tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$, or tetramethoxysilane (TMOS), $Si(OCH_3)_4$, $ZrOCl_2 \cdot 8H_2O$, H_2O and/or ethanol (ETOH) or methanol (MeOH) by using the hydrothermal technique. Either 10.830 g (for TMOS system) or 7.2237 g (for TEOS system) of $ZrOCl_2 \cdot 8H_2O$ was dissolved in the desired amount of deionized water (x ml) and mixed at room temperature to get transparent (clear) solution. Then 5 ml of TMOS (or TEOS) was added to the above transparent solution and mixed for about 30 min by stirring. The mixture was sealed in the hydrothermal vessels, Parr bombs and heated at 100°-200°C and for 3-48 hr. Either NH_4OH or HCl was used as a catalyst in some cases. The hydrothermal products were characterized by X-ray powder diffraction using a Picker-Siemens diffractometer with Ni-filtered $CuK\alpha$ radiation and by transmission electron microscopy using a Philips 420 instrument.

Results and Discussion

(I) Synthesis from TMOS-ZrOCl₂·8H₂O

First, the effect of water content on the crystallization of zircon was studied. In Figure 1, X-ray diffraction patterns for samples with different amounts of water (x) are shown. At x=5 ml, the dominant crystalline phase formed at 200°C was monoclinic zirconia under these hydrothermal conditions. When gels made from TEOS-ZrOCl₂·8H₂O were heated in air from 120°-1350°C, the tetragonal form of zirconia formed at 320°C and the monoclinic phase appeared only at >800°C (4). Thus the present hydrothermal conditions yielded monoclinic zirconia at much lower temperature than the heat treatment in air. In the present study, at x<20 ml the crystalline phases were zircon and monoclinic zirconia. With increasing amounts of water, the quantity of zircon phase increased. At x=20 ml, single phase of zircon was obtained probably as a result of the complete hydrolysis of Si alkoxide along with ZrOCl₂ leading to the formation of a single phase gel followed by its crystallization. Thus simultaneous hydrolysis of alkoxide and ZrOCl₂ to form a single phase gel appears to be the most important factor which is controlling the formation of zircon. The peaks of (200) and (400) are relatively sharp, but other peaks are broad (Fig. 1). This result shows that the crystallite size is rather small and has the a-axis orientation. The zircon crystallites prepared hydrothermally from TEOS-EtOH system were reported to have lens-shaped morphology (6) and this morphology may have led to the a-axis orientation.

When methanol (5 ml) was added to the above TMOS-ZrOCl₂ solution of x=20 ml and treated hydrothermally at 200°C the XRD peaks became sharper when compared with the sample without methanol (Fig. 2). The addition of methanol appears to promote the crystallinity of the zircon phase slightly.

The effect of acid or base additions was also examined, and the results are shown in Figure 3. There was little or no effect of acid on the

crystallization of zircon (Fig. 3). On the other hand, the addition of base led to a sharpening of the XRD peaks of zircon as can be seen from Figure 3.

(II) Synthesis from TEOS-ZrOCl₂·8H₂O-EtOH-H₂O

X-ray diffraction patterns of hydrothermally reacted samples resulting from different amounts of EtOH and H₂O are shown in Figure 4. As expected from the results for TMOS, zircon phase increased as the amount of water increased. At low water contents, crystalline phases were again zircon and monoclinic zirconia just as in the case of TEOS-ZrOCl₂ starting materials and these results can be explained in the same way.

The effect of time and temperature on the crystallization of zircon was studied using fixed volumes of ethanol and water (20 ml for each) along with constant amounts of TEOS and ZrOCl₂·8H₂O. The results are shown in Figure 5. Under these conditions, the boundary between crystalline and amorphous phases is rather sharp which is indicated by a broken line (Fig. 5). This boundary is located at lower temperature and time when compared to the earlier work of Frondel and Collette (5). The low temperature synthesis of zircon achieved here can be attributed to the higher reactivity of the starting materials compared to those of Frondel and Collette (5) who used mixed ZrO₂-SiO₂ diphasic gels.

Transmission electron microscopy (Fig. 6) was used to determine the particle size and morphology of the above hydrothermal products. Figure 6A reveals massive amorphous phase after treatment at 135°C for 6 hrs which is consistent with the XRD results (Fig. 5). However, treatment for a longer duration i.e. 24 hrs at 135°C led to the crystallization of zircon phase (Fig. 5). Treatment of the mixture at 150°C for a short duration resulted in non-uniform sized zircon (Fig. 6B) while treatment for a longer duration led to uniform sized zircon (Fig. 6C). Increasing the temperature of treatment to 175°C also resulted in uniform sized powders but at a shorter duration (Fig. 6D). The size of zircon powder increased upon treatment for a longer duration at 175°C (Fig. 6E). Figure 6F shows the zircon powders which

resulted at 200°C upon treatment for 48 hrs. There is virtually no difference between the zircon powders made at 175° and 200°C when treated for the same length of time. Thus it appears, a critical size (~650 nm) for the zircon powder was attained in the approximate temperature range of 175°-200°C. Although the zircon powders appear spherical they are not spherical as revealed by their morphology on the edge (Fig. 6). Furthermore, the core of the spherical-shaped particles is less dense than the edge as can be clearly seen in Figs. 6E and 6F. Thus the morphology of the particles is either red blood cell-like or somewhat doughnut-like although there is no hole in the middle. It is not known for certain whether the individual particles are single crystals or an assembly of many small crystals with the same crystallographic orientation. The latter case is more likely than the former based on the morphology of the zircon in Fig. 6B which shows very small zircon crystals along with large non-uniform sized particles.

References

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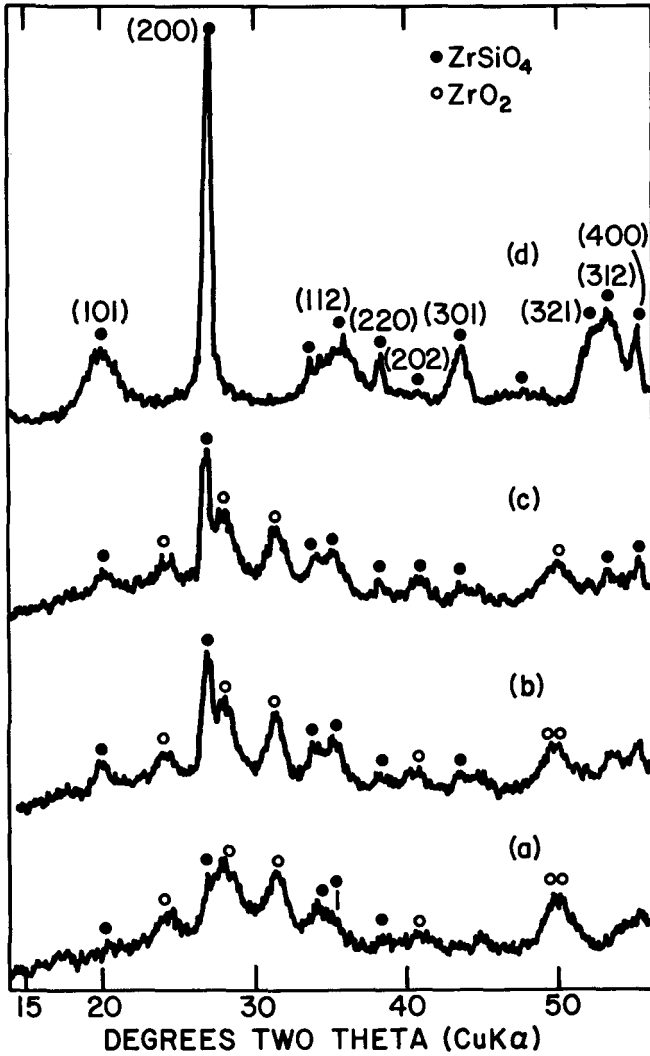


Figure 1. X-ray diffraction patterns showing the effect of water content on the crystallization of TMOS-ZrOCl₂·8H₂O-H₂O mixtures which were hydrothermally treated at 200°C for 2 days: (a) 5 ml H₂O; (b) 7 ml H₂O; (c) 10 ml H₂O; and (d) 20 ml H₂O.

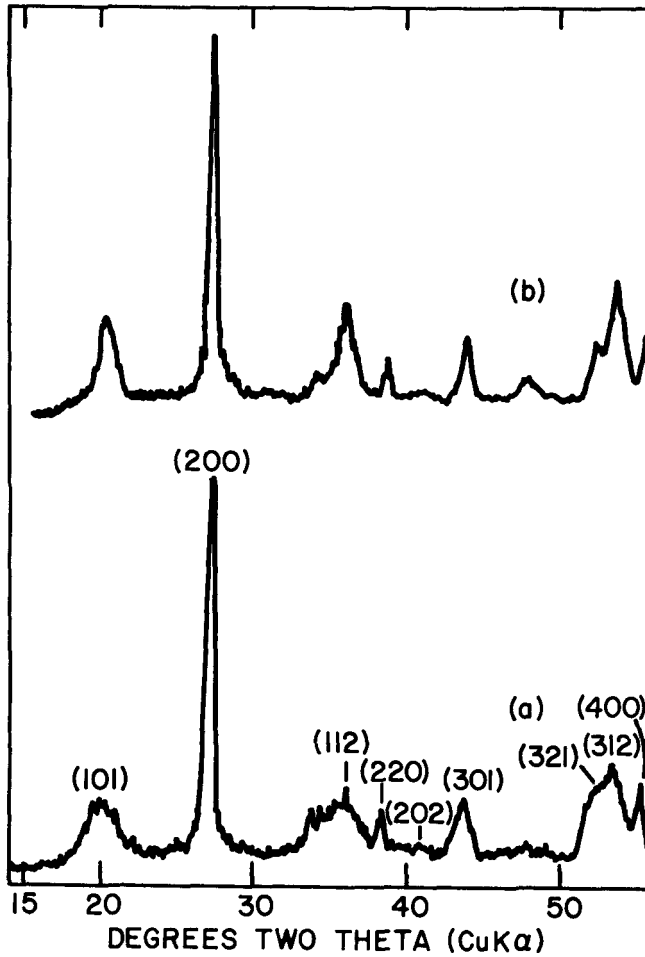


Figure 2. X-ray diffraction patterns of zircon from TMOS (5 ml)- $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (10.83 g)- H_2O (20 ml) without (a) and with (b) methanol (5 ml) treated hydrothermally at 200°C for 2 days.

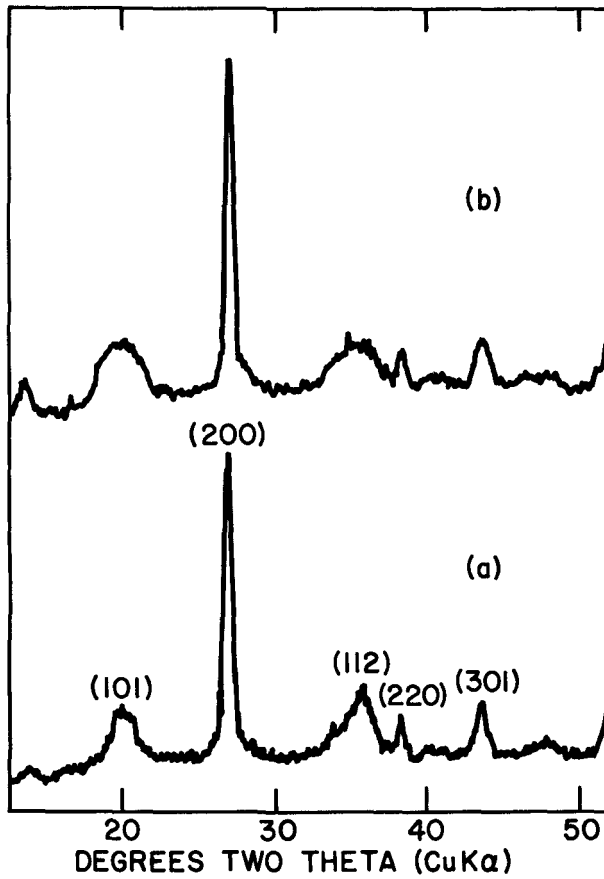


Figure 3. X-ray diffraction patterns showing the effect of (a) acid and (b) base on the crystallization of zircon. Zircons were prepared from TMOS-ZrOCl₂·8H₂O and (a) NH₄OH (1.0×10^{-2} mol/l) or (b) HCl (1.0×10^{-2} mol/l).

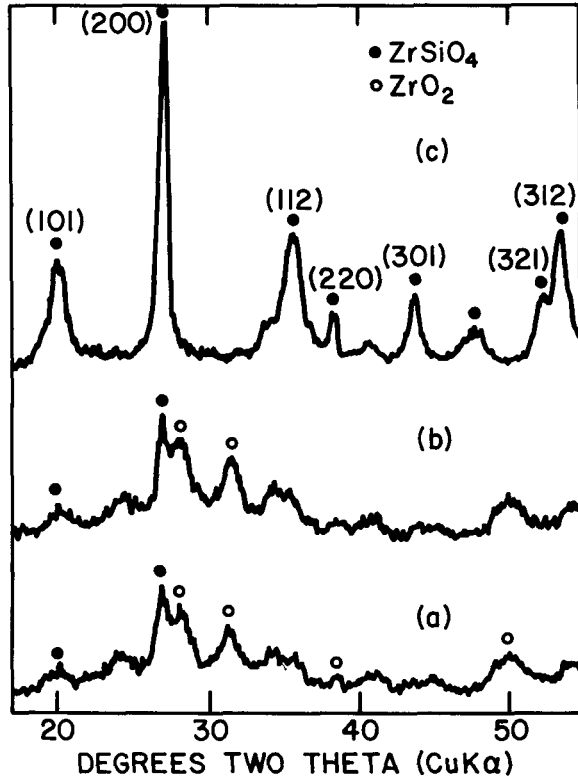


Figure 4. X-ray diffraction patterns of different samples hydrothermally treated at 200°C for 2 days. Starting compositions were TEOS (5 ml)- $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (7.2237 g), and (a) EtOH (40 ml); (b) EtOH, 40 ml- H_2O (5 ml); (c) EtOH, 20 ml- H_2O (20 ml).

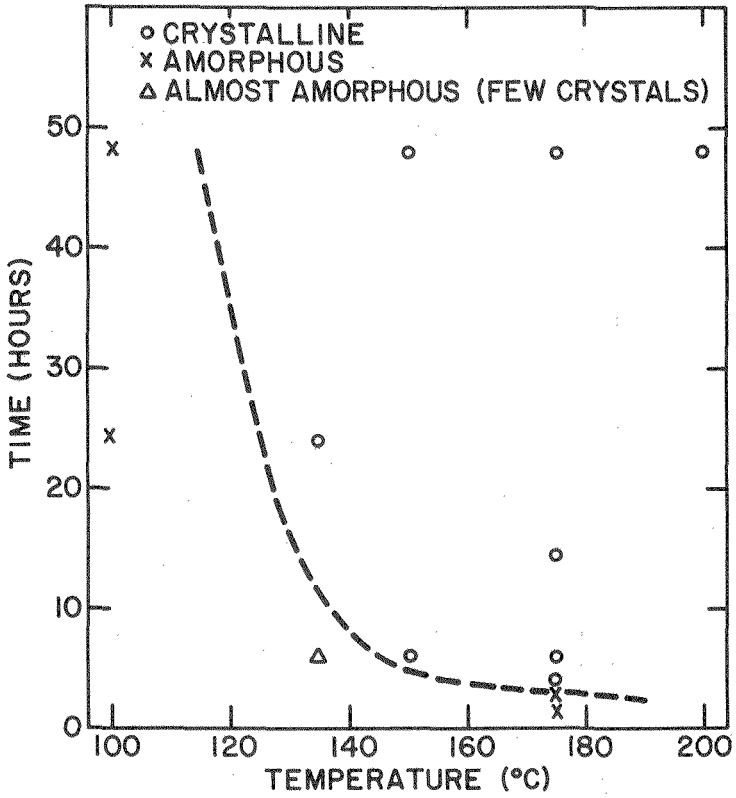
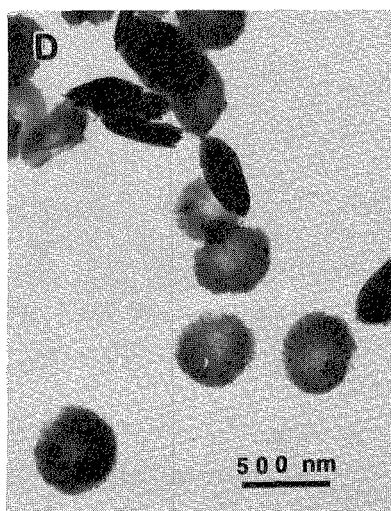
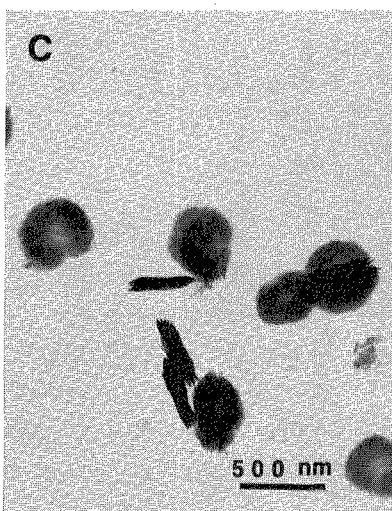
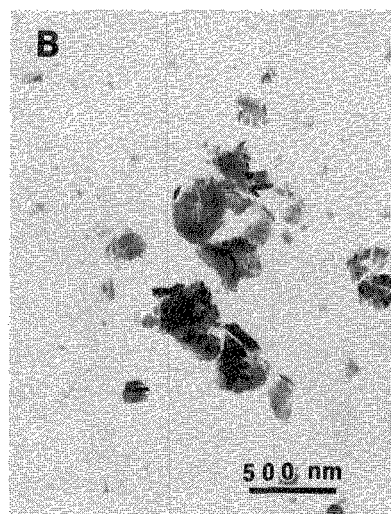
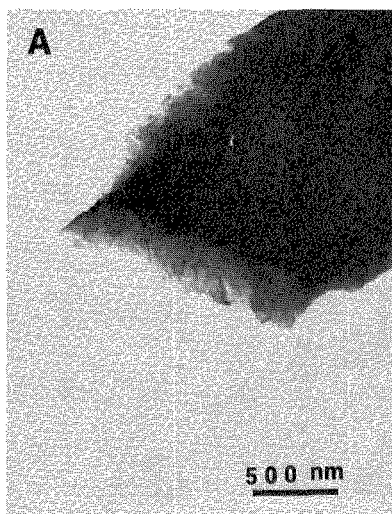


Figure 5. Effects of temperature and treating time on the crystallization of zircon from TEOS (5 ml)-ZrOCl₂·8H₂O (7.2237 g)-EtOH (20 ml)-H₂O (20 ml).



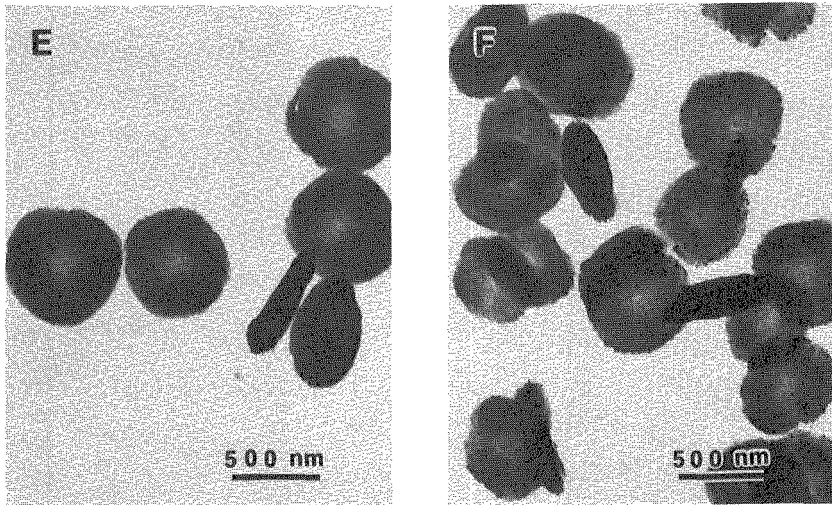


Figure 6. Transmission electron micrographs of zircon crystallization from TEOS (5 ml)-ZrOCl₂·8H₂O (7.2237 g)-EtOH (20 ml)-H₂O (20 ml) under hydrothermal conditions: (A) Amorphous mass with few crystals after treatment at 135°C for 6 hrs; (B) non-uniform sized zircon after treatment at 150°C for 6 hrs; (C) uniform sized zircon after treatment at 150°C for 48 hrs; (D) uniform sized zircon after treatment at 175°C for 6 hrs; (E) uniform sized zircon after treatment at 175°C for 48 hrs; (F) uniform sized zircon after treatment at 200°C for 48 hrs.