

High-pressure region of the silica isotypes

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With 3 figures

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Auszug

Die SiO_2 -Modifikationen, sowie BeF_2 , AlPO_4 , AlAsO_4 , AlVO_4 , MnAsO_4 , GaPO_4 , GaAsO_4 , GaSbO_4 , BPO_4 , BVO_4 , BAsO_4 , FePO_4 und FeAsO_4 wurden im Bereich von Atmosphärendruck bis etwa 60.000 bar und von Zimmertemperatur bis annähernd 600°C untersucht. Die Hochdruck-Apparatur wurde an Hand der Quarz-Coesit-Umwandlungen auf Reproduzierbarkeit, Reversibilität und Erreichbarkeit des Gleichgewichts sorgfältig geprüft. Bei 500°C wandeln sich SiO_2 und BeF_2 bei Drucken von 20.400 bzw. 21.600 bar aus der Quarzform in die Coesitform um und geht BPO_4 bei 46.000 bar aus der Cristobalit- in die Quarzform über.

Die Umwandlung von MnPO_4 , FePO_4 , GaPO_4 und AlPO_4 erfolgt um 450°C und 55.000 bar. In diesem Bereich wurde keine Umwandlung von AlAsO_4 und GaAsO_4 beobachtet. Tridymit und Cristobalit konnten nicht in neue metastabile Hochdruckformen übergeführt werden. Die p - t -Kurven dieser Reaktionen wurden für einen engen Zustandsbereich ermittelt.

Abstract

The region extending from ambient conditions up to approximately 600°C and 60,000 bars has been examined for the various polymorphs of SiO_2 , and for BeF_2 , AlPO_4 , AlAsO_4 , AlVO_4 , MnAsO_4 , GaPO_4 , GaAsO_4 , GaSbO_4 , BPO_4 , BVO_4 , BAsO_4 , FePO_4 and FeAsO_4 .

Reproducibility, reversibility and attainability of equilibrium have been thoroughly explored for the high-pressure apparatus, using the quartz-coesite reaction. At 500°C , SiO_2 and BeF_2 transform from the quartz form to the coesite form at 20,400 and 21,600 bars respectively, and BPO_4 transforms from a cristobalite to a quartz form at 46,000 bars. MnPO_4 , FePO_4 , GaPO_4 and AlPO_4 all transform to new forms near 55,000 bars at 450°C . There are no new forms of AlAsO_4 or GaAsO_4 in this range. Tridymite and cristobalite cannot be transformed metastably into other new high-pressure forms. The p - t curves for these reactions have been determined over a narrow range.

* Contribution No. 58—26.

Introduction

With the discovery of coesite or 'silica-C'¹ an entirely new chapter of inorganic chemistry was opened, since it became clear that many new phases could be prepared under high pressure (> 10,000 bars). Since then some work has been done, especially by petrologists, on systems of petrologic interest at these pressures. This work has not, in general, led to a large number of new phases, since nature had already provided the high pressure to generate most of these phases. No other systematic work was known at these pressures and temperatures. Together with attempts to synthesize various phases, including diamonds, a program of systematic high-pressure studies was started in 1955. Some results of these studies have been reported by us at the annual meetings of the Geological Society of America in 1956, 1957 and 1958.

An obvious choice for an area in which such systematic work would be meaningful was the silica structures. The quartz-coesite transition has been studied by numerous workers, the results of MACDONALD² being the most complete of those published. Nothing is known about the effect of pressure on the many analogous phases. Thus one might expect, on the basis of bond strengths alone, that BeF₂ would transform, if it did, to a coesite structure at a much lower pressure than does SiO₂; or likewise one would think that, since GaPO₄ has an average $\frac{\text{anion}}{\text{cation}}$ ratio much nearer the rutile ratio, that it would perhaps invert to rutile in this pressure range. Nothing quantitative is known about the effect of pressure on radius ratio, and hence one cannot predict the magnitude of pressures which might be required to go from one structure to another. An empirical approach is therefore not only necessary in this area of solid-state chemistry, but is virtually the only useful one.

Apparatus

The *p-t* range under consideration has been reached for sustained periods only in a very few laboratories. The industrial organizations (such as The General Electric Company and Swedish ASEA) which have prepared diamonds have not published any description of their apparatus. COES¹, however, has done so, and a detailed drawing of his

¹ LORING COES, A new dense crystalline silica. *Science* **118** (1953) 131 and personal communication (1954).

² G. J. F. MACDONALD, Quartz-coesite stability relations at high temperatures and pressures. *Am. J. Sci.* **254** (1956) 713-721.

apparatus is available³. It is the prototype for an entire family of apparatuses which have since been built for this range. Another family is based on the designs of BASSET⁴ and of BRIDGMAN⁵ as modified by GRIGGS and KENNEDY⁶. The apparatus used in the present study belongs to the latter family which is herein called an (externally heated) uniaxial pressure device.

The assembly consists of a pump delivering pressure (which is automatically controlled and recorded) to the low-pressure side of a hydraulic ram. The ram in a suitably strong frame brings the total

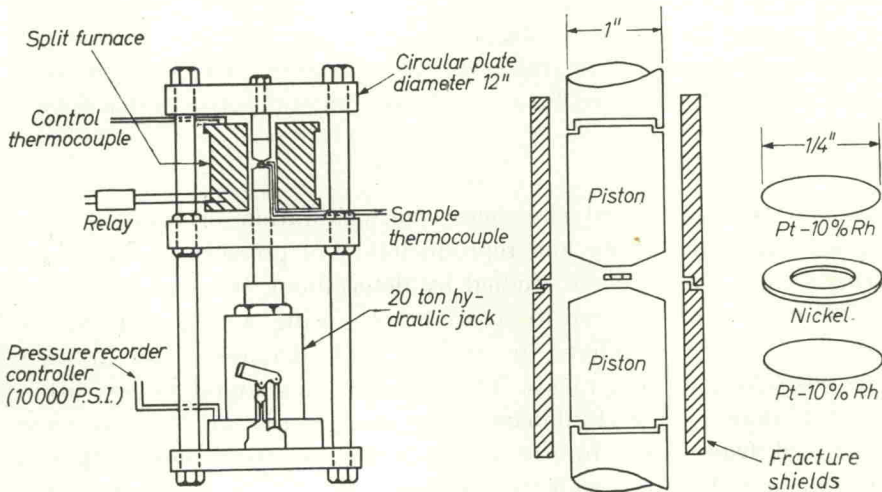


Fig. 1. Schematic layout of uniaxial high-pressure apparatus with accessories. Details of high-pressure pistons and sample assembly.

force to bear on a small area piston and sample assembly. This is shown in detail in Fig. 1. The sample is pre-pelleted into a nickel ring 0.010 inches thick and surrounded by two platinum-rhodium sheets, thus giving an essentially noble-metal container. The temperature is measured by a thermocouple very close to the sample sandwich, and is easily fixed within $\pm 5^\circ\text{C}$. Several types of pistons are

³ RUSTUM ROY and O. F. TUTTLE, Investigations under hydrothermal conditions. "Physics and Chemistry of the Earth", Vol. 1. Pergamon Press, London and New York (1956).

⁴ JAMES BASSET. Apparatus for carrying out physical or chemical experiments under pressure. Comptes rend. [Paris] **85** (1927) 343-345.

⁵ P. W. BRIDGMAN, The physics of high pressure. G. Bell, London (1949).

⁶ D. T. GRIGGS and G. W. KENNEDY, A simple apparatus for high pressures and temperatures. Am. J. Sci. **254** (1956) 722-735.

in use, cemented carbides, hardenable steels, and sintered oxides (for higher temperatures at lower pressures). Water or a "mineralizer" solution is often added to the pelleted sample before enclosing in the platinum-rhodium. Either the pressure or temperature is raised first, depending upon the result sought, and the apparatus used is capable of maintaining these p - t conditions for periods of one week or more. Runs of 20–40 hours length were made standard to avoid problems of incomplete reaction or metastability, and this is an important innovation; many runs of week-long duration were made in this same range.

For most rapid quenching a cold air blast was used to cool the samples rapidly before releasing the pressure. The samples were extracted and examined by x-ray diffraction and petrographic microscopy.

Results

We have discussed elsewhere⁷ our calibration of such devices. Briefly, the uniformity and reproducibility of pressure on the metal ring-sample surface were studied by determining the pressure of the SiO_2 quartz-coesite transition at 500°C , using a series of sample assemblies which differed in their overall diameters and in their metal-to-sample area ratios. This pressure was found to be within ± 0.4 kilobar of 20.4 kilobars even though the area ratios were changed from 3.5:1 to 0:1 and overall diameters were 0.25 and 0.50 inches. The uniformity of pressure was also evident in the consistent results obtained with different-diameter sample assemblies in high-pressure studies⁸ of the olivine-spinel transition in the system Mg_2GeO_4 — Mg_2SiO_4 .

The direct comparison of uniaxial pressure with hydrostatic pressure probably will never be realized over the full range of uniaxial pressures attainable. However, we have found that uniaxial and hydrothermal results at low pressures agree for the univariant p - t relation⁸ of the olivine-spinel transition of Mg_2GeO_4 . GRIGGS and KENNEDY⁶ also reported continuity of hydrothermal and uniaxial p - t relations for a number of systems. Suffice it to report that it is clear that in such apparatus the *reproducibility and uniformity* of the

⁷ FRANK DACHILLE, E. C. SHAFER and RUSTUM ROY, High pressure studies of the system GeO_2 — SiO_2 . In press.

⁸ FRANK DACHILLE and RUSTUM ROY, High pressure studies of the system Mg_2GeO_4 — Mg_2SiO_4 with special reference to the olivine-spinel transition. Am. J. Sci. (In press.)

pressure are within ± 5 per cent. Calibration of absolute pressure in the range of temperature and pressure has so far not been attempted in a serious way in any laboratory, and until this is done, absolute pressure values will remain somewhat questionable. The results obtained with each substance studied can be considered in turn, and a short list of critical data is given in Table 1. The results presented here are based on some 250 separate runs.

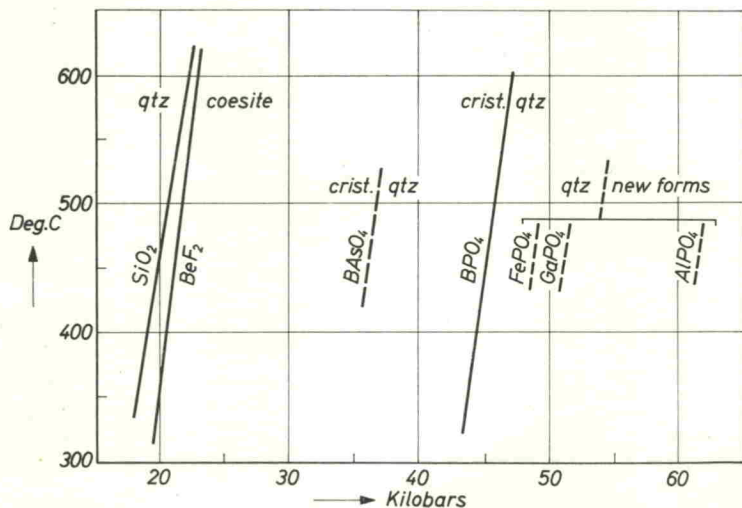


Fig. 2. Univariant pressure-temperature lines separating the fields of pairs of polymorphs for various compounds. (*Note— MnPO_4 quartz form reacts inconsistently at lower pressures than shown for the FePO_4 .)

SiO_2 . The p - t curve determined by a large number of runs in the calibration study is shown in Fig. 2. Coesite was prepared and then used as a starting material to demonstrate reversibility. The curve shown here agrees very well with that given by MACDONALD¹, but disagrees radically with scattered results reported by other workers^{9,10}.

In the attempts to determine the structure of coesite some difficulty was encountered by RAMSDELL¹¹ and by ZOLTAI and BUERGER¹²

⁹ H. T. HALL, Proceedings of a symposium, *High temperature, a tool for the future*. Stanford Research Institute, Menlo Park, California (1956).

¹⁰ F. R. BOYD and J. ENGLAND, Personal communication (1957), and Quartz-coesite transition. *Carnegie Institution Yearbook* 58 (1958/59) 87–88.

¹¹ L. S. RAMSDELL, The crystallography of coesite. *Am. Min.* 40 (1955) 975–982.

¹² TIBOR ZOLTAI and M. J. BUERGER, The crystal structure of coesite, the dense, high pressure form of silica. *Z. Kristallogr.* 111 (1959) 129–141.

Table 1. *Short list of some experimental results*

Composition	Starting material	Pressure (kilobars)	Temp. (°C)	Time (hrs.)	Results
SiO ₂	Silicic acid	20.5	499	48	Qtz.
	Silicic acid	20.7	500	20	Qtz. + tr. coes.
	Silicic Acid	21.7	494	36	Coes. + minor qtz.
	Silicic acid	24.0	586	48	Coes. + tr. qtz.
	Silicic acid	18.6	405	96	Qtz. + tr. coes.
	Silica glass	20	594	120	Qtz.
	Silica glass	22	502	48	Coes. + qtz.
	Tridymite	34	525	72	Qtz. + tr. coes.
	Tridymite	20.2	495	72	Qtz. + coes.
	Cristobalite	19.3	500	72	Qtz.
	Cristobalite	34.0	548	120	Coes.
	Coesite	19.3	590	60	95% qtz.
	Coesite	19.0	545	40	85% qtz.
BeF ₂	Quartz form	21.7	575	72	Qtz. form
	Quartz form	22.7	570	72	Qtz. + coes.
	Coesite	17.3	450	80	Qtz. + minor coes.
	Glass	22.7	550	48	Coes. + minor qtz.
	Glass	20.0	315	150	Coes. + minor qtz.
	Glass	19.3	348	80	Qtz.
	Glass	20.7	560	50	Qtz.
BPO ₄	1:1 Acids	44.8	331	40	Crist. + tr. qtz.
	1:1 Acids	46.2	475	55	Crist. + minor qtz.
	1:1 Acids	42.8	330	40	Crist.
	1:1 Acids	47.6	480	44	Qtz. + crist.
	1:1 Acids	47.0	622	10	Crist. + qtz.
	Cristobalite	48.2	480	40	Qtz. + minor crist.
	Cristobalite	51.4	460	46	Qtz.
BA ₂ O ₄	Cristobalite	34.5	453	20	Crist.
	Cristobalite	36.5	449	21	Qtz. + crist.
	Cristobalite	40.7	420	22	Qtz.
	Cristobalite	49.0	442	22	Qtz.
AlPO ₄	Gel	33	500	40	Qtz.
	Cristobalite	48	480	18	Qtz.
	Quartz	56	432	21	Qtz.
	Cristobalite	63	528	20	Qtz. + new phase
	Tridymite	55	469	24	Qtz. + new phase
AlAsO ₄	Quartz	29	472	24	Qtz.
	Quartz	48	436	24	Qtz.
	Quartz	54	400	42	Qtz.

Table 1 (continued)

Composition	Starting material	Pressure (kilobars)	Temp. (°C)	Time (hrs.)	Results
GaPO ₄	Cristobalite	35	334	120	Qtz.
	Cristobalite	53	446	22	New phase + qtz. + tr. crist.
	Cristobalite	56	450	40	New phase + qtz.
FePO ₄	ppt. Fe(NO ₃) ₂ and Na ₂ HPO ₄	50	436	70	Qtz. + new phase
		53	446	20	New phase
MnPO ₄	Mn ₂ O ₃ + H ₃ PO ₄ , amorphous	27	388	40	Mainly crist. + reactants
	Mn ₂ O ₃ + H ₃ PO ₄ , amorphous	35	456	40	Qtz. + tr. new phase
	Mn ₂ O ₃ + H ₃ PO ₄ , amorphous	50	429	70	New phase + qtz.
	Cristobalite	53	413	24	New phase + qtz. + crist.
GaSbO ₄	Rutile form	52	418	7	Rutile
	Rutile form	43	423	24	Rutile

Abbreviations: Crist. = cristobalite, Qtz. = quartz, tr. = trace. The text summarizes pertinent results for other compositions.

in fixing Z , the number of molecules/unit cell. We have redetermined the unit-cell parameters from an accurately measured and indexed powder pattern, and by a sink-float method also remeasured the density as 2.93 ± 0.02 . When these corrections are made, as has been done in Table 2, Z is clearly established as 16.

BeF_2 . This substance, which is nearly a perfect model¹³ for SiO_2 , was found also to have a coesite polymorph. However, the pressure required for its formation* was considerably more than expected, and in fact is slightly above that required for SiO_2 (Fig. 2). Thus, although the melting behavior (BeF_2 melts at 560°C) reflects rather directly the effect of the diminished interionic electrostatic forces, neither the atmospheric-pressure polymorphism nor the high-pressure polymorphism appears to fit this pattern. Only an average refractive index

* Note added in proof. Recent work with a modified piston design shows that BeF_2 coesite and the quartz forms of AlAsO_4 and GaAsO_4 persist at pressures up to 100,000 bars.

¹³ D. M. ROY, RUSTUM ROY and E. F. OSBORN, Fluoride model systems, III: The system $\text{NaF}-\text{BeF}_2$ and the polymorphism of Na_2BeF_4 and BeF_2 . *J. Am. Ceram. Soc.* **36** (1953) 185-190.

of the new form could be obtained: 1.345. Powder x-ray data are given in Table 2 for comparison with that of the SiO_2 coesite.

BPO_4 . Another interesting case studied in some detail is BPO_4 , which was known only in the cristobalite structure. In an earlier study¹⁴ it was noted that an anomalous possible quartz polymorph of BPO_4

Table 2
 SiO_2 coesite BeF_2 coesite

hkl	SiO_2 coesite			BeF_2 coesite		
	d_{obs}	d_{calc}	Intensities Film Diff.	d_{obs}	d_{calc}	Intensities Film Diff.
020	6.217	6.198	vw	5.949	5.961	vw
021	4.40*	4.385	vw	4.19*	4.216	vw
130, 111	3.432	3.439	m	3.310	3.306	m
002, 040, $\bar{2}21$	3.098	3.099	vw	2.984	2.981	vw
220, (041)	2.77*	2.772	m	2.668	2.666	vw
131	2.68*	2.705	m	2.605	2.601	w
201, $\bar{2}41$	2.350	2.343	w	2.256	2.253	vw
112, 150	2.303	2.302	m	2.216	2.214	vs
240, $2\bar{2}\bar{3}$	2.195	2.191	m	2.108	2.107	s
151, 310, 132	2.034	2.038	m	1.960	1.960	m
330	1.846	1.848	vw	1.76*	1.777	w
$\bar{2}61$	1.789	1.789	m	1.723	1.721	w
260, 222, (043)	1.716	1.717	m	1.651	1.653	w
113, $\bar{3}52$, $17\bar{1}$	1.711	1.703	m	1.640	1.638	w
$a = c =$	$7.16 \pm .01 \text{ \AA}$			$6.88 \pm .01 \text{ \AA}$		
$b =$	12.39 \AA			11.92 \AA		
	(axial ratio = 1.730)			(axial ratio = 1.732)		
$Z =$	16			16		
ϱ (meas.) =	2.93 ± 0.02			—		
ϱ (x-ray) =	2.90			2.55		

* Spacings marked by an asterisk were measured less accurately than the rest. Since the materials are pseudohexagonal, many reflections contribute to any one powder line. The reflections listed are those which appear to contribute most to the intensities, as judged by comparison with single crystal photographs, and are listed in order of decreasing contribution. Only the strongest reflection from each zone is listed; it should be remembered that the other reflections in that zone may also contribute. Indices in parentheses are of reflections which might theoretically contribute, but appear to be very weak or absent.

appeared to be formed in some of the low-pressure hydrothermal runs. This phase had refractive indices and density incompatible with the expected increases from the cristobalite form.

In the present study the authentic quartz form of BPO_4 was prepared at 50,000 bars and later a p - t curve was determined for its cristobalite-quartz transition which is shown in Fig. 2. Starting materials were 1:1 mixture of boric and phosphoric acids, and also the preformed cristobalite form. Even in the 5–6 mg samples used, very

¹⁴ E. C. SHAFER, M. W. SHAFER and RUSTUM ROY, Studies of silica structure phases, II: Data on FePO_4 , FeAsO_4 , MnPO_4 , BPO_4 , AlVO_4 and others. Z. Kristallogr. 108 (1956) 263–275.

well-formed crystals with the characteristic habit of doubly terminated quartz were obtained, large enough for single-crystal study. The powder pattern is clearly analogous to that of SiO_2 quartz, and single-crystal rotation and Weissenberg photographs confirm this in detail. The unit cell with three BPO_4 molecules has $a = 4.470 \pm 0.005 \text{ \AA}$, $c = 9.926 \pm 0.01 \text{ \AA}$, with $c/a = 2.2$, which is double the ratio for the quartz unit cell with 3SiO_2 . The indexed powder patterns and a more detailed discussion of the x-ray crystallography of the BPO_4 (and BAsO_4) quartz form are given by DACHILLE and GLASSER¹⁵. Refractive indices obtained were $N_\omega = 1.639 \pm 0.002$, $N_\epsilon = 1.647 \pm 0.002$. The density is 3.05 ± 0.02 by the sink-float method using a centrifuge. This compares with an x-ray density of 3.069.

BAsO_4 . The quartz form was prepared from the mixed oxides at 40,000 bars and 420°C . A p - t curve was not worked out in detail, but it probably passes through a point as low as 36,000 bars at 450°C . The samples are white and grind easily to a white powder. A microscopic examination shows that basal and prismatic cleavages are nearer perfect than in SiO_2 or BPO_4 , and that the material has high birefringence for a quartz structure. Clear uniaxial-positive interference figures are obtained. Refractive indices are $N_\omega = 1.730 \pm .002$ and $N_\epsilon = 1.757 \pm .002$. X-ray powder and single-crystal data are given elsewhere¹⁵ so that it will be sufficient to report $a = 4.562 \pm 0.005 \text{ \AA}$, $c = 10.33 \pm 0.01 \text{ \AA}$.

BVO_4 and AlVO_4 . The structures of these compounds are of interest because they could serve to set some limits to the fields assigned to quartz- and rutile-like phases in ionic radius-ratio plots of the type of Fig. 3. If radius ratios were the dominant factors, AlVO_4 should have the rutile structure, but BRANDT¹⁶, MILLIGAN¹⁷ and SHAFER, SHAFER and ROY¹⁴ have shown that this is not the case. The use of pressures up to 50,000 bars, which might be expected to shift the radius ratios further into the rutile field, has failed to produce such a phase. Pressures up to 33,000 bars also failed to produce quartz- or rutile-like phases of BVO_4 .

¹⁵ FRANK DACHILLE and L. S. DENT GLASSER, High pressure forms of BPO_4 and BAsO_4 ; quartz analogues. *Acta Crystallogr.* **12** (1959) 820–821.

¹⁶ KARIN BRANDT, X-ray studies on ABO_4 compounds of rutile type and AB_2O_6 compounds of columbite type. *Arkiv Kemi, Mineral., Geol.*, **17A** (1943) 1–8.

¹⁷ W. O. MILLIGAN, L. M. WATT and H. H. RACHFORD JR., X-ray diffraction studies on heavy metal orthovanadates. *J. Physic. and Colloid Chem.* **53** (1949) 227–234.

High-pressure forms of both these compounds—different from those obtained at atmospheric pressure—appear at pressures above 30,000 bars and 400°C. The new forms have a metallic character which is more noticeable in the boron compounds. The small sample wafers are black, flexible but with a fibrous fracture, and present some difficulty in grinding because of the tendency of lath-like fragments or

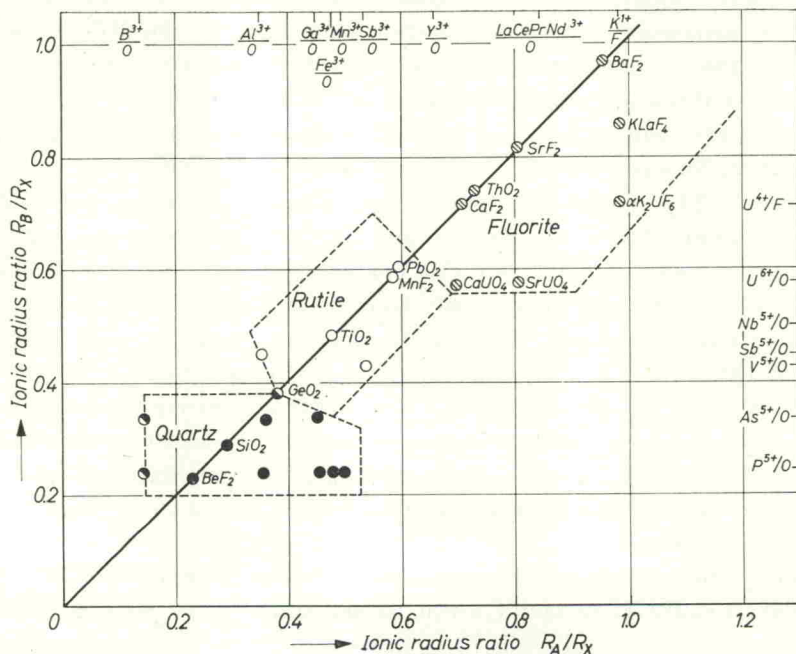


Fig. 3. Ionic radius ratio plot of structure fields of ABX_4 compounds closely related to some structures of AX_2 compounds. Compounds of other structure types are not plotted, but their respective fields helped locate the three shown. Ternary compounds in the fluorite field may have more than one form, and some have "distorted" fluorite structures.

flakes to adhere to the surfaces. There are indications that BVO_4 decomposes to the oxides at temperatures above 400°C and pressures below 30,000 bars. Further work at higher pressures is in progress on these compounds.

$AlPO_4$, $GaPO_4$, $FePO_4$, $MnPO_4$. These four compounds all invert to new forms near the limits of the apparatus, and could not be studied adequately. The p - t relations of these quartz-to-high-pressure forms are shown in Fig. 2. It will be noted that the pressure required for the

appearance of the high-pressure forms increase in the order Mn-Fe-Ga-Al phosphate. This may be a manifestation of the degree of "comfortable fit" in the quartz structure—that is, AlPO_4 (very definitely in the quartz field according to radius-ratio criteria) will maintain this structure to higher pressures than will MnPO_4 , which is on the border of the quartz field (Fig. 3).

X-ray powder patterns and single-crystal studies show that these new forms are not analogues of coesite, and further, that they do not appear to be related to each other. This is the first phase of AlPO_4 which does not match a phase of SiO_2 . Details of the optical and x-ray crystallography of these phases and some others discussed herein will be reported later¹⁸.

AlAsO_4 , GaAsO_4 , FeAsO_4 , MnAsO_4 . The atmospheric-pressure quartz forms of AlAsO_4 and GaAsO_4 remain stable to pressures of 50,000 bars at 400°C. These conditions likewise failed to alter the non-quartz form of FeAsO_4 prepared by SHAFER, SHAFER and ROY¹⁴. The MnAsO_4 composition as oxides yielded the pyroarsenate as the chief product at these conditions.

SiO_2 (*tridymite and cristobalite*). Attempts were made to prepare new dense forms which may be related to tridymite and cristobalite, even if such forms would be metastable with respect to quartz or coesite. In our temperature range this proved impossible. In the shortest runs in which any transformation occurred, coesite or quartz were always formed from the tridymite or cristobalite.

The results described herein reveal the very interesting possibility of preparing quenchable high-pressure forms of a high proportion of common inorganic compounds. Simple relationships, which might, for instance, be predicted between pressure of transition and radius ratio or ionic charge, do not appear to obtain.

Acknowledgement

We are indebted to Dr. L. S. DENT GLASSER for checking and improving the coesite powder-pattern indexing against her own single-crystal data. This work forms a part of a study in crystal chemistry supported by the Chemical Physics Branch, US. Army Signal Corps, under contract No. SC 71,214 and SC-74,951.

¹⁸ L. S. DENT GLASSER and FRANK DACHILLE, High pressure forms of silica analogue compounds. In preparation.