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GROWTH OF SINGLE CRYSTALS OF ZrO_2 AND HfO_2 FROM PbF_2 ¹A. B. CHASE AND JUDITH A. OSMER, *Aerospace Corporation,
El Segundo, California*

Baddeleyite (ZrO_2) and its analog (HfO_2) have been studied extensively over the past few years in order to determine the nature of their phase transformations. Upon heating to approximately 1050° C., baddeleyite inverts from monoclinic to tetragonal structure with a diffusionless phase transformation. HfO_2 undergoes a similar transformation at about 1650° C. (Wolten, 1963).

Microscopic crystals of monoclinic ZrO_2 have been prepared by fusion of ZrO_2 in borax (Doelter, 1926). Newkirk and Smith (1965) reported that ZrO_2 could be grown from $LiMoO_3$ -fused-salt systems; however, no data were given on either crystal characterization or crystal growth procedures. The purpose of this note is to outline a method for the preparation of macroscopic ZrO_2 - HfO_2 solid-solution crystals. It has been found that ZrO_2 - HfO_2 crystals can be readily grown from a PbF_2 -fused-salt system. The melts from which the largest ZrO_2 crystals were grown contained 10 mole % ZrO_2 and 90 mole % PbF_2 and were program cooled from 1040 to 800° C. The largest HfO_2 crystals were obtained from a melt composed of 5 mole % HfO_2 , 95 mole % PbF_2 and were program cooled from 1250 to 1000° C.

Because of a considerable change in the solubilities of ZrO_2 and HfO_2 in PbF_2 and a large change in the transformation temperature of the two compounds and their solid-solution crystals, fairly large changes in the growth parameters are required to obtain good crystals throughout the ZrO_2 - HfO_2 system. Only the basic data concerned with the preparation of the end members are discussed here. The variations in composition and temperature required to obtain crystals of intermediate composition are listed in Table 1.

The materials employed were $\approx 99.7\%$ pure ZrO_2 , $\approx 99.9\%$ pure HfO_2 , and a purified grade of PbF_2 . The powders were mechanically mixed (in 100-gram lots) and fused in tightly covered 50-ml standard-form platinum crucibles. The crucibles were placed in either of two Super-Kanthal heated horizontal muffle furnaces that have vertical and horizontal temperature gradients of less than 0.5° C./in. The melts were held at either 1040° C. or 1250° C. for 4 to 8 hr and cooled at a uniform rate (2 to 4° C./hr) to 800 to 1000° C., depending on the material to be grown. At the lowest temperature used for crystal growth, the crucibles were

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TABLE 1. NORMAL RUNS WITH RESULTS FOR ZrO₂-HfO₂ CRYSTAL GROWTH

Melt Composition			High Temp, °C	Low Temp, °C	Cooling Rate, °C/hr	Comments
Mole % ZrO ₂	Mole % HfO ₂	Mole % PbF ₂				
10	—	90	1050	690	2.6	Clear platelets 4×2×1 mm; grew near melt surface
10	—	90	1050	850	3.0	Clear platelets 4×4×1 mm; grew near melt surface
9	1	90	1040	800	4.0	Clear platelets 3×3×1 mm to 5×5×2 mm; grew near melt surface
7	3	90	1040	800	4.0	Clear platelets 3×3×1 mm; grew near melt surface and on bottom of crucible
5	5	90	1040	800	4.0	Clear platelets 5×4×1 mm; grew near melt surface and on bottom of crucible
3	7	90	1040	800	4.0	Clear platelets 2×2×0.5 mm; grew near melt surface and on bottom of crucible
—	5	95	1250	1000	4.0	Clear platelets 2×2×1 mm; grew on crucible walls

removed from the furnaces and allowed to cool to room temperature. Approximately 25 wt % of the melt was lost by evaporation during ZrO₂ runs and 45 wt % was lost during an HfO₂ run. The major portion of the loss was probably PbF₂, which has an appreciable vapor pressure at these temperatures. The crystals were recovered by digesting the contents of the crucibles in hot 20% nitric acid and were identified by microscopic examination and confirmed by standard x-ray techniques. The average yield was approximately 65 to 70% of the original ZrO₂ or HfO₂ in the melt.

The ZrO₂ crystals obtained from a typical melt ranged from 2×3×0.5 mm to 5×8×1 mm and were attached to the crucible walls near the surface of the melt. The crystals were generally subhedral, with a habit of {100} > {110} > {011}. The HfO₂ crystals were somewhat smaller, with the largest crystals being 2×3×1 mm. Their habit was the same as the

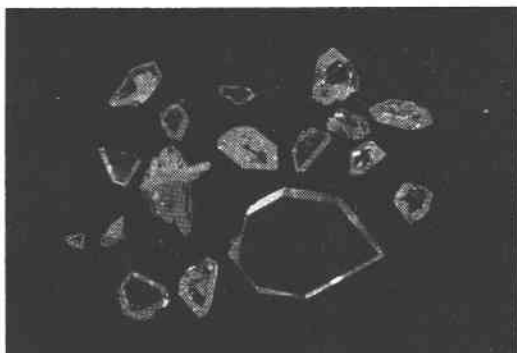


FIG. 1. A representative sample of ZrO_2 crystals (2 \times).

habit for the ZrO_2 crystals. Representative crystals are shown in Fig. 1.

The bulk of the ZrO_2 crystals exhibited (100) twinning with each crystal being composed of two or three twin-related individuals with the composition plane generally bisecting the crystal. Many of the crystals showed a further twin relationship; that is, they appeared to be related by (110) twinning (Fig. 2). Moreover, it appeared to be mechanical twinning rather than true growth twinning. The crystals grew at 90 deg from each other from a translucent rod-shaped nucleus. It is thought that the monoclinic ZrO_2 crystals grew on rod-shaped crystals which had grown as the higher temperature tetragonal modification. These crystals twinned when they were cooled below the transformation temperature, becoming monoclinic.

The HfO_2 crystals are rarely twinned, but, when they are, they exhibit (100) twinning.

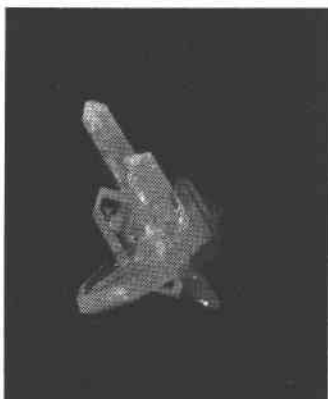


FIG. 2. A cluster of ZrO_2 crystals related by (110) twinning (5 \times).

The ZrO_2 , HfO_2 , and ZrO_2 - HfO_2 crystals are colorless and appear to be of good optical quality.

The authors wish to express appreciation to G. M. Wolten who identified and characterized the crystals by x -ray techniques.

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CACOXENITE FROM ARKANSAS

D. JEROME FISHER, *University of Chicago, Chicago, Illinois*

While A. L. Kidwell¹ was a graduate student at the University of Chicago he added to my phosphate collection samples of cacoxenite obtained by him from Arkansas in August 1948. Since this material is not listed in the A.S.T.M. index, and few data appear in the abstract by Gordon (1950), and these are in conflict with what appears in Danas' System (II 997), I have recently subjected Kidwell's material to x -ray and optical study.

According to Kidwell the material came from the Isom Avants prospect pit in the bed of a dry branch in the NW. $\frac{1}{4}$, SE. $\frac{1}{4}$, sec. 1, T.4S., R. 30W., in Polk County about 2 miles southwest of the old Shady post-office (abandoned now for some years). This is in the Ouachita Mountains near the middle of the west boundary of the state. The mineral occurs as fracture fillings in the novaculite; associated species in this area include strengite, beraunite, rockbridgeite, laubmannite, turquoise, and possibly diadochite, as well as iron and manganese oxides. The geology of the area has been described by Miser and Purdue (1929). In an earlier report Miser (1918) mentions the occurrence of "dufrenite" (rockbridgeite ?) associated with the manganese deposits as green globular aggregates with a radiating structure. Penrose (1891) gave a brief description of the C. C. Avant (iron) claim in sec. 1.

The Arkansas specimens consist of brecciated limonite-stained novaculite with fracture fillings of limonite. The cacoxenite occurs lining cavities in the limonite. It consists of radiating globular masses up to about

¹ Ph.D. 1949. Present address: Esso Production Research Co., Houston, Texas