

PROGRESS REPORT NO. 3

THE INFLUENCE OF HIGH PRESSURES AND HIGH TEMPERATURES ON TRANSFORMATIONS AND COORDINATION IN CRYSTALLINE AND VITREOUS CERAMIC MATERIALS

W.F. Claussen, R.C. DeVries, and J.D. Mackenzie

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TO

WRIGHT AIR DEVELOPMENT CENTER

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INTRODUCTION

The broad objective of this study is to gain an understanding of the crystal chemistry, phase equilibria, and structural relationships of ceramic materials formed under conditions of high pressure and temperature. Experimentally this will be accomplished by: (1) subjecting selected materials (which are known or expected to exhibit coordination changes leading to denser phases or forms) to various combinations of pressure and temperature (up to approximately 2000°C and 100,000 atmospheres); and (2) subsequent examination with various techniques to define the phases and structures produced. The work includes corroboration of previous work at high pressures and temperatures, extension of the investigations to more extreme conditions, and the study of new systems. Emphasis will be placed on the examination of the structural and stability aspects of the resulting phases.

The study can be divided into two parts on the basis of the structural types of the two ceramic systems to be investigated. Part A covers the investigation of silica and other inorganic compounds of similar structure. The structural changes in both the crystalline and the glassy forms will be investigated. This part is under the supervision of J.D. Mackenzie and W.F. Claussen. Part B is a study of the two-component $SiO_2-Al_2O_3$ system and some isotypic systems formed by the separate or combined substitution of GeO₂ for SiO₂ and Ga₂O₃ for Al₂O₃. This part is supervised by R.C. DeVries and W.F. Claussen.

PART A

Compared with work on crystalline systems, few high-pressure studies have been made on vitreous phases. It is generally considered that the density of a glass is necessarily less than that of the corresponding crystalline phase. Bridgman and Simon (1953), however, have demonstrated that vitreous silica may be compacted until its density is greater than that of cristobalite. In crystalline silica, the different arrangements of SiO₄ tetrahedra in the continuous network can give rise to polymorphs having grossly different properties. Thus, cristobalite of density 2.32 is fairly rapidly attacked by hydrofluoric acid, whereas coesite of density 3.00 is completely inert. It is interesting to subject vitreous silica to high pressures and temperatures and to investigate (a) if the preparation of a glass of density greater than that of quartz ($\rho = 2.65$) is possible, and (b) its different physical and chemical properties.

During this period, nine more high pressure experiments have been carried out, three on vitreous germania and six on vitreous silica. A summary of the experimental conditions is presented in Table I. Only platinum capsules were used and the cell employed was similar to that shown in the previous report. Pressure was applied at a rate of approximately 2000 atm/sec and the sample maintained at the maximum pressure for 2 minutes. Both x-ray and microscopic examinations were made immediately and also four weeks after the experiment to ensure no devitrification of the glass had taken place.

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Run No.	Substance	Pressure (atm)	Temp (°C)	Refractive Index	Density	Density Increase (%)
275	SiO ₂	90,000	150	1.510	2.470	11.2
340	SiO ₂	80,000	400	1.522	2.524	13.7
341	SiO ₂	80,000	500	1.528	2.558	15.2
423	SiO ₂	100,000	300			
424	SiO ₂	100,000	500	n värdestadagt		
450	SiO ₂	100,000	150			
451	SiO ₂	100,000	300		2.550	
444	SiO ₂	100,000	600		2.595	
420	GeO ₂	100,000	250	1.694	4.16	13.3
421	GeO ₂	100,000	400	1.720	4.25	15.8
422	GeO ₂	100,000	RT	1.668	4.00	9.0

TABLE I Summary of High-Pressure Experiments on

Vitreous Silica and Germania

The observed refractive indices of the compacted glass are recorded in column 5 of Table I while the density data are given in column 6. In the last report, the density data were evaluated from a plot of refractive index and density of crystalline silica, it being assumed that values of the compacted glass will fall on this smooth curve. Over this period, calibration of the liquid density columns have been completed for the density range 2.0 to 3.0 g/cc. For silica, therefore, density could be determined directly. In Fig. 1, the density-refractive index relationship for the compacted glass is seen to follow the smooth curve as assumed previously. No density column has yet been prepared to cover the range 4.0 to 5.0 g/cc, and so the density results for germania were still evaluated from the measured refractive index.

It is observed in Table I that, for germania, glasses of density equal to that of the crystalline phase have now been prepared. For silica, however, the highest density observed was 2.56 as compared to the density of 2.65 for crystalline quartz.



Fig. 1 Density-refractive index relationship for crystalline and compacted silica.





HARDNESS MEASUREMENTS

In view of the large increases observed of the density and refractive index of the glasses, it was thought that the hardness of the samples might show a similar variation. The hardness of compacted silica of various densities were accordingly measured with a Kentron microhardness tester. Samples of suitable size and surface were uncommon because of the small dimensions of the pressure cell. The results obtained on nine samples are shown in Fig. 2. It is seen that both the deviations and scatter were too large to warrant any conclusion. Hardness measurements of this type will therefore not be carried out again in the coming period.

SOLUBILITY IN HF SOLUTIONS

Coes (1953) had demonstrated that the solubility of ordinary vitreous silica and all the known modifications of crystalline silica in dilute hydrofluoric acid is a direct function of density. This is not known for compacted glass. Over this period, an empirical technique has been developed for studying this property of the dense glass. Selected pieces weighing about 10 mg were put into 5 per cent HF solutions for 24 hours. The loss of weight was then determined. The method is necessarily approximate because of the variation in shapes and sizes of the samples. Only a few measurements have been made so far and the results are inconclusive. These experiments will be continued in the next period. Germania will also be examined.

In the coming period, density columns covering the range of 4.0 to 5.0 will be prepared for the germania samples. Infrared studies will be made on the compacted glass to determine if any significant structural changes have occurred. Further high-pressure experiments will be carried out in an attempt to prepare vitreous silica and germania of even higher density. More accurate measurements of temperature will be made by the use of thermocouples in the high-pressure cells in order to obtain PVT relationships for both vitreous silica and germania.

PART B

INTRODUCTION

During the third quarter of the contract period, emphasis has been given to the study of the decomposition and transformation of the naturally occurring polymorphs of Al_2SiO_5 . This departure from the expressed intention (second quarterly report) to focus on the substitution of Ga_2O_3 for Al_2O_3 in Al_2SiO_5 was made because of the consistent failure to produce any of the desired polymorphs from gel or mechanical mixtures in the Ga_2O_3 -SiO₂ system and the only limited success in the Al_2O_3 -SiO₂ system. Either reaction rates in both systems are too slow to reach what has been considered to be equilibrium at high pressures and temperatures in these systems or the assemblages found (Ga_2O_3 plus glass and corundum plus glass, respectively) do indeed represent equilibrium in the P-T region studied. The P-T conditions for the runs that have been made were based on the work of Clark <u>et al.</u> (1) (or an extrapolation of the results of that study), who concluded that the frequently found crystalline assemblage of Al_2O_3 and SiO₂ was metastable.

By studying the decomposition of natural kyanite, and alusite, and sillimanite, the stability regions can be determined from a different direction than that offered by the synthetic approach, and such information

S.P. Clark, Jr., E.C. Robertson, and F. Birch, Am. J. Sci., <u>255</u>, 628-640 (1957).

can then be used as a guide for future work with synthetic materials. As a result, a tentative curve for the decomposition of kyanite as a function of temperature and pressure has been determined, and some new observations on reaction paths and relative reaction rates for the decomposition of the polymorphs have been made. The data for kyanite are not in agreement with the previous work⁽¹⁾ in which kyanite and sillimanite were synthesized from kaolinite, andalusite, and sillimanite.

EXPERIMENTAL

High-Pressure Cell

The same cell type previously described in the second quarterly report was used. The cell assembly was the same as described recently in regard to diamond synthesis.⁽²⁾ The internal heater in most of the runs was a graphite cylinder separated from the sample by a cylinder of alumina. The sample was enclosed in Pt or 80 Pt-20 Rh foil.

Temperature and Pressure Measurement

Several runs have been made with the above cell with a thermocouple of which the Pt capsule containing the sample is a part. In these runs a plot of watts vs temperature was made and the reproducibility of the plot was found to be \pm 50°C. With this information it is possible to make the runs without inserting a thermocouple in every run, and considerable time is saved without appreciable sacrifice of precision. Most of the runs are made this way with an occasional use of a thermocouple to check the watts vs temperature curve. No correction has been applied for the change of emf as a function of pressure.

The problem of an absolute pressure calibration is a difficult one, and we are in the unsatisfactory position of being able to state with certainty only the precision of the pressure measurement (\pm 2000 atm). The pressure calibration is made by measuring the change in resistance of Bi, Tl, or Ba wires with pressure at room temperature. The pressure transmitting medium adjacent to the wire is silver chloride. It obviously would be more satisfactory to have fixed points that could be determined under the same conditions as the runs.

2. Chemical and Engineering News, 24-25 (November 29, 1959).

Starting Materials

Naturally occurring kyanite and andalusite from Minas Gerais, Brazil, and sillimanite from Dillon, Montana, were used. The specimens were examined optically and found to be free of other phases. A chemical analysis for the kyanite sample is currently being made.

A few runs using mechanical mixtures of kaolinite and a synthetic aluminum trihydrate and some additional runs using previously described gels were also made.

Identification of Samples

In addition to the usual x-ray techniques and the transmitted polarized light methods of identification, all runs are also being examined by reflected light in polished section in order to see the microstructural relationships of the phases. This has proved to be a very sensitive technique for observing the beginning stages of the changes taking place. Identification still requires the combination of all the techniques.

RESULTS AND DISCUSSION

The data are summarized in Tables II through IV and are shown graphically in Figs. 3 and 4.

More data are needed to firmly establish the kyanite decomposition curve shown as the heavy dashed line in Fig. 3, but the general trend is clear. At one atmosphere, decomposition was observed in 48 hours at about 1100°C. This is in agreement with the work of Greig. (3) Clark <u>et al.</u> (1) report no decomposition of kyanite at 1000°C in 4 days at 1 atm. At 1500°C and 45,000 atm, kyanite is stable while decomposition is observed at the same temperature at 35,000 atm. Other data consistent with the curve determined from kyanite are the partial conversion of sillimanite to kyanite at 1700°C and 50,000 atm and the synthesis of kyanite from a gel at 50,000 atm in the temperature range 1500° to 1800°C. Kyanite has also been synthesized from a gel at 20,000 atm and about 1200°C, but not reproducibly, and there is some doubt as to the temperature of the successful run.

3. J.W. Greig, J. Am. Ceram. Soc., 8 (8), 465-484 (1925).

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Results of Experiments with Kyanite

Run No.	Starting <u>Material</u>	Temp (°C)	Pressure (atm) x 10 ³	Time (min)	Heater	Phases Present and Remarks
1624	Ky*	1850	30	4	Gt	Mullite, corundum, glass =
1634	Ку	1830	50	10	G	Kyanite beginning to decompose, some glass and corundum at grain boundaries
1641	Ку	1820	20	10	G	Mullite, glass
1642	Ку	1790	40	5	G	Kyanite decomposing at grain bound- aries, some glass and corundum
1648	Ку	1530	25	45	G	Mullite, glass, corundum at grain boundaries of original kyanite
1649	Ky	1500	30	35	G	Mullite, undecomposed kyanite, glass
1652	Ку	1850	45	10	G	Kyanite decomposition evident, glass and corundum at grain boundaries
1653	Ку	1500	35	13	G	Kyanite decomposition uncertain
1654	Ку	1950	50	10	G	Kyanite, considerable decomposition, mullite, corundum, glass
1655	Ку	1720	.35	10	G	Kyanite decomposition, corundum and glass at grain boundaries
1656	Ку	1350	30	15	G	Kyanite decomposition uncertain
1657	Ку	1320	20	15	G	Mullite, some undecomposed kyanite, glass, corundum (?)
1659	Ky	1910	45	10	G	Considerable decomposition of kyanite; mullite, glass, corundum at grain boundaries
1674	Ky	1500	45	30	G	Kyanite
1675	Ку	1300	15	30	G	Mullite, corundum, glass

*Ky = Kyanite

 $\mathbf{t}G = Graphite$

‡Glass or material amorphous to x-rays.

Run No.	Starting Material	Temp (°C)	Pressure (atm) <u>x 10³</u>	Time (min)	Heater	Phases Present
1609	Andalusite	1000	15	80	G*	Andal, corundum
1629	Andalusite	1820	35	7	G	Mullite, glass, trace corundum
1630	Sillimanite	1790	35	5	G	Glass, corundum
1672	Sillimanite	1700	50	13	G	Kyanite, corundum, coesite (?), glass
1673	Sillimanite	1670	25	20	G	Glass, corundum
*G	= Graphite					

TABLE III

Results of Experiments with Andalusite and Sillimanite

TABLE IV

Results of Experiments with Gel Mixtures and Others

Run No.	Starting Material	Temp (°C)	Pressure (atm)	Time (min)	Heater	Phases Present		
1613	Gel	1000	20	120	G*	Quartz, corundum		
1614	Gel	>1000 <1300	20	180	Ni	Kyanite, corundum		
1620	Gel	1025	25	180	Ni	Quartz, corundum		
1623	Gel	1900	30	2	G	Corundum, glass		
1650	$Gel + H_2O$	1300	35	60	G	Corundum, glass		
1658	Gel	1800 1500	50 50	5 30	G	Kyanite, corundum, glass		
1660	$Gel + H_2O$	1900	50	15	G	Corundum, glass		
1664	Gel	1300	25	40	Ni	Corundum, glass		
1669	Gel	1000	20	300	Ni	Corundum, glass		
1667	Kaolin and Gibb †	1700	35	15	G	Corundum, glass		
1668	Kaolin and Gibb †	1700	20	15	G	Corundum, glass		
*G =	*G = Graphite							

†Gibb = Gibbsite

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Fig. 3 Decomposition of kyanite as function of temperature and pressure (heavy dashed line). The solid line and the light dashed line are taken from Clark <u>et al.</u> (1) To the right of the curve above about 20,000 atm, there is evidence that the equilibrium assemblage may be corundum plus glass. Kyanite is stable to the left of the curve. The rectangle represents the precision of the temperature and pressure measurement. K = kyanite; S = sillimanite; A = andalusite; C = corundum; M = mullite; Gl = glass; Cs = coesite.





When kyanite decomposed, the first evidence usually was the formation of glass and small crystals of Al_2O_3 from the fine-grained material at the grain boundaries [Fig. 5(a)]. The larger crystals of kyanite break down to form mullite* and glass [Figs. 5(a), (b)] and then at longer times or at higher temperatures the increased formation of Al_2O_3 is seen [Fig. 5(c)]. Although more data are needed for a firm conclusion, the tentative interpretation is that the final products from the decomposition of kyanite at high temperatures and pressures (above about 20,000 atm) are Al_2O_3 (corundum) and SiO_2 -rich glass, but the reaction path may involve the formation of mullite before the final stage is reached.



- Fig. 5 Polished and etched sections as seen in reflected light, bright field. HF etchants: C = corundum; Gl = glass; M = mullite; K = kyanite.
 - HF etchants; C = corundum; Gl = glass; M = mullite; K = kyanite.
 (a) Run No. 1648. Corundum and glass at original kyanite grain boundaries; mullite and glass within original kyanite grains.
 - (b) Run No. 1649. Remnants of kyanite surrounded by mullite plus glass.
 - (c) Run No. 1624. Large mullite crystals (light grey) in glass (darker grey). Corundum crystals (white) in mullite.
 - (d) Run No. 1630. Corundum and glass formed from sillimanite.

*Below about 25,000 atm both indices of refraction and the x-ray patterns are consistent with those reported for mullite. There may be some increase in refractive indices at higher pressures.



Fig. 5

Andalusite appears to decompose in the same way as kyanite, but sillimanite transforms very quickly to Al_2O_3 plus glass and the intermediate mullite stage has not been seen [Fig. 5(d)]. The behavior of sillimanite under these conditions seems qualitatively consistent with the results with kyanite after the mullite stage is reached in large crystals. It would be expected that mullite and sillimanite would decompose in a similar way because of their structural similarity.

From the point of view of the mechanism of the reactions, it would be interesting to see if the results can be explained in terms of the respective structures and the differences in the aluminum ion coordination characteristic of each. From the point of view of phase equilibria, it is possible that the formation of corundum plus glass from the nominal Al_2O_3 :SiO₂ composition can be considered in terms of a shift of the corundum plus liquid region of the Al_2O_3 -SiO₂ system toward the silica end of the system with increasing pressure. An extrapolation of the preliminary results suggests that the Al_2O_3 -SiO₂ phase diagram at high pressure would show a large region of corundum plus liquid with kyanite melting incongruently into this region.

The decomposition curve of kyanite as presented here explained in part the predominance of corundum plus glass in most of the runs that have been made with gels and other starting materials in the present study. The P-T curves of Clark <u>et al.</u> (1) are included in Fig. 1 to illustrate the obvious disagreement between their results and the present study insofar as the stability of kyanite is concerned. If one disregards the nature of the reactions taking place and considers only the stability region of kyanite, it would be necessary to lower the curve up to 25,000 atm in order to be in agreement with the previous work or an extrapolation of it.

KYANITE X-RAY PATTERN

The differences between peak intensities in the x-ray spectrometer patterns of synthetic and natural kyanite (mentioned in second quarterly report) have been shown to be due to preferred orientation of the latter. If finely ground natural kyanite is sprinkled onto a slide covered with a thin layer of grease, the resulting x-ray spectrometer pattern is essentially identical in all respects to that of synthetic kyanite. This technique reduces the amount of preferred orientation when mounting the powder of a mineral with well-developed cleavage on a flat surface via a liquid medium. Random orientation is apparently achieved in the synthetic material because of the fine grain size and the intergrown arrangement of the crystals.

PROGRAM FOR THE NEXT QUARTER

During the final quarter it is proposed to (1) complete the determination of the P-T curves of the Al_2SiO_5 polymorphs from both the synthetic and decomposition directions; (2) to try to obtain some data on the kinetics of the transformations; and (3) to see if the mechanisms of the transformations can be treated from the available structural data.

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