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Abstract

Full Text

SILICATES OF RARE-EARTH ELEMENTS AS CRYSTAL-CHEMICAL INDICATORS

SOLID SOLUTIONS OF TRICALCIUM SILICATE WITH LANTHANUM OXYORTHOSILICATE

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The study of solid solutions of one of the principal cement minerals—tricalcium silicate—with other compounds reveals, to a certain extent, the crystal-chemical features of its structure. Some information on this question is presented in ([1–3]).

Isomorphism between calcium and rare-earth elements, as well as yttrium, in natural minerals (loparite, apatite, eudialyte, rinkolite, etc. ([4])) is very widespread. In synthetic silicate minerals, however, isomorphism between calcium and rare-earth elements began to be studied comparatively recently, together with the development of the chemistry of rare-earth silicates. The study of the properties of yttrium and rare-earth silicates has shown that they can be used as distinctive crystal-chemical indicators, making it possible to reveal clearly important properties of another substance and its solid solutions. Thus, in ([4]) it was shown that, in the formation of solid solutions of $3CaO \cdot SiO_2$ with $Y_2O_3 \cdot SiO_2$, owing to the incorporation of yttrium ions into the lattice of tricalcium silicate, certain features of $3CaO \cdot SiO_2$ and its solid solutions were most clearly manifested, namely: variations in CaO content, complex polymorphism, change of crystal system, limiting concentrations of solid solutions, etc.

We studied solid solutions of tricalcium silicate with lanthanum oxyorthosilicate. The closeness of the ionic radii of Ca^{2+} and La^{3+} (0.99 and 1.14 Å, respectively, according to Ahrens), as well as the possible structural similarity of these compounds, which belong to the oxyortho type, may promote the formation of solid solutions between these minerals. Mixtures of tricalcium silicate with lanthanum oxyorthosilicate were investigated with a content of the latter from 1 to 25 wt.%.

For the synthesis of the investigated preparations, the starting substances were carefully prepared: $CaCO_3$ was obtained by precipitation from solutions of calcium nitrate and ammonium carbonate; SiO_2 was used in the form of finely powdered rock crystal, purified of iron impurities by boiling in hydrochloric acid. Samples pressed in the form of tablets were fired 2–3 times at 1400–1450° until complete binding of calcium oxide. The content of free CaO was determined by the alcohol-glycerate method.

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Fig. 1. DTA curves

Figure 1: Fig. 1. DTA curves

Crystallo-optical, X-ray diffraction, differential-thermal, and chemical methods revealed the distinctive character of the solid solutions formed, similar to those in the system $3CaO \cdot SiO_2$—$Y_2O_3 \cdot SiO_2$ (^{5}).

Crystallo-optically, in transmitted and reflected light, it was found that lanthanum oxyorthosilicate as an independent phase appears in samples containing more than 5 wt.% $La_2O_3 \cdot SiO_2$. From this it may be assumed that the limiting composition of the solid solution contains 5 wt.% $La_2O_3 \cdot SiO_2$. However, in studying crystals of solid solutions in preparations with a larger amount of $La_2O_3 \cdot SiO_2$, it was found that their mean refractive index continues to increase from 1.72 for $3CaO \cdot SiO_2$ to 1.726 for the solid···

solution with 5 wt.% $La_2O_3 \cdot SiO_2$ to 1.732 for crystals of the solid solution in the specimen with a total $La_2O_3 \cdot SiO_2$ content of 12 wt.%. This phenomenon indicates that saturation of the solid solution with lanthanum oxyorthosilicate also occurs beyond the limits of phase homogeneity, and that the limiting composition of the solid solution contains somewhat more than 5 wt.% $La_2O_3 \cdot SiO_2$. The slow saturation of the solid solution with lanthanum oxyorthosilicate is apparently connected with the difficulty of attaining equilibrium in this system.

Fig. 1. DTA curves. **A**—quenched specimens; **B**—annealed specimens: 1—pure $3CaO \cdot SiO_2$; 2—with 2% $La_2O_3 \cdot SiO_2$; 3—with 3% $La_2O_3 \cdot SiO_2$; 4—with 5% $La_2O_3 \cdot SiO_2$; 5—with 7% $La_2O_3 \cdot SiO_2$; 6—with 12% $La_2O_3 \cdot SiO_2$; 7—with 15% $La_2O_3 \cdot SiO_2$.

Crystal-optical study revealed yet another feature of the solid solutions in the system under investigation, one that we had previously found also in the system $3CaO \cdot SiO_2$–$Y_2O_3 \cdot SiO_2$. All specimens contained, along with the principal phase—the solid solution—also β-$2CaO \cdot SiO_2$ and a certain amount of γ-$2CaO \cdot SiO_2$. The amount of dicalcium silicate increased from specimen to specimen as the addition of $La_2O_3 \cdot SiO_2$ increased. The formation of $2CaO \cdot SiO_2$ is apparently caused by the fact that the vacancies in the structure of $3CaO \cdot SiO_2$ (6), equal in size to calcium atoms and equal to them in number, may be occupied by particles of equal volume. In the present case these vacancies are occupied by calcium. This, on the one hand, creates the possibility of obtaining a silicate with a $CaO : SiO_2$ ratio greater than $3 : 1$, and, on the other hand, explains the reason for the appearance of dicalcium silicate. In addition, an additional possibility is created for the incorporation of calcium into the lattice. Indeed, with the isomorphous substitution $3Ca^{2+} \rightleftarrows 2La^{3+}$, i.e., when the places of three particles are occupied by two particles of equal volume, both the number of vacancies and their sizes increase. It follows from this that the more lanthanum there is in the solid solution, the more calcium there should also be in comparison with the stoichiometry of the $3 : 1$ compound. The solubility limit of CaO in the solid solution is higher than in pure $3CaO \cdot SiO_2$. To verify this proposition, calcium oxide was additionally introduced into the specimens in order to saturate $2CaO \cdot SiO_2$ up to $3CaO \cdot SiO_2$. The chemical-analysis data for these specimens, presented in Table 1, show that the excess of CaO in the solid solution reaches 3–4 wt.% in comparison with the stoichiometry of the 3 : 1 silicate.

Table 1

No.	Initial compositions of samples*	CaO	SiO_2	La_2O_3	l.o.i.	Σ	Amount of unbound CaO, wt. %	CaO : SiO_2 in calcium silicate	Excess CaO relative to stoichiometry, wt. %
1	$3CaO \cdot SiO_2$	73.35	25.50	–	0.94	99.79	0.9	3.04 : 1	0.97
2	97% $3CaO \cdot SiO_2$ 3% $La_2O_3 \cdot SiO_2$	72.14	25.60	2.10	0.46	100.30	–	3.07 : 1	1.68
3	97% $3CaO \cdot SiO_2$ 3% $La_2O_3 \cdot SiO_2$	71.48	24.79	2.03	1.91	100.21	1.0	3.09 : 1	2.16
4	96% $3CaO \cdot SiO_2$ 4% $La_2O_3 \cdot SiO_2$	72.02	24.92	2.60	0.77	100.31	0.5	3.13 : 1	3.09
5	96% $3CaO \cdot SiO_2$ 4% $La_2O_3 \cdot SiO_2$	71.38	24.95	2.78	1.12	100.23	0.65	3.10 : 1	2.39
6	95% $3CaO \cdot SiO_2$ 5% $La_2O_3 \cdot SiO_2$	70.62	24.55	3.88	1.25	100.30	–	3.17 : 1	4.00

Fig. 2 and Fig. 3: ionization intensity curves

Figure 2: Fig. 2 and Fig. 3: ionization intensity curves

No.	Initial compositions of samples*	CaO	SiO_2	La_2O_3	l.o.i.	Σ	Amount of unbound CaO, wt. %	CaO : SiO_2 in calcium silicate	Excess CaO relative to stoichiometry, wt. %
7	92% $3CaO \cdot SiO_2$ 8% $La_2O_3 \cdot SiO_2$	69.62	24.55	5.03	0.79	99.99	–	3.16 : 1	3.78

* Calcium oxide was additionally introduced into all samples.

The formation of solid solutions in this system proceeds in a complex manner. Apparently, one may speak here of the simultaneous formation of both substitutional and interstitial solid solutions.

Fig. 2. Ionization intensity curves: 1 –pure $3CaO \cdot SiO_2$, 2 –with 2% $La_2O_3 \cdot SiO_2$, 3 –with 4% $La_2O_3 \cdot SiO_2$, 4 –with 8% $La_2O_3 \cdot SiO_2$, 5 –with 15% $La_2O_3 \cdot SiO_2$, 6 –with 25% $La_2O_3 \cdot SiO_2$.

Fig. 3. Ionization intensity curves of a hardened (1) and annealed (2) sample with 5 wt. % $La_2O_3 \cdot SiO_2$.

It is known that in complex systems such cases may occur ([7]). The components of the solid solutions in our case are $3CaO \cdot SiO_2$, $La_2O_3 \cdot SiO_2$, and CaO. In the structure of the solid solutions, in all probability, there are calcium ions playing different roles: some of the calcium ions are located in the lattice of the solid solutions, filling voids, while some are capable of being replaced by lanthanum.

Further, according to differential thermal analysis (DTA) data, the solid solutions studied possess complex polymorphism (Fig. 1). As is seen from the figure, the formation of polymorphic forms depends on the concentration of $La_2O_3 \cdot SiO_2$ in the solid solution and on the regime of preliminary heat treatment of the specimens. Preparations containing up to 2 wt.% $La_2O_3 \cdot SiO_2$ in the solid solution are characterized by the same two polymorphic transformations in the temperature range 800-1000° as $3CaO \cdot SiO_2$ without additions. The temperatures of the polymorphic transformations of the solid solutions are somewhat lower. Heat treatment has the strongest effect on specimens containing three or more percent $La_2O_3 \cdot SiO_2$. For example, quenched preparations of such composition exhibit three sharply pronounced endothermic effects. This state of the solid solutions is unstable and is probably explained by features of their structure; annealing leads to the fact that, in the temperature interval under consideration, the specimens display the same two sharply pronounced polymorphic transformations as pure $3CaO \cdot SiO_2$ and also its solid solutions containing up to 2 wt.% $La_2O_3 \cdot SiO_2$. We consider the latter state of the solid solutions, in which two polymorphic transformations are observed in the temperature interval 800–1000°, to be the equilibrium state, since a change in the annealing regime (a decrease in the cooling rate) does not change the form of the DTA curves.

Finally, the distinctive character of the solid solutions was also manifested in their X-ray study. On the X-ray diagrams (ionization intensity curves) there was observed not only a shift of the maxima, but also a change in the very form of the curves (Fig. 2). Indeed, the triplet lines characteristic of $3CaO \cdot SiO_2$, especially in the angular ranges 20–51–52° and 61–63°, with increasing concentration of $La_2O_3 \cdot SiO_2$ in the solid solution become singlets. This fact may indicate an increase in the syngony of the solid solutions in comparison with pure $3CaO \cdot SiO_2$. Such a picture occurs in quenched specimens; annealed specimens behave differently. As an example, Fig. 3 presents the curve of a specimen with 5 wt.% $La_2O_3 \cdot SiO_2$: the singlet lines in the angular ranges 20–51–52° and 61–63° have split into triplets.

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