

FLUX GROWTH AND CHARACTERIZATION OF HEXAGONAL GERMANIUM DIOXIDE SINGLE CRYSTALS¹

C. B. FINCH AND G. W. CLARK, *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.*

ABSTRACT

Single crystals of hexagonal GeO₂ up to 2×2×3 mm were grown from Li₂O·2MoO₃ and Li₂O·2WO₃ fluxes by slow-cooling from 1100 to 950°C at ≤1°C/hr. Optically clear crystals contain 50 ppm Mo (or W) and 30 ppm Li as impurities.

INTRODUCTION

Germanium dioxide (GeO₂) exists in both a low-temperature tetragonal (rutile) and a high-temperature hexagonal (α -quartz) modification. Laubengayer and Morton (1932) reported that tetragonal GeO₂ is stable below 1033°C (in presence of a KCl-LiCl eutectic), while the hexagonal phase is stable from 1033°C up to the melting point of 1116°C. Harvill and Roy (1966) observed that tetragonal GeO₂ crystallizes in the GeO₂-H₂O system at 450–700°C between 1000 and 4000 atm, in agreement with earlier phase equilibria studies of Sarver and Hummel (1960). Kotera and Yonemura (1963) found that atmosphere (O₂, N₂, H₂O) and Li₂CO₃ or KCl "catalysts" have a marked effect on the kinetics of the hexagonal→tetragonal phase transformation at 800 to 1000°C. The foregoing observations emphasize the significant role not only of temperature but also of pressure, impurities, and surrounding environment in determining the stability of either the hexagonal or tetragonal polymorph.

The present work was prompted by a lack of single crystals of either modification which have a size, purity, and perfection acceptable for measurement of the intrinsic physical properties of GeO₂. There was a particular need for 2-mm sized GeO₂ single crystals for an electron spin resonance (ESR) study of the effect of electron and neutron irradiation on formation of oxygen vacancies in this compound. Hexagonal GeO₂ crystals up to 3 mm in size resulting from this work are often of optical quality and have proven acceptable for the ESR determinations. However, the only tetragonal GeO₂ crystals which were grown are <1 mm in size and contain impurities or defects which confuse interpretation of the intrinsic GeO₂ ESR spectrum. Accordingly, this paper places emphasis on the growth and characterization of hexagonal GeO₂.

EXPERIMENTAL

Crystallization of molten GeO₂ at its freezing point (1116°C) is hindered by the glass forming tendencies of this compound (Müller and

¹ Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Blank, 1924). A review of available literature indicated that, though some work had been done on hydrothermal and vapor growth of GeO_2 crystals (Harvill and Roy, 1966; Papazian, 1956), no attempts had been made to grow GeO_2 by high-temperature solution or flux methods. Tests were initiated to find a solvent which could dissolve and recrystallize GeO_2 of acceptably high purity at 900–1100°C, a temperature range which would favor reasonable growth kinetics and minimize formation of compounds between GeO_2 and the flux. Among the many compounds explored as potential solvents (besides KCl , LiF , PbF_2 , V_2O_5 , and $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, two were found which possess low volatility, high fluidity, and stability in air while also allowing crystallization of GeO_2 , namely: $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$ and $\text{Li}_2\text{O} \cdot 2\text{WO}_3$.

These fluxes have been frequently used for single-crystal growth of other refractory oxides, including ThSiO_4 (Finch, Harris, and Clark, 1964), BeO (Newkirk and Smith, 1965), and ThO_2 (Finch and Clark, 1965). The solubility of GeO_2 in $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$ was found to be 5.1 ± 0.1 wt % at $920 \pm 10^\circ\text{C}$ and 8.0 ± 0.1 wt % at 1050°C by weight loss determinations. The solubility of GeO_2 in $\text{Li}_2\text{O} \cdot 2\text{WO}_3$ was 4.8 ± 0.1 wt % at 985°C and 7.0 ± 0.1 wt % at 1050°C by the same method.

Growth techniques involving isothermal solvent volatilization, thermal gradients, and slow-cooling (or combinations of these) were tried using both fluxes. The experiments were carried out in air employing platinum vessels heated in a suitably controlled Kanthal- or platinum-wound resistance furnace. The vessels were equipped with thermocouple wells to allow monitoring of temperatures and thermal gradients during growth. The starting materials were 99.98% pure WO_3 (Wah Chang Smelting and Refining Company), 99.9% pure GeO_2 powder (Fairmount Chemical Company) and reagent grade Li_2CO_3 and MoO_3 (J. T. Baker Chemical Company). The WO_3 was reported to contain 20 ppm Fe and 20 ppm Ni; the MoO_3 about 20 ppm of unspecified heavy metals; and the Li_2O_3 contained 500 ppm Na and 200 ppm Ca. An impurity analysis was not available for the GeO_2 starting material.

Isothermal volatilization of $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$ from GeO_2 -saturated $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$ at $1050 \pm 10^\circ\text{C}$ resulted in nucleation and growth on platinum substrates of small (≤ 1 mm), good quality hexagonal GeO_2 crystals. Attempts to grow tetragonal GeO_2 from $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$ at 925°C were unsuccessful because of negligible volatilization over a 72-hour period. Volatilization from GeO_2 -saturated $\text{Li}_2\text{O} \cdot 2\text{WO}_3$ at 1050°C was likewise so slight that no GeO_2 nucleation occurred over a one-week interval.

Thermal gradient methods led to a rapid growth of hexagonal GeO_2 crystals of poor facial development from both $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$ and $\text{Li}_2\text{O} \cdot 2\text{WO}_3$ fluxes. The ΔT necessary for adequate solution convection over a 6-cm nutrient-growth zone interval ($\geq 20^\circ\text{C}$ at 950 – 1050°C) also produced

excessive supersaturation, resulting in profuse nucleation and rapid growth of intergrown crystals. Attempts to eliminate or restrict spurious nucleation by seeding the growth zone while imposing ΔT 's less than 20°C were unsuccessful. Crystals of the tetragonal modification were grown from $\text{Li}_2\text{O}\cdot 2\text{MoO}_3$ when the growth zone temperature was below 950°C . Such crystals (≤ 1 mm in size) are dark brown and contain undetermined impurities or defects which interfere with their ESR characterization.

The slow-cooling growth technique gave the best growth results. Well-developed, optical quality hexagonal GeO_2 crystals were grown up to 3 mm on edge from both $\text{Li}_2\text{O}\cdot 2\text{MoO}_3$ or $\text{Li}_2\text{O}\cdot 2\text{WO}_3$ fluxes by slow-cooling from 1100 to 950°C at $\leq 1^\circ\text{C/hr}$. The GeO_2 crystals grown from $\text{Li}_2\text{O}\cdot 2\text{WO}_3$ proved acceptable for the ESR determinations, while those from $\text{Li}_2\text{O}\cdot 2\text{MoO}_3$ contained impurities or defects which complicated their ESR spectra. In nearly all runs with both fluxes there were a few hopper-shaped GeO_2 crystals (often up to 1 cm in size) which had considerable flux inclusions. Only hexagonal GeO_2 formed in runs terminated at 950°C . In $\text{Li}_2\text{O}\cdot 2\text{MoO}_3$ runs cooled further to 920°C , a small amount of the brown, tetragonal GeO_2 phase was produced in addition to the hexagonal. The tetragonal modification did not nucleate in the $\text{Li}_2\text{O}\cdot 2\text{WO}_3$ runs, and uniform growth of the hexagonal phase continued while cooling to temperatures as low as 920°C .

The following procedure was found adequate for the growth of good quality single crystals of hexagonal GeO_2 up to $2\times 2\times 3$ mm. Twenty grams of GeO_2 powder are mixed with 230 g of $\text{Li}_2\text{O}\cdot 2\text{MoO}_3$ or 265 g of $\text{Li}_2\text{O}\cdot 2\text{WO}_3$ powder (prepared by reacting Li_2CO_3 and MoO_3 or WO_3 powders in a platinum dish at 800°C) to form a solution saturated with GeO_2 at 1050°C . The resulting mixture is placed in a 5-cm diameter by 8-cm tall platinum crucible. The charged crucible is equipped with a thermocouple well, fitted with a cover, and inserted into a suitably controlled resistance furnace at 1100°C . The thermal geometry of the growth system is such that at thermal equilibrium the crucible floor is about 10°C cooler than the upper solution surface.

The crucible is then cooled from 1100°C at rates not exceeding 1°C/hr to 950°C at which temperature it is taken from the furnace. The liquid is quickly decanted off the GeO_2 crystals, which adhere to the crucible floor. The crucible and crystals are (for convenience) allowed to cool in air to room temperature with no visible cracking of even 3-mm sized crystals. The crystals are dislodged by indenting or tapping the outside crucible bottom and are ultrasonically cleaned in distilled water. The cleaning operation removes residual flux, but also results in some sur-

face attack on the GeO_2 since hexagonal GeO_2 is slightly soluble in H_2O (Laubengayer and Morton, 1932).

CHARACTERIZATION

The resulting colorless, transparent crystals were examined under a polarizing microscope and found to have indices of refraction identical with those reported in the literature for hexagonal GeO_2 : $\omega=1.695$, $\epsilon=1.735$ (Laubengayer and Morton, 1932). The X-ray powder pattern of the crystals coincided with data reported for the hexagonal (α -quartz) modification of GeO_2 (Swanson and Tatge, 1953).

The crystals are bounded predominantly by rhombohedral $\{10\bar{1}1\}$ faces, with prism $\{10\bar{1}0\}$ faces incompletely developed except in rare cases. The interfacial angles measured on a hexagonal GeO_2 single crystal using a two-circle optical goniometer compare favorably with those computed from an axial ratio of 1.13 (Swanson and Tatge, 1953). Additional physical properties are given in Table 1.

TABLE 1. PROPERTIES OF HEXAGONAL GeO_2 SINGLE CRYSTALS GROWN FROM $\text{Li}_2\text{O}\cdot 2\text{MoO}_3$ FLUX

| | |
|--|--|
| Habit | Rhombohedral $\{10\bar{1}1\}$ with prism $\{10\bar{1}0\}$ incompletely developed |
| Density | 4.24 ± 0.01 g/cm ³ . (Berman balance) 4.28 g/cm ³ (computed, x-ray) |
| Hardness on $\{10\bar{1}1\}$ | 7 to 7.5 (Mohs) |
| Fracture | Uneven |
| Impurities detected by spectroscopic analysis ($\times 0.5$ to $\times 2.0$) | 50 ppm Mo 30 ppm Li 1 ppm Ca < 3 to 100 ppm Al < 10 to 2000 ppm Si |

No paramagnetic chemical impurities were detected in an ESR examination of the GeO_2 crystals grown from $\text{Li}_2\text{O}\cdot 2\text{WO}_3$. After electron or neutron irradiation, the crystals displayed resonances relatable to GeO_2 glass, and believed to be the result of oxygen vacancy formation. The ESR study will be described at a later time.

ACKNOWLEDGMENTS

The authors acknowledge with thanks the assistance of O. C. Kopp for the density determinations, L. A. Harris for the microscopic and X-ray examinations, and of T. Purcell for the ESR characterizations.

REFERENCES

- FINCH, C. B., AND G. W. CLARK (1965) Single crystal growth of thorium dioxide from lithium ditungstate solvent. *J. Appl. Phys.*, **36**, (7), 2143-45.

- , L. A. HARRIS, AND G. W. CLARK (1964) The thorite-huttonite phase transformation as determined by growth of synthetic thorite and huttonite single crystals. *Amer. Mineral.*, **49**, 782–85.
- HARVILL, M. L., AND RUSTUM ROY (1966) Habit of hydrothermally grown rutile structure crystals in the light of the Hartman theory and its extension. *Proc. Int. Conf. Crystal Growth, Boston, 1966*, 563–67.
- KOTERA, Y., AND M. YONEMURA (1963) Kinetics of the transformation of germanium oxide. *Trans. Faraday Soc.*, **59**, 147–55.
- LAUBENGAYER, A. W., AND D. S. MORTON (1932) Germanium XXXIX, the polymorphism of germanium dioxide. *J. Amer. Chem. Soc.*, **54**, 2303–20.
- MÜLLER, J. H., AND H. R. BLANK (1924) The allotropy of germanium dioxide. *J. Amer. Chem. Soc.*, **46**, 2358–67.
- SWANSON, H. E., AND E. TATGE (1953) Standard X-ray diffraction patterns. *NBS Circ.*, **539**, Vol. I, 51.
- NEWKIRK, H. W., AND D. K. SMITH (1956) Studies on the formation of crystalline synthetic bromellite II macrocrystals. *Amer. Mineral.*, **50**, 44–71.
- PAPAZIAN, H. W. (1956) Energy gap and electrical conductance of hexagonal germanium dioxide. *J. Appl. Phys.*, **27**, 1253–54.
- SARVER, J. F., AND F. A. HUMMEL (1960) Alpha to beta transition in germania quartz and a pressure temperature diagram for GeO₂. *J. Amer. Ceram. Soc.*, **43**(6), 336.
- Manuscript received, December 1, 1967; accepted for publication, April 24, 1968.*