Short Communication

A Neutron Diffraction Investigation on Single Crystals of Titanium Oxide, Zirconium Carbide and Hafnium Nitride

A. Nørlund Christensen

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

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Single crystals of titanium oxide, TiO, zirconium carbide, ZrC, and hafnium nitride, HfN, were grown by different crystal growth techniques. Crystals of TiO were made in a skull crucible by directional solidification,[1] a crystal of ZrC was grown using the floating zone technique in an ambient He atmosphere of 2.3 MPa,[2] and crystals of HfN were grown by the zone annealing technique in an ambient N_2 atmosphere of 1.3 MPa.[3] The unit cell parameters of the compounds were determined from Guinier photographs taken with Cu $K\alpha_1$ radiation (λ = 1.5405981 Å) and Si (a = 5.43050 Å) as an internal standard. The densities of the compounds were measured using the method of Archimedes, and the chemical analysis of the metals of the three compounds were made gravimetrically by oxidation in air at 1000 °C to TiO_2, ZrO_2 and HfO_2, respectively. The results of these measurements are listed in Table 1.

The crystal structures of the three compounds are known; they are all isostructural with NaCl, space group *Fm*3*m* (No. 225). However, the structures of the three compounds have not been investigated previously by single crystal neutron diffraction. The investigation reported below is an attempt to correlate crystal quality with crystal growth conditions by the application of neutron diffraction rather than to do a reinvestigation of the crystal structures. In previous single crystal neutron diffraction analysis it was frequently observed that the crystals showed strong extinction when grown with techniques where a steep temperature gradient was applied over the growth interface.[4] For the three compounds investigated, TiO should then show less extinction than the crystals of ZrC and HfN.

It could be expected that the thermal gradient across the solid liquid growth interface in the floating zone growth of a crystal would reduce the perfection of the crystal and thus reduce or eliminate the extinction problem. However, it has been observed that crystals grown with a steep temperature gradient over the growth interface had a tendency to show larger extinction effects in neutron diffraction measurements than crystals grown from the melt by directional solidification growth methods. Examples of this are the following crystals: Ho_2Fe_{17}, Czochralski-grown from a cold crucible,[5] γ-NbN, grown by solid-state annealing,[6] Mo_3Si, grown by travelling-solvent growth,[7] and $MgZn_2$, grown in a Bridgman growth mode.[4] These four crystals showed strong extinction effects in single crystal neutron diffraction, and Pd_3Ce grown by directional solidification in a cold crucible showed no extinction.[4]

The extinction corrections used in the previous as well as in the present investigation were isotropic for a type I crystal with a Gaussian distribution of the crystallites.[8]

Single crystals of the compounds were cut from the samples by spark erosion and used in the neutron diffraction measurements. Spark erosion was chosen for cutting the crystal, as it is assumed that this method is a less destructive method than mechanical cutting. The dimensions of the crystals investigated are listed in Table 1. An automatic four-circle diffractometer at DR3, Risø, using 1.02 Å neu-

Table 1. Data for crystals investigated by neutron diffraction.

Compound	Unit cell parameters/Å	Density /g cm^{-3}	Chemical composition	Size of crystal/mm	Absorption, μ/cm^{-1}
TiO	4.177(1)	4.89	$Ti_{0.92(1)}O$	1.5 × 1.9 × 1.9	0.17
ZrC	4.698(1)	6.55	$ZrC_{0.95(2)}$	2.1 × 2.3 × 2.7	0.004
HfN	4.525(1)	13.39	$HfN_{0.98(1)}$	1.4 × 1.7 × 2.1	2.55

Table 2. Values of refined parameters.

No extinction correction				Isotropic extinction correction	
Atom	Site	Occupancy	B/Å^2	Occupancy	B/Å^2
TiO: R_F = 0.6 %				R_F = 0.5 %, Extinction parameter = 0.00004(2)	
Ti	4*a*	0.91(2)	0.72(3)	0.92(2)	0.72(3)
O	4*b*	1.0	0.55(2)	1.0	0.55(2)
ZrC (as grown): R_F = 3.2 %				R_F = 0.9 %, Extinction parameter = 0.00017(6)	
Zr	4*a*	1.0	0.0(5)	1.0	0.09(5)
C	4*b*	0.91(2)	0.0(6)	0.92(1)	0.11(5)
ZrC (annealed): R_F = 1.7 %				R_F = 1.7 %, Extinction parameter 0.00002(1)	
Zr	4*a*	1.0	0.36(4)	1.0	0.36(4)
C	4*b*	0.90(2)	0.33(5)	0.90(2)	0.33(5)
HfN: R_F = 1.8 %				R_F = 1.3 %, Extinction parameter 0.0004(1)	
Hf	4*a*	1.0	0.39(7)	1.0	0.10(7)
N	4*b*	0.75(3)	0.38(8)	0.72(2)	0.0(1)

trons, was used to measure the intensities, applying the standard ω–2θ scan technique. After data reduction and correction for absorption, observed and calculated structure factors were compared using the least-squares program LINUS.[9] The parameters refined were, for each case, a scale factor, two isotropic temperature factors, an occupancy factor for one of the two atoms and an isotropic extinction parameter. The neutron scattering lengths used were from Ref. 10, and the results of the refinements are listed in Table 2.

The parameters refined (occupancy factor, isotropic temperature factors and isotropic extinction parameters) are correlated. In the series of refinements only the scale factor and one group of the parameters listed above were refined, and the parameters so refined were given fixed values in the following refinements.

TiO. The compound is known to have vacancies on both sublattices. The occupancies have thus been determined from the observed density, and only the occupancy of Ti has been refined. The composition reached is in acceptable agreement with the chemical analysis. The isotropic extinction parameter is practically negligible, and the crystal of TiO grown with a very small temperature gradient over the solid–liquid growth interface is thus practically free of extinction in the neutron diffraction experiment.

ZrC. The crystal was grown by zone melting, which involves a rather steep temperature gradient over the solid–liquid growth interface. The extinction correction is considerably greater than that for TiO. To investigate if the crystal quality could be improved by annealing, this crystal was annealed in an ambient 2.3 MPa He atmosphere at 1800 °C for 20 h. The crystal was then cooled slowly to room temperature over 20 h, and used in a new neutron diffraction measurement. This new set of data showed negligible extinction (Table 2).

HfN. The crystal was grown by the zone annealing technique, which also involves a rather steep temperature gradient over the growth interface, and the extinction correction is of the same order of magnitude as for the unannealed crystal of ZrC.

The investigation shows that the crystal quality with respect to diffraction for crystals grown in high-temperature growth modes is dependent on the growth conditions, but that the quality can be improved by annealing, so that the extinction problem can be reduced considerably.

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