FLUX GROWTH AND CHARACTERIZATION OF HEXAGONAL GERMANIUM DIOXIDE SINGLE CRYSTALS

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Abstract

Single crystals of hexagonal GeO₂ up to 2x2x3 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 GeO₂ crystals (Harvill and Roy, 1966; Papazian, 1956), no attempts had been made to grow GeO₂ by high-temperature solution or flux methods. Tests were initiated to find a solvent which could dissolve and recrystallize GeO₂ of acceptably high purity at 900-1100°C, a temperature range which would favor reasonable growth kinetics and minimize formation of compounds between GeO₂ and the flux. Among the many compounds explored as potential solvents (besides KCl, LiF, PbF₂, V₂O₅, and Na₂O·2B₂O₃, two were found which possess low volatility, high fluidity, and stability in air while also allowing crystallization of GeO₂, namely: Li₂O·2MoO₃ and Li₂O·2WO₃.

These fluxes have been frequently used for single-crystal growth of other refractory oxides, including ThSiO₄ (Finch, Harris, and Clark, 1964), BeO (Newkirk and Smith, 1965), and ThO₂ (Finch and Clark, 1965). The solubility of GeO₂ in Li₂O·2MoO₃ was found to be 5.1±0.1 wt % at 920±10°C and 8.0±0.1 wt % at 1050°C by weight loss determinations. The solubility of GeO₂ in Li₂O·2WO₃ 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 WO₃ (Wah Chang Smelting and Refining Company), 99.9% pure GeO₂ powder (Fairmount Chemical Company) and reagent grade Li₂CO₃ and MoO₃ (J. T. Baker Chemical Company). The WO₃ was reported to contain 20 ppm Fe and 20 ppm Ni; the MoO₃ about 20 ppm of unspecified heavy metals; and the Li₂O contained 500 ppm Na and 200 ppm Ca. An impurity analysis was not available for the GeO₂ starting material.

Isothermal volatilization of Li₂O·2MoO₃ from GeO₂-saturated Li₂O·2MoO₃ at 1050±10°C resulted in nucleation and growth on platinum substrates of small (<1 mm), good quality hexagonal GeO₂ crystals. Attempts to grow tetragonal GeO₂ from Li₂O·2MoO₃ at 925°C were unsuccessful because of negligible volatilization over a 72-hour period. Volatilization from GeO₂-saturated Li₂O·2WO₃ at 1050°C was likewise so slight that no GeO₂ nucleation occurred over a one-week interval.

Thermal gradient methods led to a rapid growth of hexagonal GeO₂ crystals of poor facial development from both Li₂O·2MoO₃ and Li₂O·2WO₃ fluxes. The ΔT necessary for adequate solution convection over a 6-cm nutrient-growth zone interval (≥20°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 Li$_2$O·2MoO$_3$ 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 Li$_2$O·2MoO$_3$ or Li$_2$O·2WO$_3$ fluxes by slow-cooling from 1100 to 950°C at ≤1°C/hr. The GeO$_2$ crystals grown from Li$_2$O·2WO$_3$ proved acceptable for the ESR determinations, while those from Li$_2$O·2MoO$_3$ 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 Li$_2$O·2MoO$_3$ 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 Li$_2$O·2WO$_3$ 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 2×2×3 mm. Twenty grams of GeO$_2$ powder are mixed with 230 g of Li$_2$O·2MoO$_3$ or 265 g of Li$_2$O·2WO$_3$ powder (prepared by reacting Li$_2$CO$_3$ 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$_2$O (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 ($\alpha$-quartz) modification of GeO$_2$ (Swanson and Tatge, 1953).

The crystals are bounded predominantly by rhombohedral $\{10\overline{1}1\}$ faces, with prism $\{10\overline{1}0\}$ 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 Li$_2$O·2MoO$_3$ Flux**

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Habit</td>
<td>Rhombohedral ${10\overline{1}1}$ with prism ${10\overline{1}0}$ incompletely developed</td>
</tr>
<tr>
<td>Density</td>
<td>4.24±0.01 g/cm$^3$. (Berman balance)</td>
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<tr>
<td></td>
<td>4.28 g/cm$^3$ (computed, x-ray)</td>
</tr>
<tr>
<td>Hardness on ${10\overline{1}1}$</td>
<td>7 to 7.5 (Mohs)</td>
</tr>
<tr>
<td>Fracture</td>
<td>Uneven</td>
</tr>
<tr>
<td>Impurities detected by spectroscopic analysis (×0.5 to ×2.0)</td>
<td>50 ppm Mo</td>
</tr>
<tr>
<td></td>
<td>30 ppm Li</td>
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<tr>
<td></td>
<td>1 ppm Ca</td>
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<tr>
<td></td>
<td>&lt; 3 to 100 ppm Al</td>
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<tr>
<td></td>
<td>&lt;10 to 2000 ppm Si</td>
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</table>

No paramagnetic chemical impurities were detected in an ESR examination of the GeO$_2$ crystals grown from Li$_2$O·2WO$_3$. 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.

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**References**


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