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Abstract

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SOLID SOLUTIONS OF TRICALCIUM SILICATE WITH YTTRIUM OXYORTHOSILICATE

Among the little-studied properties of the basic cement mineral–tricalcium silicate–is its interaction with other components, its capacity to form solid solutions. Solving these questions is of primary importance for elucidating the crystal-chemical features of the structure and the complex polymorphism of $3CaO \cdot SiO_2$. Data on the mutual solubility of tricalcium silicate with certain substances are given in (1).

Our study is devoted to the investigation of the formation of solid solutions between this mineral and yttrium oxyorthosilicate. The choice of yttrium silicate is not accidental. It is known that, among divalent cations, calcium is closest to yttrium in ionic-radius size $\left(Ca^{2+}\ 0.99\ \text{Å},\ Y^{3+}\ 0.93\ \text{Å},\ \text{according to Pauling}\right)$, and therefore the assumption of the possibility of broad isomorphism between calcium and yttrium silicates is entirely justified. In addition, $3CaO \cdot SiO_2$ may be regarded as the oxyorthosilicate $Ca_3O[SiO_4]$, by analogy with yttrium oxyorthosilicate–$Y_2O[SiO_4]$. The possible structural similarity of these minerals (2) may be expressed in their ability to form solid solutions. At the same time, differences in optical properties, density, and other characteristics between $3CaO \cdot SiO_2$ and $Y_2O_3 \cdot SiO_2$ make it possible to use the latter as a distinctive crystal-chemical indicator, enabling more precise determination of the limiting concentrations of solid solutions, their mutual transitions, behavior upon heating, etc.

For the investigation, mixtures of tricalcium silicate with yttrium oxyorthosilicate were prepared, containing $Y_2O_3 \cdot SiO_2$–0.5; 1; 2····..8; 10; 12; 15 wt. %. The starting materials used were calcium carbonate ($CaCO_3$—100%), obtained by precipitation from solutions of calcium nitrate (chemically pure grade) and ammonium carbonate (chemically pure grade), rock crystal (99.9% SiO_2), and yttrium oxide (99.89% Y_2O_3).

The finely ground, thoroughly mixed batch was fired in the form of tablets at a temperature of 1400—1450°. After 2-3 firings, each lasting 3 hours, the specimens contained no free CaO (determined by the alcohol-glycerate method), which indicates completion of the reaction. By crystal-optical examination in reflected and transmitted light and by X-ray diffraction it was established that specimens with yttrium oxyorthosilicate contents up to 6–7% constituted a homogeneous phase—a solid solution. At contents of $Y_2O_3 \cdot SiO_2$ above the indicated amount, this silicate was detected as an independent phase.

These results indicate the existence of a limited series of solid solutions between $3CaO \cdot SiO_2$ and $Y_2O_3 \cdot SiO_2$. The limiting composition contains approximately 5 wt. % Y_2O_3. However, a detailed analysis of the data obtained by crystal-optical, X-ray diffraction, and differential-thermal methods revealed a very complex character of the solid solutions formed, expressed in the following.

1. Crystallo-optically, an unexpected phenomenon was found—the presence in all samples, along with the main phase, of weakly birefringent grains of a solid-solution phase with a bright-yellow interference color—β-$2CaO \cdot SiO_2$ and a little γ-$2CaO \cdot SiO_2$. It was noted that the amount of the β- and γ-forms increased from sample to sample as the addition of $Y_2O_3 \cdot SiO_2$ was increased and reached a maximum value of 10–15%. Repeated syntheses and chemical analysis revealed no error in the preparation of the starting mixtures. The reason for this phenomenon, in our opinion, was that, owing to the presence in the structure of tricalcium silicate of interstices equal in size and number to those occupied by calcium atoms (3), the possibility is created for the incorporation of calcium oxide in excess of the stoichiometry of the compound $3CaO \cdot SiO_2$. In addition, isomorphous substitution in the solid solutions under consideration proceeds according to the scheme $3Ca^{2+} \leftrightarrow 2Y^{3+}$. Since three calcium ions are replaced by two yttrium ions of equal size, additional vacancies arise in the structure, in addition to those already present, which facilitates the incorporation of foreign atoms.

Let us assume, first, that if calcium oxide is added to the preparations under consideration, which contain the β- and γ-forms of dicalcium silicate, in an amount calculated to saturate them to tricalcium silicate, then in these samples an excess of CaO is possible in comparison with the stoichiometric ratio of oxides in tricalcium silicate. Secondly, the more $Y_2O_3 \cdot SiO_2$ the solid solution contains, the greater this excess should be.

And indeed, chemical analysis* (see Table 1) confirms these assumptions and shows that the excess CaO increases from 0.5 wt.% in pure $3CaO \cdot SiO_2$ to 2.5–3.0 wt.% in the solid solution. The accuracy of oxide determination is: CaO $±$0.3%; SiO_2 $±$0.2%; Y_2O_3 $±$0.2%.

Fig. 1. X-ray diffraction patterns of samples in the angular region $2\theta = 51$–$52°$: 1—pure $3CaO \cdot SiO_2$, 2—with 8% $Y_2O_3 \cdot SiO_2$, 3—with 12% $Y_2O_3 \cdot SiO_2$

Table 1

No.	Initial compositions of samples*	Chemical analysis, wt.% CaO	Chemical analysis, wt.% SiO_2	Chemical analysis, wt.% Y_2O_3	Chemical analysis, wt.% i.l.	Chemical analysis, wt.% Σ	Data after recalculation to ignited substance, wt.% CaO	Data after recalculation to ignited substance, wt.% SiO_2	Data after recalculation to ignited substance, wt.% Y_2O_3	Data after recalculation to ignited substance, wt.% Σ	CaO : SiO_2 in the silicate of calcium	Excess CaO relative to stoichiometry, wt.%
1	3CaO SiO_2	73.28	25.98	–	0.89	100.15	73.83	26.17	–	100.0	3.02 : 1	0.50
2	3CaO SiO_2	73.63	26.10	–	0.37	100.10	73.83	26.17	–	100.0	3.02 : 1	0.50
3	93% $3CaO\cdot SiO_2$ 7% $Y_2O_3\cdot SiO_2$	68.89	25.61	5.39	–	99.89	68.96	25.64	5.40	100.0	3.05 : 1	1.20
4	92% $3CaO\cdot SiO_2$ 8% $Y_2O_3\cdot SiO_2$	67.61	25.58	6.55	0.37	100.11	67.79	25.64	6.57	100.0	3.04 : 1	0.97
5	92% $3CaO\cdot SiO_2$ 8% $Y_2O_3\cdot SiO_2$	67.52	25.49	6.41	1.06	100.48	67.90	25.65	6.45	100.0	3.04 : 1	0.97
6	90% $3CaO\cdot SiO_2$ 10% $Y_2O_3\cdot SiO_2$	67.23	25.01	7.55	0.58	100.37	67.37	25.06	7.57	100.0	3.13 : 1	3.09
7	90% $3CaO\cdot SiO_2$ 10% $Y_2O_3\cdot SiO_2$	66.79	24.99	7.80	0.23	99.81	67.07	25.10	7.83	100.0	3.12 : 1	2.86

Fig. 2. Infrared absorption spectra of pure $3CaO \cdot SiO_2$ and solid solutions

Figure 1: Fig. 2. Infrared absorption spectra of pure $3CaO \cdot SiO_2$ and solid solutions

* Calcium oxide was additionally introduced into all samples.

* The chemical analysis was performed by F. N. Smelovskaya in the analytical laboratory of the Institute.

2. It was shown crystallo-optically that the light refraction of the solid solutions changes only slightly, namely from 1.720–1.717 for pure $3CaO \cdot SiO_2$ to 1.726–1.722 for solid solutions with a content of $Y_2O_3 \cdot SiO_2$ of 6–7%. We accepted this preparation as the limiting solid solution. Addition of a larger amount of $Y_2O_3 \cdot SiO_2$ led to its appearance in the free state. However, analysis of the solid solutions in these heterogeneous specimens showed that their light refraction increases up to a content of yttrium oxyorthosilicate equal to 12%, and reaches the value 1.730–1.726.

Thus, the homogeneity of a specimen is not yet a criterion that the limiting composition of the solid solution has been reached. An increase in the concentration of the solid solution also occurs beyond the limits of phase homogeneity, which is probably connected with the difficulty of attaining equilibrium in this system. We encountered a similar phenomenon also in studying solid solutions of calcium alumoferrites (^{4}).

3. The X-ray investigation was carried out on the basis of intensity ionization curves obtained with a URS50I apparatus. Owing to the closeness of the values of the ionic radii of calcium and yttrium, one could hardly expect a noticeable displacement of the positions of the maxima. Nevertheless, the X-ray diffraction patterns of the solid solutions differed substantially from the X-ray diffraction patterns of pure $3CaO \cdot SiO_2$. The triplet lines characteristic of tricalcium silicate in the angular ranges 2θ—31–32°, 51–52°, 62–63°, degenerated on the X-ray diffraction patterns of the solid solutions into single lines. Fig. 1 demonstrates the change of the triplet line of the pure mineral, located in the angular range 2θ—51–52°, into a single line in the solid solution.

Fig. 2. Infrared absorption spectra of pure $3CaO \cdot SiO_2$ and solid solutions

Although there are no direct experimental data, by analogy with solid solutions of $3CaO \cdot SiO_2$ with Na_2O (^{5}) and $3CaO \cdot SiO_2$ with MgO and Al_2O_3 (^{6}), studied by other authors, the change in the configuration of the maxima is apparently connected with the transformation of the triclinic lattice of pure $3CaO \cdot SiO_2$ into a monoclinic one in the solid solutions.

Infrared absorption spectra taken in the wavelength region from 800 to 1100 cm^{-1} (Fig. 2) show that the strong bands characteristic of the pure silicate considerably decrease in intensity in the solid solutions and, as the content of yttrium oxyorthosilicate increases, become broadened. The authors express their gratitude to G. P. Stavitskaya, who obtained the spectra of the substances studied.

4. The distinctive character of the solid solutions was shown by the results of differential thermal analysis. In the study of quenched specimens, the presence of yttrium oxyorthosilicate not only lowers the temperature of the polymorphic transformations of the pure mineral, but possibly also changes its syngony. Both phenomena depend on the concentration of $Y_2O_3 \cdot SiO_2$. Addition of this silicate up to 3% (Fig. 3A) lowers the temperature of the polymorphic transformations, but has no effect on the polymorphism of the solid solutions, i.e., in the temperature range 900–1000° the same two polymorphic transformations are observed as in pure $3CaO \cdot SiO_2$:

$$\text{triclinic} \xrightleftharpoons{\sim 920^\circ} \text{monoclinic} \xrightleftharpoons{\sim 970^\circ} \text{trigonal.}$$

However, the lowering of the tempe-

the temperature of the second polymorphic transformation occurs more intensively than that of the first (Fig. 3A). As a result, the temperature interval between the two transformations narrows, and at a concentration of $Y_2O_3 \cdot SiO_2$ in the solid solution of 4-5% and higher, the two endothermic arrests merge.

Fig. 3. DTA curves: **A**—of quenched specimens, **B**—of annealed specimens: 1—pure $3CaO \cdot SiO_2$, 2—with 3% $Y_2O_3 \cdot SiO_2$, 3—with 4% $Y_2O_3 \cdot SiO_2$, 4—with 5% $Y_2O_3 \cdot SiO_2$, 5—with 6% $Y_2O_3 \cdot SiO_2$, 6—with 10% $Y_2O_3 \cdot SiO_2$, 7—with 12% $Y_2O_3 \cdot SiO_2$.

The differential thermal curves of the annealed preparations (Fig. 3B) show that, at a concentration of yttrium oxyorthosilicate of 5% and higher, two endothermic arrests again appear on the thermogram. Solid solutions with a $Y_2O_3 \cdot SiO_2$ content up to 4% behave during annealing analogously to the quenched specimens. Apparently, the lattice of tricalcium silicate, accommodating this amount of oxyorthosilicate, remains stable. This is probably connected with the structural features of tricalcium silicate.

On the thermograms of some specimens, an endothermic reaction at a temperature of about 800° is noteworthy; we explain it by the presence of an impurity of γ-$2CaO \cdot SiO_2$.

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