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A New Crystalline Silica

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A STUDY (*1*) of the role of soda in the crystallization of amorphous silica under hydrothermal conditions has uncovered a new crystalline form of silica. The new phase has characteristic physical properties different from the other known forms of silica. Its occurrence in nature is not known. The resemblance of a crystalline "intermediate" in the formation of low-cristobalite from silicic acid, reported by J. Endell (*2*), has been noted and is further discussed here.

The hydrothermal conditions of formation of the new phase were produced with equipment patterned after Morey's (*3*). The reaction vessel was a Morey-type autoclave with an internal volume of approximately 20 ml. Platinum or silver crucibles, with covers, held the reactants within the autoclave. To furnish pressure, distilled water was compressed by a high-pressure hydraulic pump and delivered to the autoclave through standard high-pressure metal tubing. The pressure was maintained at desired levels by electronic controls. Heating was accomplished by surrounding the autoclave with a Nichrome-wound furnace, also controlled electronically. The gage-pressure and temperature ranges within which the new silica was synthesized were 5000 to 18,000 lb/in.^{2} and 380° to 585°C. These limits, for the most part, were set either by the equipment or by the relative sluggishness of reaction (at the lower temperatures and pressures) and, therefore, do not define actual limits between which the new silica may be synthesized.

The initial material in the majority of experiments was Merck's "analytical reagent silicic acid." Silica gel formed by the hydrolysis of tetraethyl orthosilicate was also used successfully. To this, in a platinum (or silver) crucible, was added a small amount of alkali. Distilled water was used to fill the crucible, the cover was adjusted, and water was added to fill the reaction chamber completely. The alkali was added as NaOH, KOH, LiOH, Na_2WO_4, and as the carbonates of the same metals, all in solution form. The amount added was extremely small, for example, 1 ml of 0.0100N NaOH solution.

The concentration of base is fairly critical, because too small an amount will cause the formation of cristobalite and too large an amount, the formation of quartz. The actual concentration in contact with the silica is not known exactly, because the distribution of water in the apparatus is so dependent on the temperature. The amount of silicic acid was not a vital factor; generally, approximately 1.5 g was used as determined by the capacity of the crucibles used. Synthesis of the new silica was effected in more than 70 experiments; conversion under optimum conditions was, in general, complete. However, crystal development usually was quite poor, the product being cryptocrystalline in appearance. Only a small proportion of experiments yielded crystals of sufficient quality for optical analysis. This strong tendency to form submicroscopic crystals may well account for its lack of recognition in nature. Identification of such crystalline aggregates in some reaction products, by means of refractive index, yielded a range of values extending from 1.501 to approximately 1.508, and also from 1.528 to approximately 1.535. These differences in index resulted from the presence of intermingled, very small crystals of either cristobalite or quartz, as determined by x-ray analysis. This effect of an "average refractive index" for an aggregate has been noted before (*4*). Consequently, another reason why the new silica may have been overlooked in nature is the lack of distinguishing features by virtue of the poor crystalline development; it may even have been identified as, or with, another phase—perhaps, as a "microcrystalline variety" of silica.

Both spectrographic and chemical analysis show the reaction product to be a very pure silica. It is completely soluble in cold hydrofluoric acid. The major impurities, Na_2O, Fe_2O_3, and Al_2O_3, are present in a concentration of less than 0.01, less than 0.02, and less than 0.02 percent, respectively. The new silica crystals

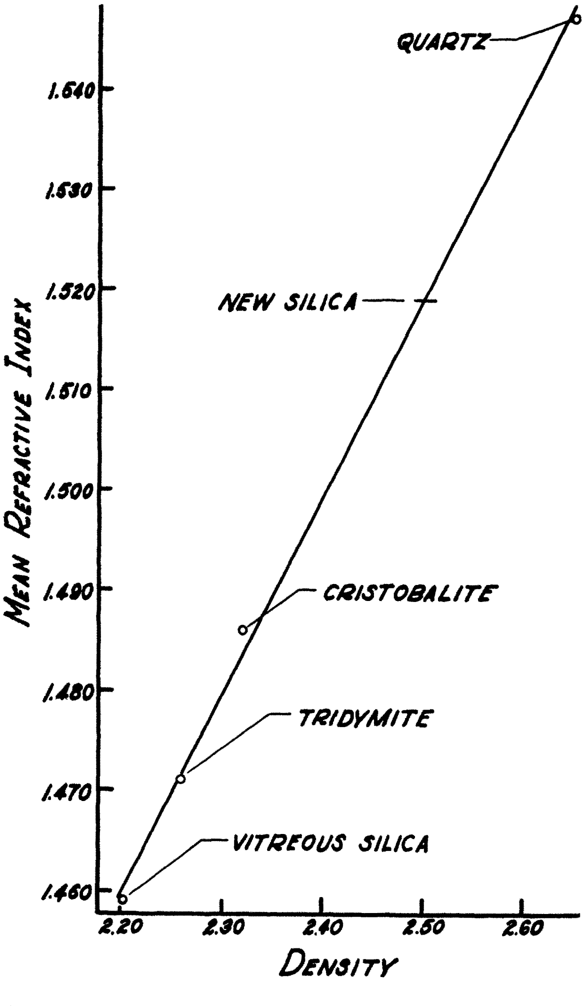

Fig. 1. Interpolation of density of new silica from plot of density versus mean refractive index of known forms of silica (off-scale plot of dense silica described by Coes (*10*) is not included).

are very stable thermally—heating at 1100°C for 37 hr showed little, if any, conversion to cristobalite. Heating for 3 hr at 1620°C changed the crystals completely to cristobalite. Conversion to the other known forms of silica in the presence of Na_2WO_4 is effected easily in the usual temperature ranges given for the stable forms.

Differential thermal analysis showed no inversions up to 1100°C. However, the indicated absence of a low-high inversion so characteristic of the other known forms of silica may have been due to the insensitivity of the apparatus or the nature of the sample and not solely to the possible nonexistence of such an inversion within the temperature range studied. The sensitivity of the instrument was such as to give only a small peak (0.27 in.) for the low-high inversion of a sample of very pure North Carolina quartz and might, in the case of a smaller heat effect, fail to register adequately. Keith and Tuttle (*5*) have noted the importance of particle size and the nature of the specimen in producing measurable thermal effects even with very sensitive apparatus. They observed that some samples of microcrystalline quartz (chert) showed measurable thermal effects only on fine grinding of the specimen to a size approaching that of the individual grains (1 to 7 μ). They also noted samples in which even this treatment did not yield a measurable thermal peak—only a change in slope gave indication of the low-high inversion. Unfortunately, the sample available for thermal analysis was microcrystalline, and it could possibly have behaved like the specimens studied by Keith and Tuttle.

Optical examination of crystals up to 50 μ in size showed them to be uniaxial negative, with $\omega = 1.522$ and $\varepsilon = 1.513$. The predominant habit is that of square platelets. Density as determined from a plot of mean refractive index (of the known forms of silica) versus density (of the respective forms) is 2.50 (Fig. 1).

Single-crystal x-ray analysis yields a primitive tetragonal unit cell with dimensions *a* and *c* of 7.46 and 8.59 A (*6*). These data taken together with the calculated value of density indicate that 12 formula weights of SiO_2 constitute the unit cell. Powder patterns using Cu K_α radiation yield the data of Table 1.

Thermal dilatation was determined on a Norelco x-ray spectrometer. A small resistance furnace served to heat the sample. Quartz was used as an internal standard (*7*); its low-high inversion being used to position a calibration curve based on readings from a thermocouple imbedded in a test sample. The results indicate that the new silica expands parallel to the *c*-axis up to 550°C (the temperature limit of reliable data gathered) and shrinks parallel to the *a*-axis up to about 250°C, at which point the true coefficient of expansion (parallel to *a*) passes through zero, becomes positive, and continues so up to 550°C. The calculated over-all effect on an aggregate is shown in Fig. 2. From this, it is seen that the new silica exhibits a negative mean linear expansion from 25°C over the range of temperature studied. The coefficient is of about the same order of magnitude as that of vitreous silica.

The similarity in structure between the new silica

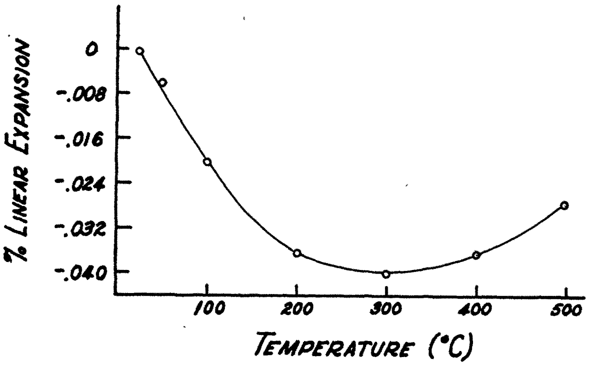

Fig. 2. Mean linear thermal expansion from 25°C of an aggregate of the new silica, calculated from expansion of unit cell parameters.

Table 1. Comparison of x-ray powder patterns of the new silica, β-spodumene, and Endell's "intermediate-I."

	New silica		β-Spodumene		Intermediate-I
hkl	*d* observed	Relative intensity	*d* observed†	Relative intensity	*d* observed
100	7.46 A	VVW*			
101	5.64	½	5.74 A	0.4	
110	5.28	½			
111	4.50	2	4.56	.1	
					4.0 A (amorph)
102	3.72	7	3.86	3.5	
201	3.42	10	3.46	10.0	3.4
112	3.33	2			
210			3.30	0.4	
211	3.11	2	3.14	1.0	
103			2.83	0.3	
113	2.516	½	2.64	.3	
222	2.246	½	2.29	.7	
213	2.174	½	2.25	.4	
004	2.148	½			2.15
312	2.067	½	2.10	.6	
114	1.988	VW			
303	1.879	½			
400	1.864	1	1.875	.1	1.85
	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			

* VW, very weak; VVW, extremely weak.
† Smaller *d* values of β-spodumene are not included here.

and β-spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, is seen by comparison of the x-ray powder patterns of the two, as is shown in Table 1. Presumably, the β-spodumene structure can be derived from that of the new silica by substitution of the larger, trivalent aluminum atom for quadrivalent silicon up to a ratio of 1 : 2. The necessary amount of monovalent lithium is contained within the interstices of the structure to offset the negative charge left over by the tetrahedrally coordinated trivalent aluminum atom. Consequently, diffraction by similar *hkl* planes results in larger *d* values for the correspondingly larger unit cell of β-spodumene.

Calculations based on this assumption and the data of Karkhanavala and Hummel (*8*) (Table 1) give approximate tetragonal unit cell dimensions for β-spodumene of $a = 7.5$ A and $c = 9.0$ A. Such a unit cell would accommodate two formula weights of β-spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$. The calculated density is 2.45 g/cm^3. The observed density is 2.35 (*9*). The actual structure of β-spodumene, however, may be a slightly distorted derivative of the foregoing. Another silicate, "μ-cordierite," may also be structurally similar to the new silica—a correlation between "μ-cordierite" and β-spodumene has been suggested by Karkhanavala and Hummel.

It is of interest to note here a study of the behavior of "silicic acid" as it changes to cristobalite under the influence of heat. Endell (*2*) has reported the occurrence of two "intermediate structures" and possibly a third during the careful heating of silicic acid over the temperature range 1000° to 1300°C. Unfortunately, the only obtainable data on the intermediates were a few x-ray reflections for each. It is interesting that the three reflections of Endell's "intermediate-I" (Table 1) correspond to three of the new silica; a fourth possible reflection of intermediate-I with $d = 3.72$ A and a fifth with $d = 4.50$ A may have been masked by a broad, amorphous peak that remained to some extent from the original silicic acid material. This resemblance of Endell's intermediate-I to the new silica, in the available x-ray patterns and in the sequence of formation, indicates but does not prove definitely a possible identity of the two.

The afore-described data establish the existence and conditions of formation of a new phase of silica, possessing a characteristic structure and physical properties. The structure of the new silica is unique and may be the basis for derivative silicate structures among which β-spodumene is an example. An apparent consequence of this structure is the interesting combination of directional thermal expansion properties leading to a small negative mean linear thermal expansion up to 550°C and higher.

References and Notes

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