

NonSilicates with CristobaliteLike Structure

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where ϵ_i is the potential energy connected with that deviation and n' the number of atoms per cc having this deviation. One then inserted n' from the Maxwell-Boltzmann distribution law and integrated over $dx dy dz$. But that is correct only if in the permitted range $L\epsilon_i < Q_0$. Otherwise, one can only integrate to such values of x, y, z in (19) that

$$L\epsilon_i = Q_0.$$

Call $\int_0^{L\epsilon_i=Q_0} dx dy dz = 1/n''$.

Then, in the simplest case, the number of evaporating atoms is

$$nk_0/n'' = \alpha' k_0,$$

where n is, as before, the number of atoms per cc, and speed of sublimation and speed of condensation have both to be multiplied by $\alpha' < 1$ in all the cases treated in I. The same is true for molecules and assumption (14''). Possibly Volmer's¹¹ experiments showing a reflection coefficient of Hg on mercury crystals of 10 percent can be explained so.

¹¹ M. Volmer and I. Estermann, *Zeits. f. Physik* **7**, 1 (1921).

Similarly for molecules, we have to change the discussion of assumption (14') so that we integrate only to such values of the coordinates in the crystal that satisfy

$$Q_0 > L(\epsilon_i + \epsilon_r).$$

The speed of sublimation $k_0\beta$ has again to be multiplied by a factor α' smaller than 1,

$$\alpha' = n\Phi_0^{-1} \int_0^{L\epsilon_i=Q_0} dx dy dz dq = \Phi'\Phi_0^{-1}$$

and the same factor enters the formula for the speed of condensation, giving rise to a reflection coefficient of $1 - \alpha'$.

The physical reason for the existence of this reflection coefficient is, of course, that the attractive forces that are responsible for the heat of sublimation can force the incoming molecule only into the fraction α' of the total coordinate space.

We have then an intermediate case between (13') and (13'') where

$$k = k_0\beta', \quad \beta' = \Phi'\Phi_s^{-1}, \quad \alpha' = \Phi'\Phi_0^{-1}.$$

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Non-Silicates with Cristobalite-Like Structure

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The cristobalite type of structure which has been previously observed in certain silicates: carnegieite, NaAlSiO_4 , and $\text{Na}_2\text{CaSiO}_4$ is now shown to occur in $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3$, and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$.

A NEW cubic compound, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, has recently been described by Brownmiller,¹ and measurements on an x-ray powder photograph of it have been published.² This powder

photograph is very similar to that of $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3$, and they both resemble the x-ray patterns of certain silicates structurally isomorphous with cristobalite (see Table I). These similarities indicate that the structure of $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and of $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ may in some way or other be related to that of cristobalite.

The well-known feature of the cristobalite structure is the existence of endless silicon-oxygen chains with large, open spaces in between. It seemed probable, therefore, that in $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ there would be corresponding chains of alumi-

¹ L. T. Brownmiller, *A Study of the System Lime-Potash-Alumina*, *Am. J. Sci.* **29**, 260 (1935).

² The reflections observed by Brownmiller correspond to cubic symmetry (length of the edge of the unit cube, $a = 7.69\text{\AA}$), except for three weak lines, corresponding to a planar spacing of 2.395, 2.000 and 1.488. He states, however, that $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ is extremely hygroscopic so there were considerable difficulties in taking the photograph; it is probable, therefore, that these weak reflections come from some alteration product on the surface of the crystals.

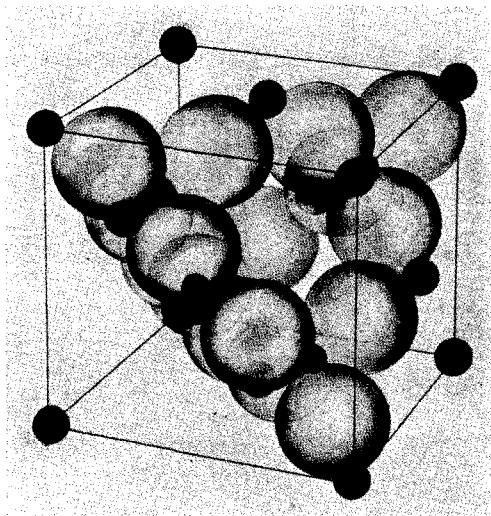


FIG. 1. The unit of the high-cristobalite structure. The large transparent balls represent oxygen ions, and the small black ones silicon ions, bringing out their relative size. The positions of the ions are very slightly displaced to give the structure a more regular arrangement than actually exists.

num-oxygen, and in $K_2O \cdot Fe_2O_3$ chains of iron-oxygen, with the potassium atoms situated in the interstices.³

TABLE I. Intensity of powder diffraction lines of α -carnegieite, Na_2CaSiO_4 , $K_2Fe_2O_4$, and of $K_2Al_2O_4$.

| Indices | Carnegieite | | Na_2CaSiO_4 | | $K_2Fe_2O_4$ | | $K_2Al_2O_4$ | |
|---------|-------------|------|---------------|-------|--------------|-------|--------------|-------|
| | Obs. | Obs. | Obs. | Calc. | Obs.* | Calc. | Obs.* | Calc. |
| 111 | 10 | 3 | 4 | 2.2 | 0 | 0.2 | | |
| 022 | 9 | 10 | 10+ | 15.1 | ss | 15.0 | | |
| 113 | 0.5 | 0.5 | 0 | 0.1 | m | 3.5 | | |
| 222 | 3 | 1 | 1 | 0.9 | w | 1.7 | | |
| 004 | 1 | 4 | 4 | 1.8 | m | 1.2 | | |
| 133 | 4 | 0.5 | 1 | 1.0 | 0 | 0.1 | | |
| 224 | 6 | 6 | 8 | 10.0 | s | 10.0 | | |
| 333 | | | | | | | | |
| 115 | 2 | 1 | 1 | 0.3 | 0 | 0.6 | | |
| 044 | 3 | 3 | 3 | 5.5 | m | 6.3 | | |
| 135 | 2 | 1 | 1 | 0.8 | 0 | 0.0 | | |
| 026 | 2 | 2 | 5 | 5.0 | s | 5.4 | | |
| 335 | 0 | 0.5 | 0 | 0 | 0 | 0 | | |
| 444 | 0.5 | 0.5 | 0.5 | 0.8 | w | 0.7 | | |
| 117 | | | | | | | | |
| 155 | 0 | 0.5 | 0 | 0 | 0 | 0 | | |
| 246 | 1 | 1 | 2 | 6.5 | m | 6.5 | | |
| 355 | | | | | | | | |
| 137 | 0.5 | — | — | 0 | 0 | 0 | | |
| 066 | — | — | — | 3.4 | w | 3.1 | | |
| 228 | — | — | — | 1.4 | w | 1.0 | | |
| 048 | — | — | — | — | w | 1.4 | | |
| 466 | — | — | — | — | w | 1.4 | | |
| d_0 | 7.37 | 7.48 | 7.99 | | | 7.69 | | |

* Observed intensities as given by Brownmiller.

³ For a description of the cristobalite structure, and of the structure of carnegieite and Na_2CaSiO_4 , which have

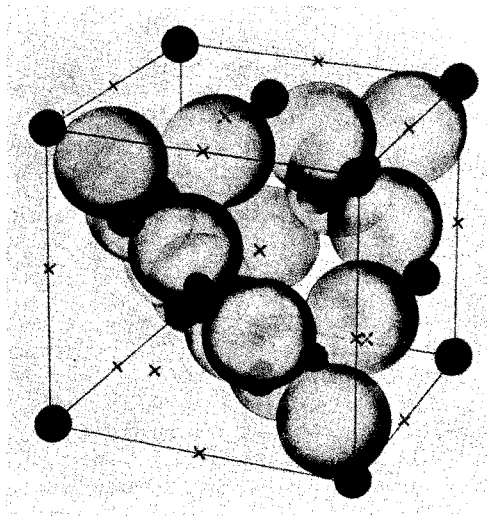


FIG. 2. The unit of the structure of $K_2Al_2O_4$ (and of $K_2Fe_2O_4$). The large transparent balls represent oxygen ions, and the small black ones aluminum ions, bringing out their relative size. In this way aluminum-oxygen chains are formed that are strictly analogous to the silicon-oxygen chains of cristobalite. The centers of the potassium atoms are indicated by crosses; the atoms themselves are so large as to fill up the interstices, touching 12 adjacent oxygens. The positions of the ions are very slightly displaced to give the structure a more regular arrangement than actually exists.

The constituent atoms in cristobalite (and in the silicates isomorphous with it) show a close approach to a face-centered arrangement with silicons close to $4b$, $4d$; and oxygens close to $16a$.⁴ In $K_2O \cdot Al_2O_3$ one would expect, therefore, Al to be in $4b$, $4d$; and the oxygens to be in $16a$, or very nearly in these positions. The only possible place for the K-atoms would then be $4c$, $4e$. The same holds, of course, for $K_2O \cdot Fe_2O_3$ with interchange of Fe and Al.

We can test this assumption by calculating the intensities which, if this represents the true structure of $K_2O \cdot Al_2O_3$ and $K_2O \cdot Fe_2O_3$, must be proportional to the observed ones.

Table I shows that there is a fair agreement between calculated and observed intensities, and it can be concluded, therefore, that the structure

the same type of structure, see Barth and Posnjak, *Silicate Structures of the Cristobalite Type: III, Structural Relationship of High-Cristobalite, α -Carnegieite, and Na_2CaSiO_4* , Zeits. f. Krist. 81, 376 (1932).

⁴ Wyckoff's notation.

of $K_2O \cdot Al_2O_3$ and of $K_2O \cdot Fe_2O_3$ is of the cristobalite type.

A few years ago it was shown that the structure of cristobalite was not exactly face-centered but actually built upon a simple lattice.⁵ Also certain silicates isomorphous with cristobalite exhibit the same small, but characteristic deviation from a face-centered lattice.⁶

An inspection of Table I shows that $K_2O \cdot Al_2O_3$ and $K_2O \cdot Fe_2O_3$ also seem to deviate slightly from the face-centered arrangement. The discrepancies between observed and calculated intensities are small, but significant; thus 400 is always stronger than demanded by the theory, which is again exactly the same phenomenon previously observed in cristobalite and its congeners. This means that the structural arrangement we have been considering so far is not accurate, it represents only the approximate or idealized structure, whereas the true structure is slightly different and actually isomorphous with the space group T^4 . (The arguments for T^4 are exactly the same as in the case of cristobalite.)

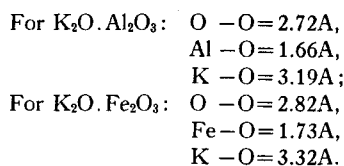
From this it follows that the true structure of $K_2O \cdot Al_2O_3$ is conditioned by no less than 8 independent parameter values: $4K + 4K$, $4Al + 4Al$, and $4O_I$ in position $4f$, each group of four with one parameter, and the remaining $12O_{II}$ in the general positions of T^4 with three parameters. These 8 parameters cannot be determined accurately from powder photographs. But in the case of $K_2O \cdot Fe_2O_3$ a trial calculation has been made which shows that the discrepancies between calculated and observed intensities are appreciably diminished by moving the oxygen atoms slightly out of the idealized positions, following thereby exactly the same procedure previously described in the case of carnegieite and Na_2CaSiO_4 .

Figs. 1 and 2 show very plainly the relation between the structure of cristobalite and the structure of $K_2O \cdot Al_2O_3$ (or $K_2O \cdot Fe_2O_3$). Al (and Fe) has coordination number 4, K has 12.

The interatomic distances in the idealized structures are as follows:

⁵ T. F. W. Barth, *Am. J. Sci.* **23**, 350 (1932).

⁶ T. F. W. Barth and E. Posnjak, *Zeits. f. Krist.* **81**, 135, 371 (1932).



It is noteworthy that the distances $Al-O$ and $Fe-O$ are smaller than usual even for coordination number 4,⁷ a phenomenon which also has its strict analogy in the silicate structures of the cristobalite type.

As has long been known, mixed crystals of α -carnegieite and cristobalite exist.⁸ But it has now been observed that α -carnegieite is able to take up also $Na_2O \cdot Al_2O_3$ in solid solution; indeed, it is possible that a continuous series of solid solutions extends all the way between carnegieite and $Na_2O \cdot Al_2O_3$.⁹ Consequently $Na_2O \cdot Al_2O_3$ must be isomorphous with carnegieite and the structure type of at least one of its modifications (potential or real) must therefore be that of $K_2O \cdot Al_2O_3$. This becomes so much the more probable since powder photographs of $Na_2O \cdot Al_2O_3$ at ordinary temperature exhibit an interesting similarity to those of low-carnegieite. To be sure, the low-carnegieite pattern merges gradually into that of low- $Na_2O \cdot Al_2O_3$ through intermediate mix-crystals with successively decreasing amounts of silica.¹⁰

Thus we see that the cristobalite type of structure is not restricted to silicates only, but that at least two aluminates and one ferrite crystallize in the same structure.

Note added in proof: In a paper by S. Hilpert and A. Lindner measurements of x-ray powder photographs of $K_2O \cdot Fe_2O_3$, $Rb_2O \cdot Fe_2O_3$, and $PbO \cdot Fe_2O_3$ have been published (*Zeits. f. physik. Chemie* **B22**, 400 (1933)). From these measurements it can be deduced that $Rb_2O \cdot Fe_2O_3$ and $PbO \cdot Fe_2O_3$ are isomorphous with $K_2O \cdot Fe_2O_3$, and consequently that these two additional ferrites also crystallize in the cristobalite type of structure.

⁷ For discussion and values of interatomic distances in relation to coordination number see W. H. Zachariasen, *Zeits. f. Krist.* **80**, 137 (1931).

⁸ Cf. Barth and Posnjak, *Silicate Structures of the Cristobalite Type: III*, *Zeits. f. Krist.* **81**, 385 (1932).

⁹ Unpublished experiments by J. F. Schairer of this Laboratory.

¹⁰ These mixtures were prepared by Dr. J. F. Schairer.