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

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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