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THE SYSTEM GeO_2-SiO_2[1]

W. S. MILLER, F. DACHILLE, E. C. SHAFER AND RUSTUM ROY
College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

ABSTRACT

Phase equilibria in the lower temperature region of the system GeO_2-SiO_2 have been determined in hydrothermal and opposed anvil pressure apparatus. A maximum of 31 mole % GeO_2 is soluble in the α quartz phase at 700°C. and 0.7 kb, the solubility decreasing with increasing pressure to a eutectic pressure (29 kb at 450°C.) above which the stable phases are SiO_2 coesite and GeO_2 rutile. No solid solution has been found in either the coesite or rutile phases, but appears to be complete in β quartz. The solubility of GeO_2 raises the α-β transition to 670°, and also raises sharply the temperature of the quartz-tridymite inversion.

INTRODUCTION

This work is a part of a study of silica and its structural analogs with special interest in the extent of solid solution between isomorphs.

GeO_2 is an interesting compound to study with respect to its crystal-chemical relationships with the common (Laubengayer and Morton, 1932) and high-pressure forms of silica (Coes, 1953; Stishov and Popova, 1953). From a study of the system GeO_2-SiO_2 one could obtain data on the amount of GeO_2 which can be accommodated in four-fold coordinated structures of silica and also learn whether any Si^{4+} can enter the six-fold coordination in the germania rutile lattice.

Further, in our earliest thinking on high pressure calibration it was proposed that a binary system with the extent of solid solution changing with pressure would provide an excellent potential continuous calibrant (Dachille and Roy, 1957). The possibility of establishing an isothermal P-χ section (at 400–500° C.) in the system GeO_2-SiO_2 for example, could provide a pressure scale out to about 80 kb.

Experimental Studies

Preparation of mixtures. In most instances, the starting samples were prepared by mixing the correct proportions of quartz-form germania and amorphous silica. The oxide mixture was mulled under alcohol, and dried. As a check against this method, other starting samples were prepared by the simultaneous hydrolysis of the two tetra-chlorides mixed in the correct proportions. If the amorphous silica used in the first method was a precipitated silicic acid there was no detectable difference between results obtained with samples prepared by the two methods.

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However, when "Cab-o-Sil" was used as the source of silica for the mix, it was sometimes found difficult to reach equilibrium, especially in the hydrothermal runs.

High pressure runs. The techniques and apparatus used for the hydrothermal and dry work (Shepherd *et al.* 1909; Roy and Osborn, 1952) and the opposed anvil runs (Dachille and Roy, 1959; Dachille and Roy, 1962) have been described elsewhere. Mixtures ranging from 1% GeO_2-99% SiO_2 to 80% GeO_2-20% SiO_2 were studied by both methods: hydrothermally at 700 bars, varying the temperature; isothermally by varying the pressure in two series of runs, one at 500° C. and the other at 450° C., the latter being used to extend the pressure limits of the apparatus used. In the hydrothermal work the samples were sealed with a small amount of water in 12 mm$\times$2 mm diameter silver or gold tubes.

It was found necessary to do all the hydrothermal work in such a "closed system" because of the high solubility of the GeO_2 (quartz). Batches of solid solutions prepared in the relatively large volumes of Morey bombs were found by x-ray fluorescence analysis to have lost appreciable germania to the water solution. In the isothermal series steel anvils (Speed Star, 66HS, or the equivalent) were used for runs under 45 kb, and anvils with tungsten carbide inserts were used for runs at higher pressures up to 130 kb. In all cases, the runs were quenched under pressure in the hope that all crystal forms present at the higher temperature might persist and be identified at room temperature. Identification was made by means of x-ray powder diffraction patterns obtained with a Norelco diffractometer. Microscopic examination also was carried out on certain samples, as described in the discussion of the results.

Evidence for solid solution was sought by determining the values of 2θ for selected diffraction peaks for the phases found and comparing them with those of corresponding peaks on patterns obtained from the respective pure phases. Those products which consisted of a single phase were used to establish a curve showing the variation with compositions of 2θ values for a particular reflection (*e.g.* quartz 112) (Fig. 1). This indicates a considerable departure from the ideal relationship. The curve was then used to determine the composition of the quartz (ss) phase in other products, which, together with the nature of the phase assemblages helped to establish phase boundaries. "Dry" runs with the GeO_2 end member were carried out in an attempt to fix the inversion temperature from the rutile to the quartz form. These were made in a platinum-wound furnace with temperatures controlled to $\pm 5°$ by Minneapolis Honeywell Pyrovane Controllers. Temperatures were read with platinum-platinum 10% rhodium thermocouples.

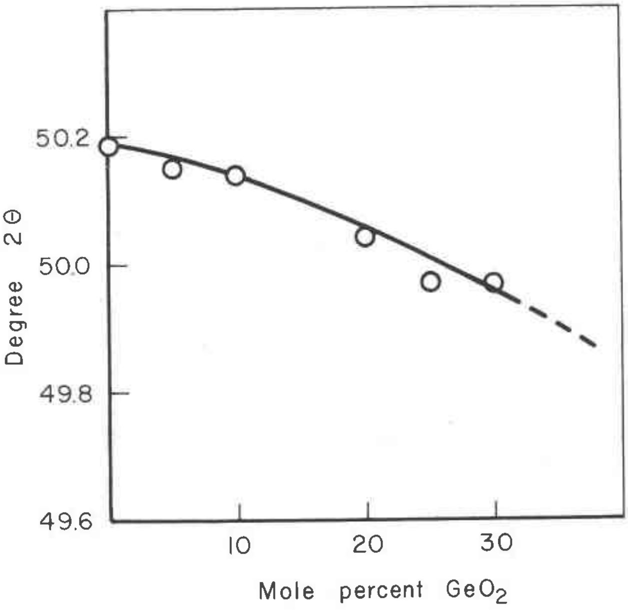

Fig. 1. Change of quartz (ss) (112) in terms of 2θ (CuKα)

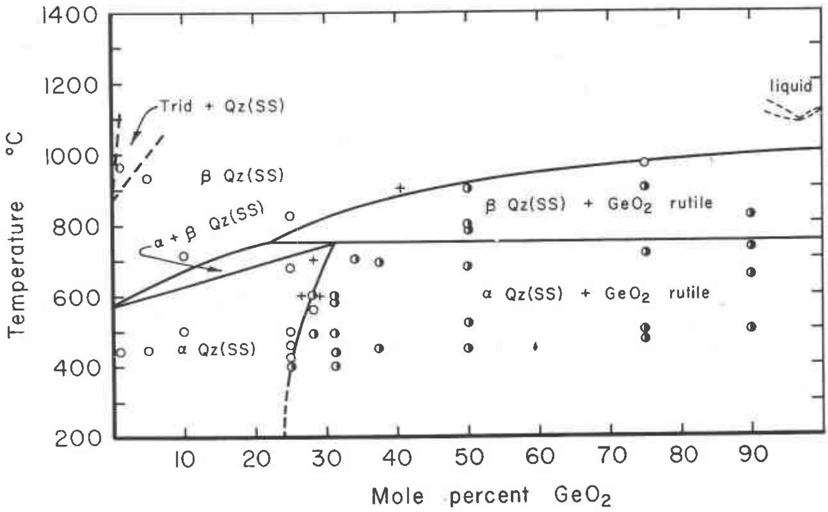

Fig. 2. Phase diagram of the system SiO_2-GeO_2 based on dry studies and hydrothermal studies at 700 bars.[1] The boundaries determined both by phases and by compositions of Qz (SS) in two-phase fields.

To complete other portions of the phase diagram attempts were made to follow the effect of solid solution on the α to β quartz transition by differential thermal analysis.

RESULTS AND DISCUSSION

Figure 2 shows the phase diagram constructed from the data obtained in the hydrothermal study. Figure 3 summarizes the results of the isothermal anvil runs in a p-x section for the system.

Hydrothermal, DTA, and "dry" studies. As shown, at relatively low pressure and temperature (700 bars at about 300° C.) germania solid solution

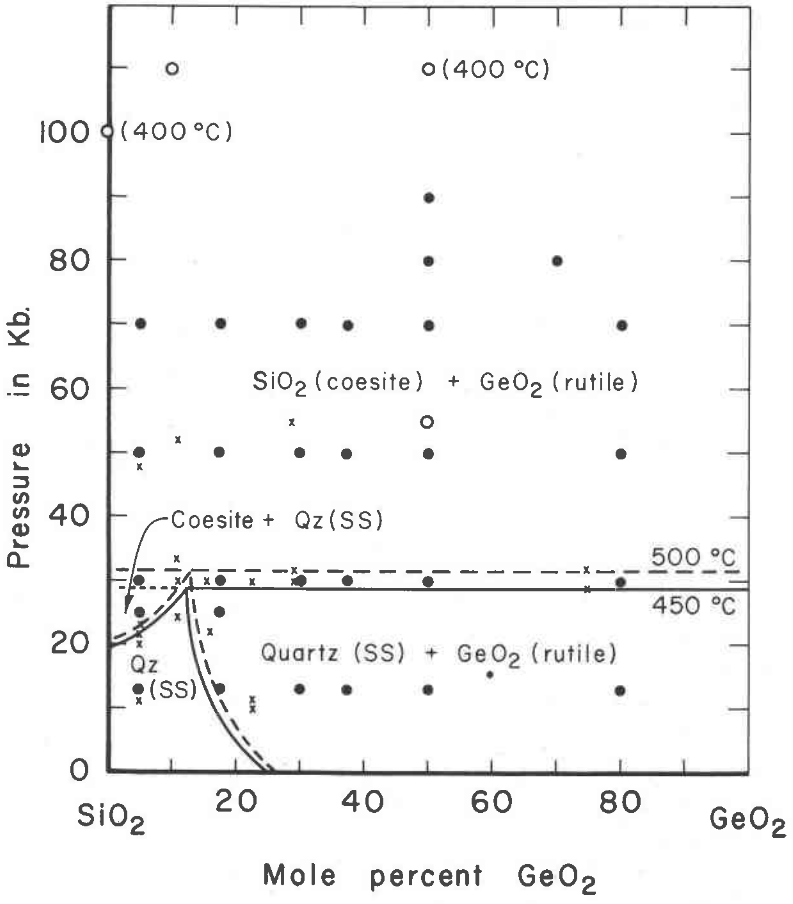

FIG. 3. Isothermal studies of the system SiO_2-GeO_2 in opposed anvils apparatus. (Data at 450° C. plotted as dots; 500° C. as X's; a few 400° runs, as open circles.)

in α quartz occurs to the extent of about 24%. Increasing the temperature to about 750° C. while holding the pressure constant results in a slight increase in solubility up to about 31%.

Compositions richer in GeO_2 yield in addition to the quartz phase, a rutile phase. Measurements made at $\frac{1}{8}$ degree 2θ per minute diffractometer scanning on the lattice constants of these rutile phases show that they have the spacings of pure GeO_2-rutile within experimental error ($\pm .015°\theta$). Thus it is concluded that no measurable amount of Si^{4+} entered the six-fold coordination of the rutile lattice under these experimental conditions.

As can be seen in Fig. 2, another complete series of solid solutions was found which could, on quenching, persist metastably as quartz at room temperature. The solid solutions have a β quartz structure up to 31% GeO_2 and presumably also in the richer GeO_2 mixtures up to 100% GeO_2, *i.e.*, GeO_2 at the liquidus should have a β quartz structure. However, it is not certain whether a particular sample contains metastable β or metastable α quartz. For this diagram to be possible it is necessary for the GeO_2 to show an $\alpha \rightarrow \beta$ quartz inversion somewhere before its melting point. No inversion was found by DTA nor by high temperature *x*-ray methods to 700° C. Subsequent to that work, however (Sarver, 1961), has found a reversible heat effect by DTA methods in GeO_2 (quartz) at 1000° ± 20° which he attributes to an $\alpha \rightarrow \beta$ transition. This would be compatible with the phase data of the present study.

The attempt to use DTA methods to observe the effect of solid solution of GeO_2 on the $\alpha \rightarrow \beta$ quartz (ss) inversion was not wholly successful. Only at very low germania concentrations were any heats of transition noted. Nevertheless it is believed that these observations provide evidence for a two-phase region in which α quartz and β quartz solid solutions exist. The evidence is seen in the fact that the temperature of the beginning of the inversion is lower in the up-temperature direction than in the cooling cycle (Fig. 4). The inversion in pure SiO_2 occurs at 573° C. while with 1% GeO_2 it is raised to 580° C.

Further support for the position of the boundary given in Fig. 2 was found in a high temperature *x*-ray determination of the thermal expansion curve; a break in the curve was found near 660° C. for a 10% GeO_2 − 90% SiO_2 solid solution (Fig. 5).

The temperature of inversion from quartz to tridymite is raised even more rapidly with increase in germania solid solution. The silica end member undergoes this change at 870° C. Beyond 2% GeO_2 the inversion temperature was out of the range of our equipment.

Liquidus data in GeO_2-rich mixtures. Liquidus temperatures were found to be quite difficult to determine in dry systems for two reasons: differen-

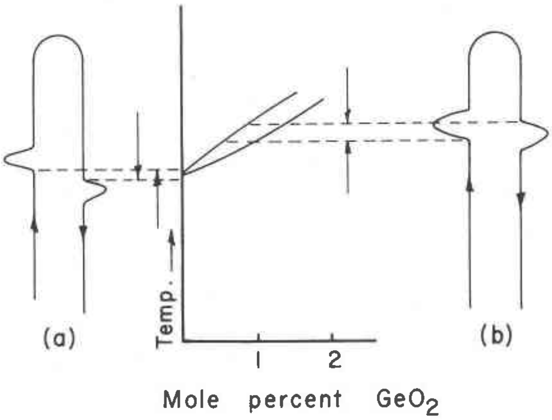

FIG. 4. Displacements of reversible heat effects through one phase and two phase fields.

tial volatilization caused changes in the composition of the mixture and one could not be certain of the "quenchability" of the phases. From the data obtained it would appear that the liquidus did not rise smoothly towards SiO$_2$ but rather that it went through a minimum suggesting the shape of the liquidus shown as a dotted line in Fig. 2.

Although no detailed attempt was made to study the ternary system GeO$_2$-SiO$_2$-H$_2$O evidence of the very marked effect of water content on

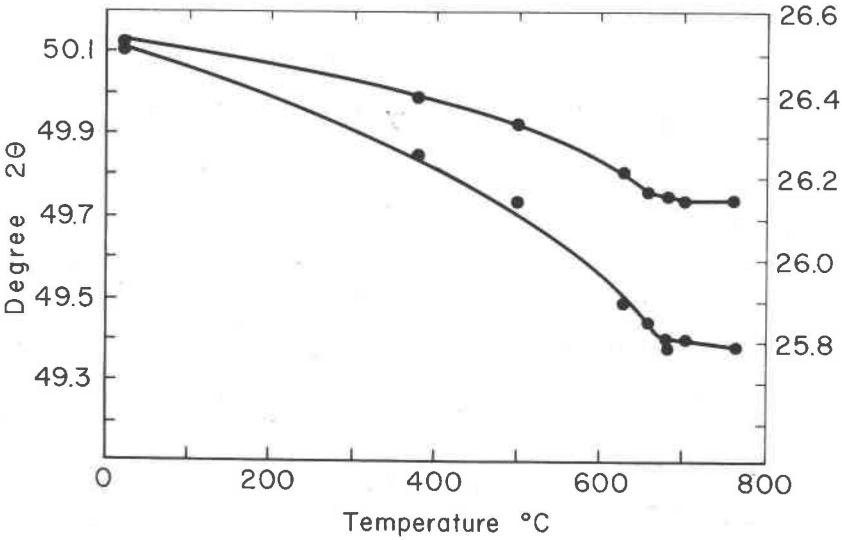

FIG. 5. Thermal expansion of 10% GeO$_2$-90% SiO$_2$ solid solution in terms of 2θ (CuKα) for the 112 and 101 planes.

liquidus temperatures was observed at certain pressures. Two 50 mole per cent mixtures (with about 10% H_2O) quenched to a (ternary) glass after 40 hours at 911° C. and 0.67 kb while a similar run made with even more water as "mineralizer" quenched to crystal phases. Also, 10 mole per cent GeO_2 mixtures (with about 15% H_2O initially) set up in the opposed anvil apparatus at 4 kb for 2 hours at 500° C. and 596° C. yielded one phase glasses. When the pressure on the glasses was raised to 19 kb and held for 24 hours they failed to crystallize at 500° C. Identical runs made without the heating period at 4 kb yielded the qz (ss) phase.

High pressure region. Increasing the pressure at constant temperature decreases the solubility when working in the rutile-quartz (ss) range between 13% and 26% GeO_2, and increases the solubility in the coesite-quartz (ss) range between 0 and 13% GeO_2. There appears to be a eutectic near 13% at the temperatures used in this study. At higher germania concentrations where the amount of GeO_2 exceeds the solubility limit the remaining germania always is found to be in the rutile form, with no evidence of solid solution of SiO_2 in this phase. Coesite is found below 30 kb in association with quartz (ss). At pressures above 31.5 kb at 500° C., or above 29 kb at 450° C., the silica appears as coesite and the germania as the rutile form. *X*-ray spacing measurements of the coesite did not show measurable shift to indicate GeO_2 in solid solutions. Under these conditions coesite is unmistakably present in mixtures containing less than 50% GeO_2. At higher concentrations the *x*-ray patterns are dominated by that of the rutile phase. Since coesite diffraction peaks could no longer be detected in spite of careful searching beyond this composition, it was thought that the silica was dissolving in the GeO_2-rutile. Stishovite (Chao, *et al.*, 1962) the very dense form of silica, has a rutile structure. However, careful measurement of the GeO_2-rutile *x*-ray diffraction spacings gave no evidence of solid solution. It is not yet known whether failure of the silica to assume the rutile structures in crystalline solution with germania under the conditions of the present experiments is real, or due to a kinetic barrier, or to the inability to "quench" a highly metastable solid solution.

The possibility also exists that a ternary melt is formed under certain p-t conditions passed through as the samples are brought to the desired p-t values where crystallization of GeO_2 (rutile) takes place rapidly while silica remains in the amorphous phase, only very slowly crystallizing as coesite.

Microscopic examination did reveal numerous amorphous grains coated with micron sized crystals of GeO_2 rutile. These grains, found in the products of 50 and 80 mole per cent mixtures, had refractive indices between 1.560 and 1.593. In the case of the 80 mole per cent products a gravity separation was used to concentrate the silica fraction which showed more clearly the presence of amorphous and coesite grains. The high refractive indices of the glass grains of their general composition range are in keeping with the findings (Cohen and Roy, 1962) on the densification of glasses under pressure. They show that silica glass and germania glass densified under conditions similar to the present ones have refractive indices of 1.53 and 1.67 approximately.

Attempts to overcome the sluggish nature of the reactions by the use of displacive shearing stresses were not successful. The silica end member, 30 and 50 mole per cent compositions subjected to pressures in excess of 100 kb under shearing conditions (Dachille and Roy, 1960) at 400–450° C. for 2.5 to 22 hours gave no satisfactory *x*-ray or microscopic evidence of the formations of stishovite, rutile phase or coesite phase solid solutions.

That the failure to obtain an SiO_2-containing rutile structure phase may be a matter of kinetics is strongly suggested also in the results of a related study with the excellent "weakened" SiO_2 model, BeF_2. It has been observed that crystallization of the quartz and coesite phases of BeF_2 from glass proceeds under appropriate pressures at very much greater rates than for the SiO_2. Furthermore, the transition of BeF_2 quartz to coesite which takes place essentially at the same p-t conditions (Dachille and Roy, 1959) as for the corresponding SiO_2 transition also proceeds at a much higher rate. It appeared reasonable to expect the formation of a rutile phase of BeF_2 at pressures above those reported in the synthesis of stishovite (about 80 kb) (Sclar, *et al.*, 1962) because of the greater ease of solid state transition reactions with this compound. However, the following runs at pressures from 100–160 kb failed to produce a rutile phase of BeF_2:

160 kb	250° C.	10 hrs.	BeF_2 qz remained qz.
160 kb	325° C.	14 hrs.	BeF_2 qz$\rightarrow$qz+coesite
100 kb	340° C.	2 hrs.	BeF_2 glass$\rightarrow$coesite

It should be noted that even with BeF_2 the solid state reactions become very sluggish below 300° C.

It is interesting that whereas there appears to be complete solid solution of SiO_2 and GeO_2 in β quartz and solid solution of GeO_2 in α quartz up to about 30%, the rutile form of GeO_2 will not accept measurable amounts of SiO_2 into its lattice at temperatures approaching 1000° C. when the pressure is 700 bars. Even at much higher pressure (110 kb) no evidence for solid solution of SiO_2 in rutile germania was found within the temperature and pressure ranges of this investigation. This, in spite of the fact that SiO_2 itself can assume the rutile structure if the pressure is high enough.

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