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Abstract

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ON THE FORMATION OF SOLID SOLUTIONS BETWEEN TRICALCIUM AND TRISTRONTIUM SILICATES

The tendency of tricalcium silicate to form solid solutions with other components is of great interest for the crystal chemistry of silicates, the chemistry and technology of cements, refractories, etc.

Experimental work in recent years has shown that $3CaO \cdot SiO_2$ is capable of dissolving a certain amount of oxides of chromium ([1,2]), cobalt and nickel ([3]), iron, manganese, phosphorus ([4]), and also titanium. Of considerable importance for cement chemistry is the question of the dissolution of magnesium oxide and aluminum oxide (or calcium aluminates) in tricalcium silicate. The composition of this solid solution, which has received the name alite, was proposed as $54CaO \cdot 16SiO_2 \cdot Al_2O_3 \cdot MgO$ ([5]). The possibility of the formation of solid solutions between $3CaO \cdot SiO_2$ and $3SrO \cdot SiO_2$ had until recently been called into question ([6]). The synthesis of tristrontium silicate itself was carried out only in 1952 ([6]); the first investigator of the system SrO—SiO_2, Eskola, found only two strontium compounds—metasilicate and orthosilicate ([7]).

According to the data of ([6]), tricalcium and tristrontium silicates are dissimilar in both physical and chemical properties and are not inclined to form solid solutions. Nevertheless, subsequent work showed that these minerals possess substantial similarity. Thus, Massazza ([8]) was able to establish that strontium silicate occurs in several polymorphic modifications. According to ([4]), the phenomenon of polymorphism is also characteristic of calcium silicate. In addition, $3SrO \cdot SiO_2$, like $3CaO \cdot SiO_2$, has limited temperature ranges of stability in the corresponding systems.

Further, one of the properties important for cement chemistry is the ability to harden upon treatment with water. In Braniski' s opinion ([9]), one variety of $3SrO \cdot SiO_2$ possesses this property.

Finally, Carlson and Wells ([10]) succeeded in synthesizing strontium hydrosilicate $3SrO \cdot SiO_2 \cdot 2H_2O$, similar in composition to calcium hydrosilicate $3CaO \cdot SiO_2 \cdot 1.5H_2O$, which is formed during hydrothermal treatment of $3CaO \cdot SiO_2$.

The closeness of the chemical properties of the elements Ca and Sr and of their ionic radii (Ca^{+2} 1.04 Å, Si^{+2} 1.20 Å), as well as the analogy considered above in the properties of the corresponding silicates, may serve as grounds for assuming the formation of solid solutions between them. However, the very considerable similarity of the optical indices of these minerals and the absence of color greatly complicate the investigation. Another major obstacle is the limited stability range of both compounds.

We have made an attempt to investigate the possibility of formation of solid solutions between the indicated minerals and the limit of solubility of $3SrO \cdot SiO_2$ in calcium silicate.

Samples of the following compositions were synthesized: pure $3CaO \cdot SiO_2$, 95 wt.% $3CaO \cdot SiO_2$ + 5 wt.% $3SrO \cdot SiO_2$, 92.5 wt.% $3CaO \cdot SiO_2$ + 7.5 wt.% $3SrO \cdot SiO_2$, 90.0 wt.% $3CaO \cdot SiO_2$ + 10 wt.% $3SrO \cdot SiO_2$.

Natural calcite, rock crystal, and strontium carbonate were used as starting materials. The finely ground, thoroughly mixed batch was fired in the form of pellets for 100 h at 1400° and then for 12-15 h at 1550-1600° in a platinum crucible in furnaces with platinum and platinum-rhodium heaters. After each firing lasting 10-15 h, the pellet was ground, pressed, and fired again. The fired samples were rapidly cooled by quenching in air.

Chemical analysis by the alcohol-glycerate method showed that, after firing under the indicated regime, samples with 5 and 7.5% $3SrO \cdot SiO_2$ contained no calcium oxide unbound in silicate. A sample with 10% strontium silicate could not be obtained without free CaO even after 40-50 h exposure at 1550-1600°. Firing the samples in a microfurnace with a tungsten heater at 1700-1800° also did not lead to the desired result.

Crystallo-optical analysis was carried out in sodium light at a constant temperature (22°). The results obtained showed that samples containing 5 and 7.5% $3SrO \cdot SiO_2$ consisted of weakly birefringent grains of tricalcium silicate, having refractive indices somewhat higher than those of the pure mineral, namely: pure $3CaO \cdot SiO_2$—1.717-1.720; with 7.5% $3SrO \cdot SiO_2$—1.720-1.724.

Fig. 1. Curves of differential thermal analysis of the investigated samples

The difference in the refractive indices of pure $3CaO \cdot SiO_2$ and of the solid solution is so slight that the data of the chemical and crystallo-optical methods had to be checked by differential-thermal and X-ray analyses.

Figure 1 presents thermal curves recorded on an apparatus for micro-thermal analysis from samples of pure $3CaO \cdot SiO_2$ (curve 1), with 5 (curve 2) and 7.5% (curve 3) $3SrO \cdot SiO_2$. The lowering of the temperature of the polymorphic transformations of tricalcium silicate with the addition of $3SrO \cdot SiO_2$, in comparison with the pure mineral, may be explained by the formation of a solid solution. The relative values of the temperatures of the endothermic reactions are as follows: for pure $3CaO \cdot SiO_2$ the first transformation takes place at a temperature of approximately 900°, the second at 950°; for the solid solution with 7.5% $3SrO \cdot SiO_2$, at 850 and 920°, respectively. The results of thermal analysis for pure $3CaO \cdot SiO_2$ agree with the data ([11]), with the only difference that the transformation temperatures under our conditions proved to be somewhat lower. The occurrence of endothermic reactions is probably associated with the polymorphic transformations of tricalcium silicate ([4,11]):

$$\text{pure } 3CaO\cdot SiO_2 \text{ triclinic } \underset{\leftarrow}{\overset{900^\circ}{\rightleftarrows}} \text{ monoclinic } \underset{\leftarrow}{\overset{950^\circ}{\rightleftarrows}} \text{ trigonal.}$$

The addition of strontium ions either does not change the lattice or distorts it so insignificantly that the high-temperature transformations of the solid solution apparently have the same character as in the pure mineral; namely, the solid solution is also characterized by two polymorphic transformations.

X-ray analysis of the samples was carried out by the asymmetric method ([12]). The X-ray patterns were taken in a precision cylindrical camera. Cu$K\alpha$ radiation was used. The effect of luminescence was weakened by the use of aluminum foil. In order to obtain, where possible, sharper interference lines, a thin ⋯

the specimen was prepared by applying the sample powder to a glass fiber 0.04–0.06 mm thick. The X-ray patterns were recorded at 18–19°. The distances between interference lines were measured on an IZA-2 horizontal comparator with an accuracy of $±$0.01 mm.

Since it was not possible to obtain sharp lines in the region of large angles θ, metallic copper was photographed in this part of the X-ray pattern in order to calculate the effective film diameter.

Figure 2 (see the inset to p. 830) shows the X-ray pattern of the solid solution containing 7.5% $3SrO \cdot SiO_2$, obtained after a 55-hour exposure.

Although it was not possible to obtain sharp lines in the region of large angles θ that would have provided data of high accuracy, nevertheless in our case the accuracy attained proved quite satisfactory. The arithmetic mean error for the averaged d was $±$0.001 and was approximately the same for all the lines used.

Below are given the values* of the interplanar spacings for pure $3CaO \cdot SiO_2$ and its solid solution containing 7.5% $3SrO \cdot SiO_2$. Six of the sharpest and strongest interference lines were selected in the range of angles θ from 16.1 to 31.2°:

d_{av} of pure $3CaO \cdot SiO_2$	2.7553	2.6028	2.1807	1.7605	1.5399	1.4885
d_{av} of solid solution	2.7636	2.6120	2.1866	1.7663	1.5426	1.4893
$d\Delta$	0.0083	0.0092	0.0059	0.0058	0.0027	0.0038

Analysis of the X-ray data clearly indicates the presence of solid solutions in the system $3CaO \cdot SiO_2$–$3SrO \cdot SiO_2$ and confirms the results obtained by the crystal-optical and differential-thermal methods.

According to the experimental data, the solubility limit of tristrontium silicate in tricalcium silicate is approximately 7.5 wt.%.

On the basis of existing ideas concerning the regularities of solid-solution formation and isomorphism, it may be assumed that the example under consideration is an example of substitutional solid solutions, or solid solutions of the first kind, the ions substituting for one another having the same valence. The case of isovalent isomorphism of the ion pair $Ca^{2+} \rightleftarrows Sr^{2+}$ has been very little studied and is of great interest for the crystal chemistry of silicates and the theory of solid solutions.

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* The mean values of measurements of four films of samples from two syntheses are given.

Note: Figure translations are in progress. See original paper for figures.

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