

straight line seems to be due to a lack of homogeneity. This is substantiated by the closer approach of the points to the line after additional heating periods. As with the sulfides, the solubility limit is 50 mole per cent. and the lattice constant is increased as the vacancies are filled by strontium ions.

### Discussion

The results of the experiments described in Section I, Experimental, indicate that the complex form of cerium(III) sulfide described here is identical with the complex phase described by Eastman, Brewer, *et al.*, when traces of oxide are present. The cubic phase, which has been shown to be a distinct phase from the complex phase, is stabilized in the presence of strontium sulfide in solid solution as well as by the removal of oxide by solution in a molten flux. The stabilizing effect of strontium sulfide on the cubic form in the presence of oxygen, even when a flux is absent, may possibly be due to the separation of strontium oxide as a separate solid phase. The manner in which lithium fluoride and sodium chloride enter the  $Ce_2S_3$  lattice has not been determined, but it is possible that the alkali metal ions enter into certain interstices between the sulfide ions with an equivalent number of halide ions entering in other interstitial positions. Another possibility, of course, is the substitution of three alkali ions for one cerium ion by filling vacancies in the cation lattice. In this case, the displaced cerium ions might form a separate cerium halide phase. In view of the shrinkage of the lattice with lithium fluoride and the expansion with sodium chloride, it may be that the halide ion is

entering the sulfide lattice. However, the effect is rather small and a determination of the exact mechanism of solid solution may not be readily feasible.

The solid solutions of strontium sulfide and selenide in the corresponding cerium compounds represent cases of filling of a defect structure by the incorporation of cations of lower charge than those originally present. They differ from the solid solutions of cerium(II) sulfide in cerium(III) sulfide in that the additional metallic binding forces are not present either in the original compound of the divalent metal or in the solid solutions. With the alkaline earth metals, the binding is predominantly ionic and the cerium sulfide or selenide lattice expands when a large cation-like strontium is added, and contracts when a smaller cation-like calcium or magnesium is added. It is noteworthy that divalent europium forms a "normal" sulfide with no metallic binding. It should be of some interest to determine whether other rare earths which would have one or two "d" or "f" electrons in the divalent state, would also form semimetallic sulfides and selenides like CeS and CeSe.

**Acknowledgment.**—We wish to express our gratitude to Professor I. Fankuchen for his invaluable advice on the interpretation of X-ray diffraction data and to Professor Leo Brewer who so generously provided us with samples of his materials and information in advance of publication.

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[CONTRIBUTION FROM THE INSULATION DEPARTMENT, WESTINGHOUSE RESEARCH LABS.]

## A New Highly Silicious Soda-Silica Compound

BY LEON McCULLOCH

A new soda-silica compound, of silica to soda ratio between 9.4 and 13.1 to one, has been made by crystallization of silicious sodium silicate solutions at 100°. The crystals are rectangular plates, single and in groups. Being readily prepared and easily filtered and washed without change, this compound should invite investigation. Incidental mention is made of a sodium tetrasilicate having an X-ray pattern unlike the one found in the literature.

A new soda-silica compound high in silica has been obtained by crystallization of silicious sodium silicate viscous solutions. Analyses of several such products give silica-soda ratios between 9.4:1 and 13.1:1. The most silicious compound heretofore reported has a ratio 4.0 or 4.3:1, the tetrasilicate.

The new silicate is made by the prolonged heating of a silicious solution of the following formula:

Silica gel or silicic acid (Dry but not anhydrous)	15 parts
Sodium hydroxide (pellets)	3.6 parts
Water	30 parts

This ratio of  $SiO_2:Na_2O$  is about 5.0:1. Commercial sodium silicate solutions are below 4.0:1 in ratio.

The ingredients were enclosed within Pyrex ampoules (1" × 6") or friction-top tin cans (quarter pint) kept at 100° in a laboratory oven. These containers were inverted frequently to cause flow and stirring of the viscous solution. Within a week

or two, the mass became clouded. In three or four weeks, precipitation was complete, yielding well-settled sediment and clear, thin liquor. Three such liquors had silica-soda ratios of 3.7, 3.6 and 3.8. Nine of the sediments, washed and dried, had ratios between 9.4 and 13.1. The analyses are collected into Table I, and also in Fig. 1, where  $Na_2O$  is plotted against  $SiO_2$ . Analyses were made of three of the liquors, also of some suspensions and sediments damp from a centrifuge, and of the sediments

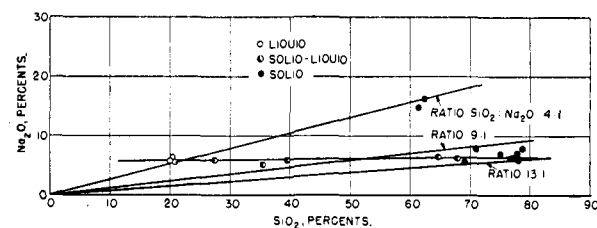


Fig. 1.—Silicious sodium silicates.

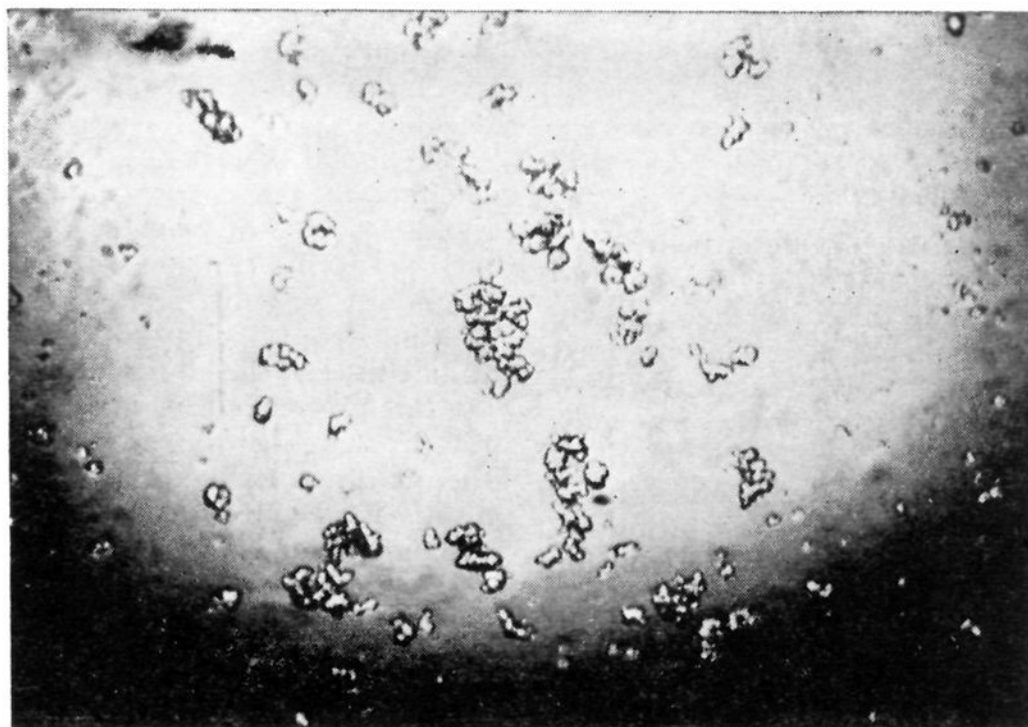


Fig. 2.—Nodules, SiO<sub>2</sub>:Na<sub>2</sub>O 12.7:1; magnification 100.

TABLE I  
ANALYSES OF SILICIOUS SODIUM SILICATE CRYSTALLIZATION PRODUCTS

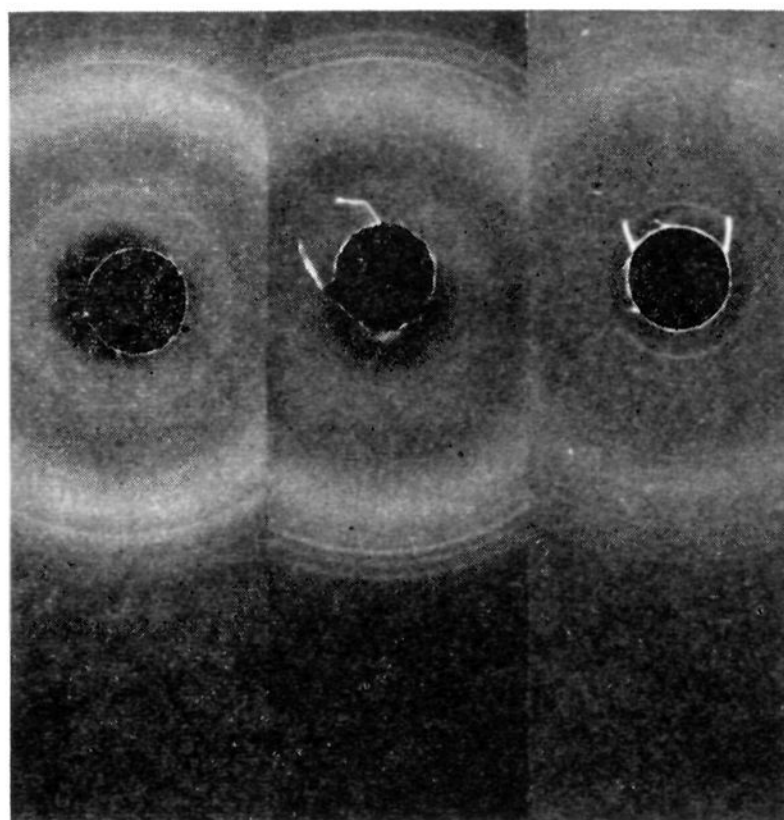
Preparation	Na <sub>2</sub> O	SiO <sub>2</sub>	H <sub>2</sub> O	Molecular ratio SiO <sub>2</sub> :Na <sub>2</sub> O
From ampoule, aged 3 years at room temperature				
Clear liquor	5.7	20.2	74.1	3.7
Suspension	5.9	27.4	66.7	4.8
Wet sediment	5.9	39.5	54.6	6.9
Sediment drained by centrifuge	6.5	64.7	28.8	10.4
Sediment washed by dialysis within cellophane tube, dried at 35°	5.9	78.0	16.1	13.1
From ampoule, aged 6 months at room temperature				
Clear liquor	6.0	20.6	73.4	3.6
Suspension	5.1	35.5	59.4	7.3
Sediment washed by dialysis, dried at 35°	6.2	77.3	16.5	12.8
From ampoules, recent, using silicic acid				
Sediment washed with water by centrifuge and decanting, dried at 35°	7.8	71.1	21.1	
	7.8	71.0	21.2	9.4
From ampoule, recent				
Clear liquor	5.6	20.7	73.7	3.8
Sediment drained by centrifuge	6.3	67.8	25.9	11.1
Sediment washed with water on suction filter, dried at 35°	6.3	76.9	16.8	12.7
From tin can, spontaneous crystallization				
Sediment washed with H <sub>2</sub> O on suction filter, dried	5.8	69.1	25.1	12.2
Sediment washed with 1% NaOH in H <sub>2</sub> O, then CH <sub>3</sub> OH, dried	6.2	77.4	16.4	12.8

From tin can, seeded

Sediment washed with 5% NaOH, then CH <sub>3</sub> OH, dried	7.9	78.7	13.4	10.0
Washed with 5% NaOH, then CH <sub>3</sub> OH, dried	7.0	75.2	17.8	11.1

“Tetra silicate” from “Star” sodium silicate

Washed with 1% NaOH in H <sub>2</sub> O, then CH <sub>3</sub> OH, dried 35°	16.1	62.3	21.6	4.0
Washed with 5% NaOH in H <sub>2</sub> O, then CH <sub>3</sub> OH, dried 35°	14.9	61.5	23.5	4.3



Tetra                      13:1                      9.4:1  
SiO<sub>2</sub>:Na<sub>2</sub>O = 4:1

Fig. 3.—X-Ray powder diffraction; copper radiation filtered through nickel.

washed and dried. A constant percentage of  $\text{Na}_2\text{O}$  is observed, the liquors and the precipitate having nearly the same soda content as the original mixture—an interesting coincidence.

A crystalline product was made in a shorter time by the use of "seed" which was added but not especially mixed into the mass. The grain size of this product was smaller and its ratio lower: 10.0, 11.1:1. A similar product crystallized spontaneously had a ratio 12.2, 12.8:1. The crystals appear through the microscope usually as groups of rounded nodules (Fig. 2). Mild grinding yields suspensions of flake-like particles, showing streamline reflection of light.

A product from precipitated "silicic acid," not silica gel, made without seeding, was more flake-like than nodular in its particles. This had the lowest ratio, 9.4:1. Its X-ray diffraction pattern (Fig. 3) differs from that of another made spontaneously from silica gel. Through a microscope (Fig. 4) and an electron microscope (Fig. 5), it appears as thin rectangular plates, as does also one of the products from silica gel (Fig. 6). Possibly there is more than one compound within this range, perhaps there is solid solution. Further work is called for.

The discovery of this reaction acquired significance from a review in 1950 entitled "The System  $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  at 50, 70 and 90."<sup>1</sup> The most silicious compound reported there was the tetrasilicate, to which the formula  $3\text{Na}_2\text{O}\cdot 13\text{SiO}_2\cdot 11\text{H}_2\text{O}$  was ascribed.

It happened about this time that the writer found a sodium tetrasilicate as a voluminous precipitate from a gallon of "Star" sodium silicate after several years storage. Analyses gave a ratio of 4.0 and 4.3:1 in this precipitate after separating by decanting, washing with dilute aqueous  $\text{NaOH}$ , then with methyl alcohol (see Table I and Fig. 1). Microscopic and X-ray examination found it to be crystalline. Its X-ray pattern (Fig. 3) differs from that given by Baker, Jue and Wills<sup>2</sup> (see Table II). Through the microscope it appeared as clusters of rhombic leaflets (Fig. 7). It is quite unlike the new highly silicious compound. Sodium tetrasilicate hydrate is said to exist in high and low temperature forms.

TABLE II

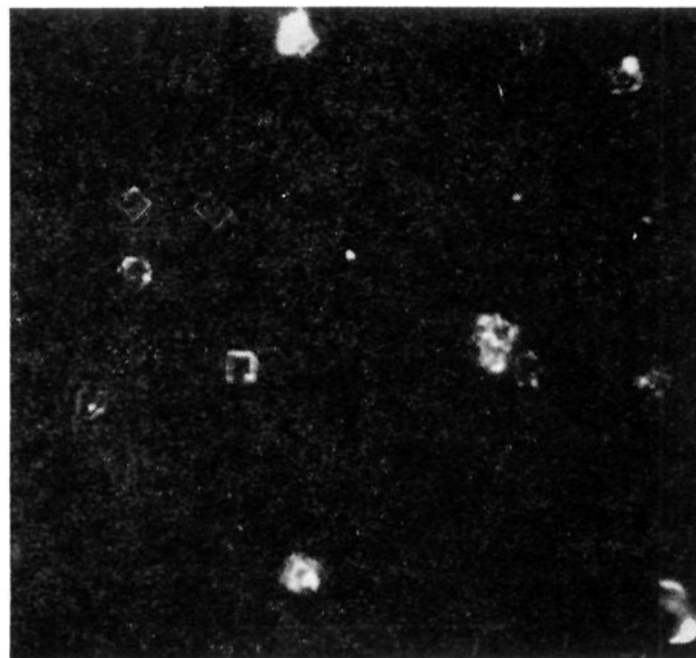
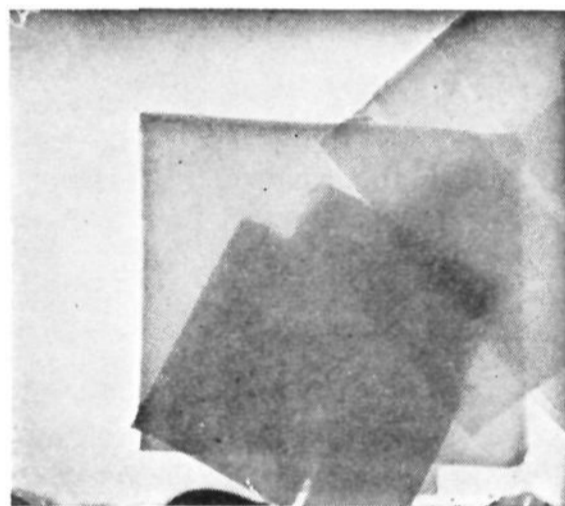
INTERPLANAR SPACINGS "d" BY X-RAY POWDER DIFFRACTION

This Laboratory (Filtered Copper)	Tetrasilicates		Silicates high in silica	
	Philadelphia quartz	3.17 W	Ratio 13.1 (Filtered copper)	Ratio 9.4 (Filtered copper)
7.8 S	9.40 S	3.17 W	5.24 VW	11.2 S
4.67 M	5.21 VS	3.02 M	3.67 VW	4.81 M
3.62 S	4.76 VW	2.91 W	3.59 VW	4.10 M
3.54 W	3.73 S		3.47 VS	3.63 VW
3.28 W	3.44 MS		3.32 M	3.49 M
2.70 W			3.16 S	3.30 W
				3.06 M

The preparation and purification of the new

(1) C. L. Baker, L. R. Jue and J. H. Wills, THIS JOURNAL, 72, 5369 (1950).

(2) Previous reference. The interplanar spacings "d" were supplied by C. E. Imhoff, Allis-Chalmers, by personal letter.

Fig. 4.— $\text{SiO}_2:\text{Na}_2\text{O}$  9.4:1; magnification 970.Fig. 5.— $\text{SiO}_2:\text{Na}_2\text{O}$  9.4:1; magnification 8700; electron microscope.Fig. 6.— $\text{SiO}_2:\text{Na}_2\text{O}$  11.1:1; magnification 8700; electron microscope.

highly silicious sodium silicate is simple and rapid, making the study very attractive to anyone having the time and the preparation to attempt it. The resulting addition to silicate chemistry might be substantial.

Credit for the chemical analysis is due J. F. Reed;

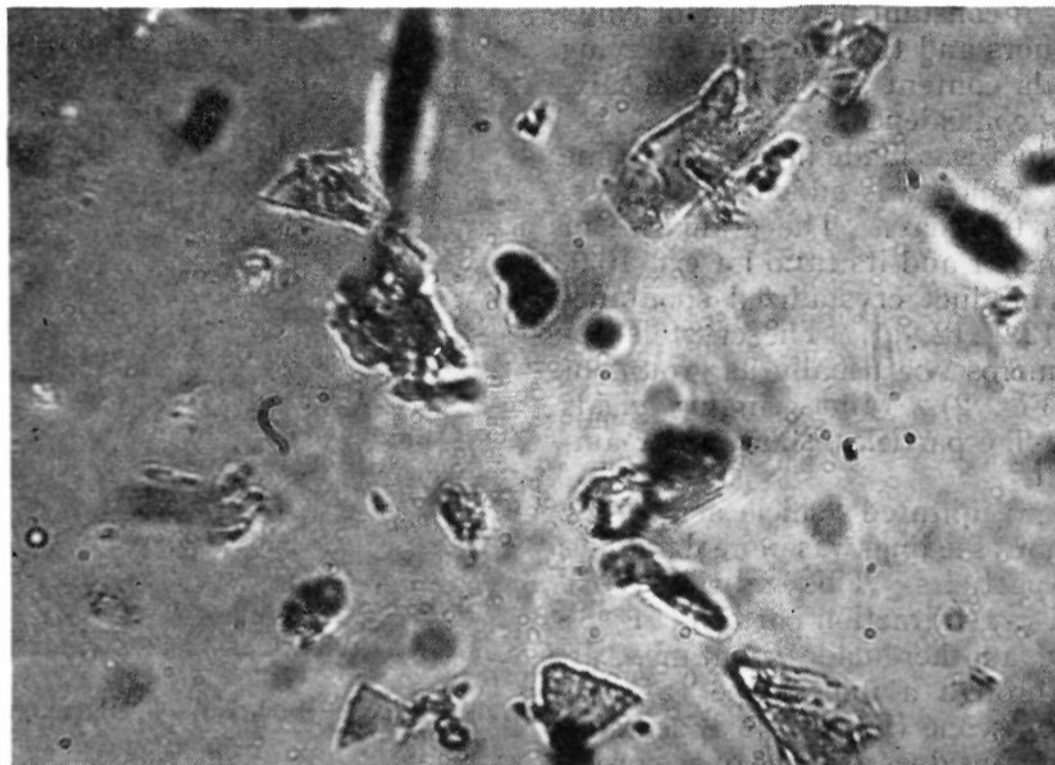


Fig. 7.— $\text{SiO}_2:\text{Na}_2\text{O}$  4.0:1; tetrasilicate; magnification 970.

for the X-ray diffraction patterns, Joan Von Hoene; for the microphotography, Mrs. Genevieve Lachmanek; and for the electron microscope photo-

graphs, Wm. McMillan and E. A. Gulbransen.  
EAST PITTSBURGH, PENNSYLVANIA  
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