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A CHALCEDONY-LIKE VARIETY OF GERMANIA

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Abstract

A fibrous variety of GeO_2 (quartz type) was produced hydrothermally. It has anamolous physical and optical properties which are analogous to the corresponding form of silica, chalcedony. Accordingly, this variety may be termed chalcedonic germania.

Refractive indices determined for single crystals of GeO_2 (quartz type) are slightly different from those previously reported.

Introduction

During hydrothermal studies in the system GeO_2—H_2O, single crystals of GeO_2, analogous to quartz, were produced under certain conditions. With a slight variation in conditions, a fibrous modification with distinct optical and physical properties was formed, and is subsequently referred to as chalcedonic germania.

To prepare the quartz-type crystals of GeO_2, germanium dioxide glass, in the form of irregular lumps of about 0.5 gram each, was reacted at 200° C. and 12 atmospheres with 5 ml. of distilled and demineralized water. In runs of about 2 hours, the glass was converted *in situ* to the hexagonal form as shown by optical examination and *x*-ray powder patterns. However, this is a metastable form. GeO_2 (rutile type) is the low temperature form according to Laubengayer and Morton (1932), with a transformation to the hexagonal form at about 1033° C. Apparently at 200° C. in the presence of water, GeO_2 glass first reacts to give the metastable hexagonal form. With runs at higher temperatures or for longer periods, the product was invariably the rutile-type of GeO_2.

The optically and physically distinct chalcedonic modification was produced by the same methods, except that the autoclave was rapidly cooled by quenching with water.

GeO_2 (Quartz Type)

The hexagonal crystals of GeO_2 were identified by the *x*-ray powder diffraction data in the ASTM card file, and gave the same pattern as the chalcedonic germania.

The refractive indices reported in the literature by Laubengayer and

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Morton (1932) need revision. Careful measurements were made by the immersion method using sodium light and temperature corrections with calibrated liquids. The birefringence was also determined, using a Berek compensator. A summary of the morphological and optical properties is given in Table 1.

Chalcedonic Germania

The following observations show chalcedonic germania has anomalous properties in relation to the quartz form. Further, these properties are very similar and comparable to those of the chalcedonic form of silica.

As shown in Fig. 1, the chalcedonic germania looks like a hemispherical variety of ordinary chalcedony. It consists of microscopic, fibrous, fan-shaped aggregates; the larger aggregates being about 0.1 mm. in size. Although the fibrous character is marked, individual fibers are so narrow that they are difficult to distinguish. In orientation, the fibers range from approximate parallelism to strongly divergent groups. Under crossed nicols, most of the fibers show approximate straight extinction, but some have extinction angles ranging from small up to about 30°. Also, some of the fiber groups exhibit wavy or varying extinction in different places along their length. Almost all of the fibers or fiber groups are length-slow, but a few are length-fast. In addition, traces of concentric banding are occasionally present. In color, much of the germanium chalcedony appears distinctly brown in transmitted light in contrast to the colorless appearance of the quartz form of GeO_2. However, the color is gradational, and the fibrous aggregates vary, often along the length of the fiber bundles, from a distinct brown to colorless. All of the above mentioned properties appear to be the same or highly similar to those found in chalcedony.

Table 1. Morphological and Optical Data on GeO_2 (Quartz-Type)

Habit (A) Rhombohedrons, approximately cubes.
(B) Equally developed + and − rhombohedrons (geometric hexagonal dipyramids) with hexagonal prism

Uniaxial, optic sign +	Previously reported
$\omega=1.697\pm0.001$	$\omega=1.695$
$\epsilon=1.724\pm0.003$	$\epsilon=1.735$
Birefringence 0.027 ± 0.002	B=0.040
Length slow (+elongation)	

The refractive indices of germania chalcedony are compared in Table 2 to the quartz-type of GeO_2 and also to the refractive indices of the cor-

TABLE 2. REFRACTIVE INDICES OF QUARTZ AND CHALCEDONY AND THE CORRESPONDING VARIETIES OF GeO_2

Chalcedony	Chalcedonic germania
1.533–1.539 1.530	1.653 1.633
Quartz $\omega=1.544$ $\epsilon=1.553$	Quartz type of GeO_2 $\omega=1.697$ $\epsilon=1.724$

responding silica varieties as given by Winchell (1951). The refractive indices of chalcedonic germania are variable as are those of chalcedony, and those given in Table 2 refer to the more chalcedonic material. Actually, refractive indices of some of the fan-shaped aggregates range from

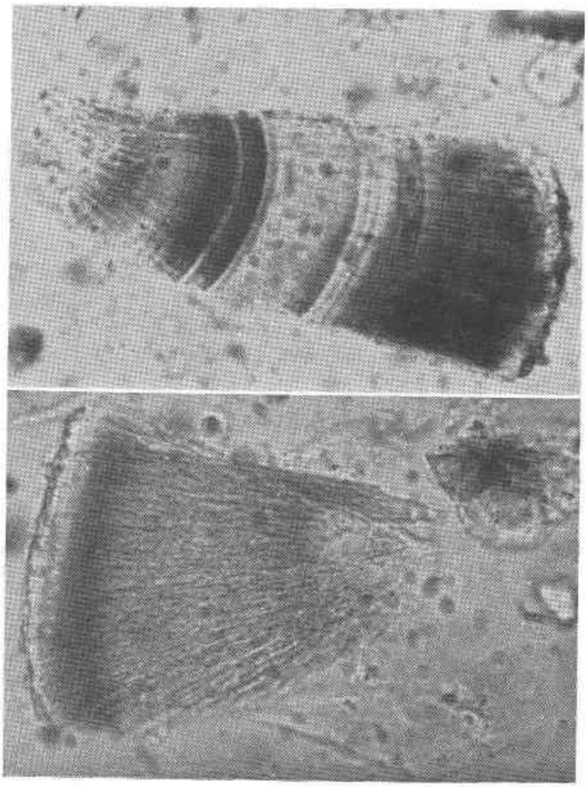

Fig. 1. Chalcedonic germania showing banding (above) and fibrous texture. Ordinary light. Magnification 600×.

those given for the chalcedonic variety up to those of the quartz type. This change appears to be gradational along the length of some of the fibrous aggregates. Corresponding with gradational changes in refractive indices, there is a gradational change in color from a distinct brown for the chalcedonic material of lowest refractive indices to colorless for the quartz form. In the case of chalcedony Folk and Weaver (1952), by using the electron microscope, showed that small cavities are present and that these produce a brownish color in transmitted light. Refractive index and specific gravity were also shown to vary in proportion to the abundance of the holes. According to Pelto (1956), the brown color is due to the preferential scattering of blue light by suitably small submicroscopic pores. Thus, the brown color of germanium chalcedony which is associated with low refractive indices, along with variation toward lighter color with higher refractive indices, supports the idea that the anomalous properties of germanium chalcedony are also due to the presence of submicroscopic holes.

The specific gravity could not be accurately measured because of the presence of small amounts of the quartz form and the variable nature of some of the material. However, a reliable estimate can probably be calculated by the use of refractive indices and chemical composition in the same manner as has recently been emphasized to give reliable densities for minerals by Jaffe (1956) and Allen (1956). Using the Gladstone-Dale relation, the specific refractivity of GeO_2 was calculated as .165 from refractive indices measured on the quartz form and x-ray density. Using this specific refractivity and refractive indices, the calculated specific gravity of the germanium chalcedony referred to in Table 2 is 3.9 and compares to 4.28 for the quartz type.

The chalcedonic germania was identified structurally by x-ray powder pattern and derived unit cell measurements which are compared in Table 3 to those given by Donnay and Nowacki in Crystal Data, 1954. In addition, infrared absorption spectra in the range 2–15 microns, which were obtained for both the quartz and chalcedony forms, gave essentially identical and characteristic patterns except for minor differences in intensities.

Table 3. Comparison of Unit Cell Measurements

Chalcedonic germania	Quartz type GeO_2 (from Crystal Data)
Hexagonal $a_0=4.96$ Å $c_0=5.65$	Hexagonal $a_0=4.972\pm.005$ kX $c_0=5.648\pm.005$

In summary, the properties of chalcedonic germania are very similar and comparable to those given for chalcedony: Winchell (1951), Rogers and Kerr (1942), Folk and Weaver (1952), and Pelto (1956). Chalcedonic germania is essentially a fibrous variety of the quartz form of GeO_2 with anomalous physical and optical properties. There is thus the common problem of anomalous properties of the chalcedonic forms of GeO_2 and SiO_2. Chalcedony, according to Pelto (1956), is regarded by recent workers as microcrystalline quartz with submicroscopic pores containing water; while earlier workers supported the idea of interstitial, amorphous silica. In the present investigation, the gradational relationship between the chalcedonic and quartz varieties, as well as the relation between refractive indices and color, support the concept that the chalcedonic varieties are quartz forms with submicroscopic holes.

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