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HYDROTHERMAL INVESTIGATION OF GeO_2

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INTRODUCTION

Germania (GeO_2) is an interesting compound from a crystalchemical viewpoint because it is a dioxide exhibiting the two important structures: the rutile-type with six-coordinated cation and quartz-type with four-coordinated cation. The polymorphism in GeO_2 under atmospheric pressure was first studied by Laubengayer and Morton (1932) and Sarver (1961). According to them, the rutile-type GeO_2 is stable below 1050°C above which temperature it transforms slowly to the quartz-type which melts at 1116°C. The reverse process can only be completed in the presence of a mineralizer. Several investigations have questioned the transformation temperature. Shafer and Roy (1957) reported that it should be lowered to 1007°C under atmospheric pressure. This value was later verified by Robbins and Levin (1959), and Majumdar (1958) placed the transformation temperature at 1002°C.

EXPERIMENTAL METHOD

Work on the stability relations in the system GeO_2-H_2O was undertaken to provide basic information on the conditions for hydrothermal growing the polymorphs. Materials used were reagent grade GeO_2 with the quartz-type structure, laboratory-prepared GeO_2 glass, and hydrothermally synthesized rutile-type GeO_2. Each was contained in a separate platinum capsule. The p-t field of interest in the system necessitated low-water content in the charge. The required amount of water was obtained by filling each capsule with water vapor at 100°C and 1 atmospheric pressure. This was done by placing a drop of water at the bottom of the capsule, adding the GeO_2 starting material, and suspending a set of these capsules over boiling water for periods of two to three hours. The water in the capsule evaporated in the steam bath, thereby replacing the air in the capsule with water vapor. The capsules were removed singly, and immediately crimped shut and welded. They were usually bloated at the end of the run, demonstrating that a vapor phase was present, and the water added was in excess of the amount required to saturate a glass if formed. In the few cases where the capsule had collapsed, leaks were detected and the runs were always repeated. Three capsules, each containing one of the three different starting materials, were

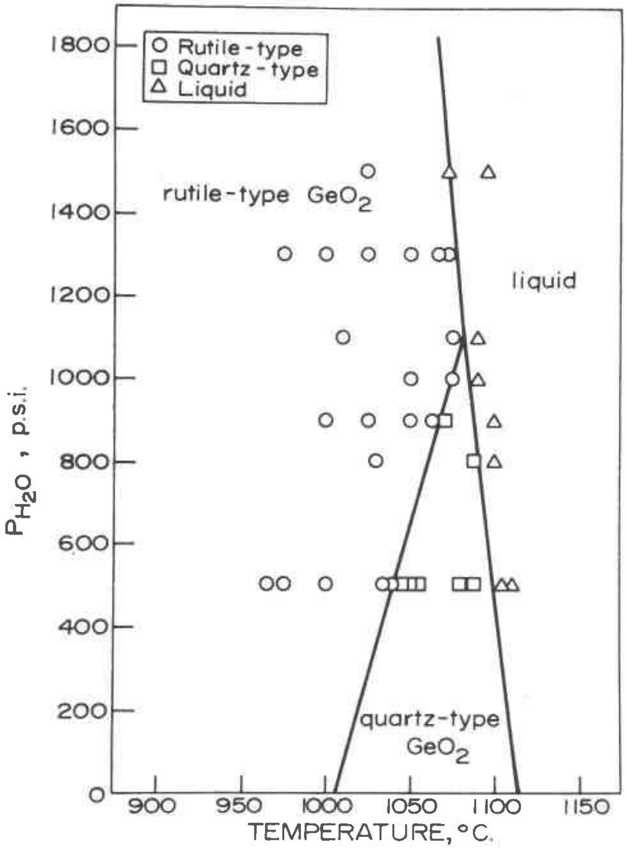

Fig. 1.

bonded together by platinum wire forming a sample assemblage, and treated simultaneously.

The pressure vessel used was a modified cold-seal type with ¼-inch ID and fabricated from Rene 41[1]. Argon was used as the pressure medium to balance the water pressure in the sample capsules. The vessel was heated externally in a Tem-Pres hydrothermal system. The temperature was measured by either chromel-alumel or Pt-Pt 10 Rh thermocouples, depending on the temperature involved. The vessel was air-quenched at the end of the run. This was satisfactory since the equilibrium established at high temperature and pressure was not changed during the cooling period. Phase identification was made using petrographic microscopy, and X-ray diffraction.

The stability relations in the system GeO_2-H_2O were studied in the temperature range between 900° and 1150°C with pressure up to 1500 psi. It was found that a minimum of four hours was required for the reaction to reach equilibrium or at least indicate the direction of equilibrium. Runs of longer than six hours duration were not feasible because the

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[1] High temperature superalloy manufactured by Union Carbide Corporation.

TABLE 1. SUMMARY OF CRITICAL RUNS IN THE SYSTEM GeO_2-H_2O

Source	PSI	°C	Hrs.	Results	Source	PSI	°C	Hrs.	Results
R	1500	1073	5	G	R	900	1100	$5\frac{1}{4}$	G
Q	1500	1073	5	G	Q	900	1100	$5\frac{1}{4}$	G
G	1500	1073	5	G	G	900	1100	$5\frac{1}{4}$	G
R	1500	1025	5	R	R	900	1070	$5\frac{1}{4}$	Q+R
Q	1500	1025	5	R	Q	900	1070	$5\frac{1}{4}$	Q
G	1500	1025	5	R	G	900	1070	$5\frac{1}{4}$	Q
R	1300	1075	5	R	R	900	1063	$5\frac{1}{4}$	R
Q	1300	1075	5	R	Q	900	1063	$5\frac{1}{4}$	R+Q
G	1300	1075	5	R	G	900	1063	$5\frac{1}{4}$	R+Q
R	1100	1090	5	G	R	900	1054	$5\frac{1}{4}$	R
Q	1100	1090	5	G	Q	900	1054	$5\frac{1}{4}$	R
G	1100	1090	5	G	G	900	1054	$5\frac{1}{4}$	R
R	1100	1075	5	R	R	800	1100	$5\frac{3}{4}$	G
Q	1100	1075	5	R	Q	800	1100	$5\frac{3}{4}$	G
G	1100	1075	5	R	G	800	1100	$5\frac{3}{4}$	G
R	1000	1090	$5\frac{3}{4}$	G	R	800	1087	$5\frac{1}{4}$	Q
Q	1000	1090	$5\frac{3}{4}$	G	Q	800	1087	$5\frac{1}{4}$	Q
G	1000	1090	$5\frac{3}{4}$	G	G	800	1087	$5\frac{1}{4}$	Q
R	1000	1075	$5\frac{1}{4}$	R	R	500	1110	$5\frac{1}{4}$	G
Q	1000	1075	$5\frac{1}{4}$	R	Q	500	1110	$5\frac{1}{4}$	G
G	1000	1075	$5\frac{1}{4}$	R+Q	G	500	1110	$5\frac{1}{4}$	G
R	1000	1050	$5\frac{1}{4}$	R	R	500	1046	$4\frac{3}{4}$	Q
Q	1000	1050	$5\frac{1}{4}$	R	Q	500	1046	$4\frac{3}{4}$	Q
G	1000	1050	$5\frac{1}{4}$	R	R	500	1036	4	R
					Q	500	1036	4	R
					G	500	1036	4	R

R = Rutile polymorph.
Q = Quartz polymorph.
G = Glass.

capsules often became corroded and leaked. Even within this limit of six-hour duration the corrosion of capsule was also a problem in some runs with high-water pressures. The uncertainties in the individual runs were estimated to be ±10°C and 25 psi.

RESULTS AND DISCUSSION

The experimental results are shown in Figure 1 with a summary of critical runs tabulated in Table 1. Below 1100 psi., both crystalline polymorphs of GeO_2 and the glass were found in some quenched samples. With increasing pressure up to 1100 psi., the temperature of the quartz-rutile transformation increased from 1007° to 1083°C. Thus, the quartz-type GeO_2 has a wedge-shaped field of stability in the p-T diagram.

The data indicate that above 1100 psi., the rutile-type GeO_2 exists in equilibrium directly with the liquid (glassy GeO_2 in quenched samples) along an univariant p-T curve, and the quartz-type GeO_2 has no stability field. When GeO_2 glass was used as the starting material, the quartz-type GeO_2 grew initially even in the field of the rutile-type polymorph. However, in the stability field of the rutile polymorph, this stable phase later crystallized. This fact, plus the formation of rutile-type GeO_2 from quartz-type GeO_2 under the identical physical conditions, proves that the quartz-type GeO_2 produced from the initial devitrification was metastable with respect to the rutile-type polymorph. The rutile-type GeO_2 melts at lower temperatures with increasing pressure. A triple point at which quartz-type, rutile-type and liquid GeO_2 are in equilibrium exists at 1083° and 1100 psi.

The results obtained demonstrate that reversible equilibrium was achieved, but the reconstructive transformation occurred through a solution process. The phase diagram for the system GeO_2-H_2O is similar to that for the system SiO_2-H_2O. The densities of the phases involved are 6.239 for rutile-type GeO_2, 4.228 for quartz-type GeO_2, and 3.6277 for GeO_2 glass at room temperature. As in the case of the system SiO_2-H_2O, the slopes of the phase boundaries is dependent on the differences between the densities of the phase involved. The reaction path is controlled by the relative solubility of the phases, and the ease of nucleation of the crystals. Their relative solubilities in water are:

$$GeO_2 \text{ (glass)} > GeO_2 \text{ (quartz-type)} > GeO_2 \text{ (rutile-type)}$$

The quartz-type GeO_2 is readily soluble in water and so sometimes recrystallizes appreciably during the heating process. GeO_2 glass is also appreciably soluble in water and recrystallizes first to the quartz-type form which is readily nucleated. The quartz-type GeO_2 formed will slowly invert to the rutile-type polymorph at temperatures below the inversion temperature. The process is facilitated by the presence of seeds of the stable polymorph. Because of differences in solubility, ease of nucleation, and structural relationships between the various phases, both stable and metastable equilibrium reactions and crystal growth occur in this system. The hydrothermal growth of single crystals of the quartz-type GeO_2 occurs under conditions in which it is metastable with respect to the rutile-type polymorph.[1] On the other hand, the growth of crystals of the rutile-type polymorph (Harvill and Roy, 1966) represents a stable process.

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COPPER ZONING IN PYRITE FROM CERRO DE PASCO, PERU

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INTRODUCTION

A review of 785 pyrite analyses (Fleischer, 1955) indicates that 75 percent contain more than 10 ppm copper, 10 percent contain more than 1 percent copper, and the maximum concentration reported is about 6 percent copper. The conclusion was reached that "it seems probable that most, if not all, of (the copper) is present as admixed chalcopyrite or other copper minerals" (*Ibid*, p. 1005). A review of the literature indicates that this is a widely held view. Analyses by all standard techniques are suspect, unless it can be shown that the material is inclusion-free. However, electron microprobe analysis, having a resolution of one micron, is ideally suited to the study of minor elements and their distribution. Probe analysis has recently confirmed the presence of significant amounts of copper held in solid solution in pyrite (Frenzel and Ottemann, 1967). The present note further documents this fact.

ANALYTICAL METHODS

The minor element content of sulfides from Cerro de Pasco, Peru, was studied by electron microprobe analysis (Applied Research Laboratories, EMX) of carbon-coated, polished sections. The analytical conditions were as follows: sample current, 0.03 microamps; accelerating voltage, 20 kV; probe diameter, 2 microns; and counting time, 40 seconds. Low counting rates obviated dead-time corrections. Drift and background corrections were applied to all data. Atomic number, fluorescence, and absorption corrections were not applied. Due to the low amounts of copper, these corrections would have little effect on the

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