

Memo Report C-54-137

CHEMISTRY RESEARCH DEPARTMENT

Research Laboratory

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“Seventh Symposium On Crystal Chemistry As Applied To Ceramics”

Rutgers University, New Brunswick, N. J., June 4, 1954—A Report on papers presented.

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Abstract: A report on Silica Symposium, Rutgers University, June 4, 1954. Some high-pressure, high-temperature work described.

This is a class 4 technical report. Its distribution in the General Electric Company is highly restricted. It may not be sent outside the United States.

L. Coes, The Norton Co. – “A New Dense Silica”

Apparatus was described for obtaining 45,000 atms. Pressure simultaneously with temperatures to 1000°C. Drawings of the apparatus are given in Figs. 1 and 2. The “mold” cavity is one quarter inch in diameter. The capsule containing the material to be subjected to pressure and temperature is about one half inch long. Pressure generated in the sample as a function of press load was obtained by extrapolation from one calibration point; i.e., observation of the bismuth transition near 25,000 atms. Coes thinks the pressure is known to ± 3000 atmospheres at 45,000 atmospheres.

The temperature in the sample was determined by a thermocouple placed in the thermocouple well of Fig. 1. This thermocouple was compared with a thermocouple placed in the position normally occupied by the sample to obtain the necessary calibration. The thermocouple in the well was also checked against the melting points of copper and aluminum. (These were melted in the capsule.)

The upper limit of pressure (45,000 atmospheres) is fixed by the strength of the carboloy pistons. The Al_2O_3 liner normally shows no tendency to fail in tension cracks perpendicular to the center line of the system. Under some conditions, however, (especially when the softer grades of carboloy are used for pistons) the pistons tend to “mushroom” at the ends. This “mushroom” pushes into the liner causing it to crack and fail.

Coes’ high pressure apparatus requires a very rigid press that maintains very good alignment as the load is imposed. He found “three-post” presses best met his requirements. (These may have been built by Elmes Engineering Division of American Steel Foundries, Cincinnati 29, Ohio. This company specializes in a standard line of three-post “hobbing” presses.)

The capsule in Coes’ equipment will hold about one-tenth cubic centimeter of material. This is about the same sample size as that used in the “Belt”¹. The Norton Company has presses available for scaling up their capsule volume by a factor of 1000. (This would require about a 2000-ton press at 45,000 atmospheres.) As yet, they have not built apparatus for use in these large presses.

The information disclosed by Coes on dense silica (now called Coesite) was essentially that given before.^{2,3} The following information concerning the Norton Company’s high-pressure program was obtained in conversation with Coes:

1. Two micron size crystals of Coesite are unaffected by twenty-four hour boiling in either concentrated hydrofluoric acid or concentrated sodium hydroxide solutions.
2. Professor Lewis S. Ramsdell, Univ. of Michigan, obtained some Coesite crystals one year ago for the purpose of studying the x-ray structure. This has proved to be difficult. Most of the crystals are twinned. They seem to be dimensionally hexagonal but with only monoclinic symmetry. There seems to be a c axis glide, $a = c$ and $\alpha\beta = 120^\circ$.
3. Coes is disappointed in the small number of new crystals that have been found in their high-temperature, high-pressure work. A few new garnets, Coesite and some pyroxenes just about cover the field. Some particular modifications are favored at high pressure and temperature but they are not new materials. For instance, magnetite (Fe_3O_4) will form from Fe_2O_3 at high pressure – high temperature.
4. Oxidation often takes place in the capsule by virtue of hydrogen (from H_2O , NH_3 , etc. used as mineralizers) escaping through the wall or being picked up by the wall. (We have observed the same phenomena in the “Belt”.)
5. Coes says graphite (from carbon producing reactions) almost always forms instead of diamond even though the high-pressure, high-temperature reaction is carried out in the diamond stable thermodynamic region. For example, in the reaction $\text{Ag}_2\text{CO}_3 + \text{Si} \rightarrow \text{SiO}_2$ (Coesite) + $\text{AgO} + \text{C}$, the carbon formed at 35,000 atmospheres and 800°C is formed as graphite. This is to be expected since the thermodynamic conditions favor graphite. However, graphite is also formed from this reaction at 45,000 atmospheres and 800°C. These conditions, says Coes, are thermodynamically favorable to diamond.
6. Coes says the diamond synthesis is still a real problem.
7. In the oxidation of SiC at 800°C and at pressures over 35,000 atmospheres, Coesite forms around crystalline carbon. Below 35,000 atmospheres, quartz and graphite form separately.

¹ H. Tracy Hall, “The ‘Belt’: Ultra-High-Pressure, High-Temperature Apparatus, RL-1064, March 1954.

² H. Tracy Hall, “Diamond Making at the University of Utah”, Memorandum April 13, 1953.

³ L. Coes, Jr. “A New Dense Crystalline Silica”, Science 118, 131-2 (1953).

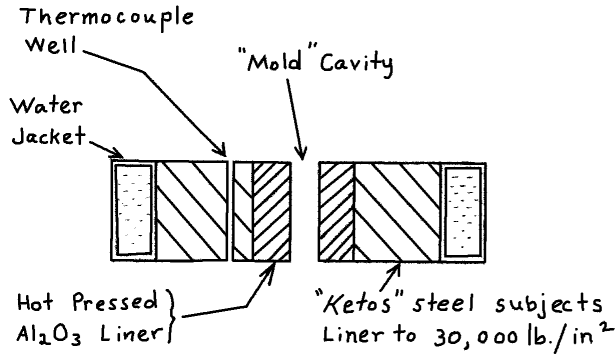


FIG. 1 HIGH PRESSURE ASSEMBLY USED AT NORTON COMPANY

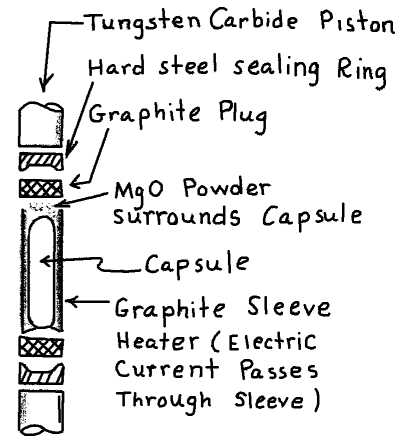


FIG. 2 "MOLD" ASSEMBLY (GOES INSIDE MOLD CAVITY of FIG. 1)

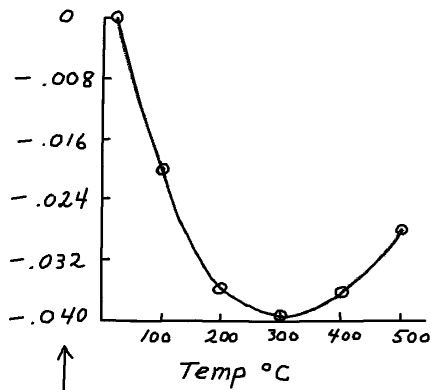


FIG. 3 MEAN LINEAR THERMAL EXPANSION of KEATITE

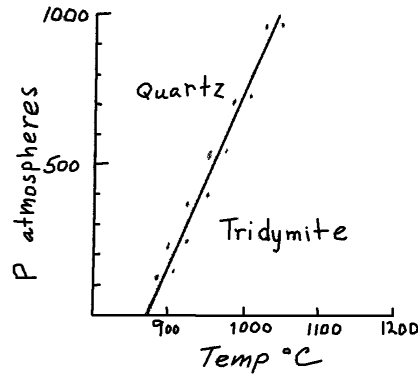


FIG. 4 QUARTZ - TRIDYMITE EQUILIBRIUM AS FUNCTION of PRESSURE and TEMPERATURE

H. J. H 6-18-54

Keat, The Norton Co. - "A New, Crystalline Silica"

Keat has produced a crystalline form of SiO_2 now called Keatite. This material is produced at 385 - 585°C at 10,000 lbs./sq.in. pressure. The reaction materials are 1 ½ g. silicic acid plus 1 ml. of 1/100 N NaOH. Lithium and potassium hydroxides as well as carbonates or tungstates will also catalyze Keatite formation. The reaction vessel was made of platinum.

If the alkali concentration is too great, quartz is formed. If too small, cristobalite forms rather than Keatite. Sometimes cristobalite and quartz form with, and intergrow with Keatite. The Keatite forms as tiny, square plates usually less than ½ micron across.

Between room temperature and 1100°C, no inversions have been observed for Keatite. Thirty-seven hours heating at 1100°C causes no change in structure. At 1400°C, Keatite changes to cristobalite.

The crystal is uniaxial negative with $\epsilon = 1.513$ and $\omega = 1.522$. A density vs. index of refraction plot for the various forms of silica indicates the density of Keatite should be about 2.50.

The thermal expansion has been determined by x-ray methods. The a_0 axis contracts with increasing temperature. The c_0 expands. The mean linear expansion calculated from the unit cell parameters is given in Fig. 3. X-ray powder pattern (Cu K α radiation) information on Keatite is given in Table I. This indicates that Keatite is similar to high temperature β spodumene.

hkl	d	Relative Intensity
100	7.46Å	VVW
101	5.48	½
110	5.28	½
111	4.50	2
102	3.72	7
201	3.42	10
112	3.33	2
211	3.11	2
113	2.516	½
222	2.246	½
213	2.174	½
004	2.148	½
312	2.067	½
114	1.988	VW
303	1.879	½
400	1.864	1
	1.667	½
	1.636	VW
	1.589	VW
	1.562	½
	1.489	½
	1.441	VW
	1.412	½
	1.389	VW
	1.366	VW
	1.321	VW
	1.246	VW

Robert B. Sossmann, Rutgers U., New Brunswick, N.J. – “A General View of the Known Phases of Silica

Fourteen crystalline and two vitreous phases of silica are now known. They are listed below:

1. quartz (low) <573°
2. quartz (high) 573° - 870°
3. Tridymite I 440 - 867°
4. Tridymite II 230 - 440°
5. Tridymite IIIA 117 - 230°
6. Tridymite IVA <117°
7. Tridymite IIIB 163 - 230°

8. Tridymite IVB <163°
9. Crystobalite high A ↘
10. Crystobalite low A → globular under microscope ↘
11. Crystobalite high B ↘ Subject to history
12. Crystobalite low B → hexagonal ↗
13. Coesite 500-800°C, 35,000 ats.
14. Keatite 385-585°C, 680 ats.
15. Ordinary vitreous silica
16. Bridgman's high pressure vitreous silica (50,000 ats.)

O.F. Tuttle, Penn. State College. – “The System SiO₂-H₂O at High Pressure and Temperature”

Tuttle studied the quartz-tridymite equilibrium line as a function of temperature and pressure (to 1000 atmospheres). The line is shown in Fig. 4. Water was the fluxing agent. At 100 atmospheres, Tuttle observed that liquids were obtained with SiO₂ + a tiny amount of water at temperatures as low as 600°-700°C. Alkali was not required to obtain this tremendous lowering of the liquids. Tuttle suggests that silica vessels might be easily shaped at 1000 atmospheres and 600°C by simply adding a small amount of water to the silica.

James E. Austin, U.S. Steel, Kearny, N.J. – “Inversion Temperatures Of Trydymite”.

Tridymite was carefully purified from a tungsten melt (the fluxing of mineralizing agent) and also from old silica brick. Inversion temperatures were determined with an interferometric dilatometer. They are 117, 163, 210, 300 and 475°C

Alfred H. Weber, Dept. Physics, St. Louis University. – “A Neutron Diffraction Study of Vitreous Silica”

These results check with previous x-ray results.

I learned at this meeting that Dr. Hatten S. Yoder, Geophysical Lab., Carnegie Institution, Washington 8, D.C. has made some of Coes' garnets. This means they have facilities for at least 30,000 atmospheres at 800°C. High-pressure, high-temperature research is also being carried on at the Bureau of Standards. A list of institutions known to be engaged in high-pressure, high-temperature work follows. Men associated with the project, where known, are given. The maximum sustained pressure simultaneously with temperature they are probably working at is also given.

(1) The Norton Co.	L. Coes, Jr.	45,000 ats.	1000°C
(2) Harvard	Bridgman, Kennedy	10,000	1200-large volume apparatus
(3) U. of Michigan	C.B. Slawson (Sponsor O.N.R.)	30,000	1000
(4) Geophysical Lab.	H.S. Yoder	30,000	1000
(5) Bureau of Stds.	?	?	?
(6) U. of Utah	S.S. Kistler	45,000	1000
(7) G.E. Co.	A.J. Nerad, et al	100,000	3000
(8) DuPont?	Paul Arthur, Jr. ?	?	?
(9) Carbide & Carbon	?	?	?

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