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Abstract

Full Text

CHEMISTRY

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SOLID SOLUTIONS IN THE SYSTEM Ca_2SiO_4 –Ca_2GeO_4

The crystal-chemical similarity between calcium orthosilicate and orthogermanate was established by Shtrunts and Jakob (*1*). A further analogy with respect to the physicochemical properties of these compounds, and also between Ca_3SiO_5 and Ca_3GeO_5, was revealed in (*2, 3*). Therefore, a physicochemical investigation of calcium germanates as analogues of calcium silicates is of interest for the chemistry of cements, refractories, etc.

Dicalcium germanate, according to (*3*), crystallizes in two polymorphic forms. The low-temperature variety of Ca_2GeO_4 has an olivine-type structure (*1*) and will hereafter be denoted by us as l.t. (low-temperature) Ca_2GeO_4. The high-temperature form of Ca_2GeO_4 is stable above 1450° and, according to X-ray analysis (the most characteristic lines: 3.27, 2.94, 2.82, 2.71, 2.17, 1.97, 1.73, 1.60, 1.57, 1.49), is completely identical with α-Ca_2SiO_4. Hence one may expect the existence of isomorphism between dicalcium silicate and dicalcium germanate. The study of this question is of interest in light of the elucidation of anionic isomorphism for Ca_2SiO_4, on which only limited data are available in the literature (*4-8*). For this purpose we studied solid solutions between dicalcium silicate and dicalcium germanate.

Fig. 1. Dependence of the birefringence for annealed specimens in the system Ca_2SiO_4–Ca_2GeO_4 on their composition.

To study the phase equilibrium of the system, 23 compositions were prepared. The starting materials used for preparing the mixtures were $CaCO_3$ (chemically pure), crystalline SiO_2 (99.9%), and amorphous GeO_2 (99.9%) in one series of experiments, and γ-Ca_2SiO_4 and l.t. Ca_2GeO_4 in another. It should be noted at once that the results of the experiments for both series were identical. Carefully mixed batches were pressed in the form of cylinders, and the latter were fired in a silite furnace at a temperature of about 1500°. After the first firing, mixtures

Fig. 2. X-ray patterns of solid solutions

Figure 2: Fig. 2. X-ray patterns of solid solutions

containing more than 60 mol.% and less than 40 mol.% Ca_2GeO_4 were homogeneous, while mixtures with intermediate Ca_2GeO_4 content consisted of two phases. After additional firings with intermediate grinding, homogeneity was achieved for all compositions. After firing, the specimens were cooled slowly together with the furnace; in this process all compositions containing from 0 to 42.5% Ca_2GeO_4 crumbled into powder, whereas specimens with a higher Ca_2GeO_4 content retained the shape of sintered compacts.

The synthesized products were investigated by microscopic, X-ray, and differential thermal analyses. X-ray recording was carried out on a URS-50I ionization unit using CuKα radiation at a rate of 1°/min.

As a result of the microscopic investigation, the existence of two single-phase regions was established in the system. Compositions containing from 0 to 42.5% Ca_2GeO_4 are represented by elongated, weakly birefringent

prismatic crystals with straight extinction, positive elongation, and strongly pronounced twinning along the elongation axis. Compositions with a Ca_2GeO_4 content from 43.75 to 100% were observed in the form of rounded or fragmental crystals with much higher birefringence. The change in refractive indices for the synthesized samples as a function of their composition is shown in Fig. 1. The graph shows

Fig. 2. X-ray patterns of solid solutions: **a, ,** $-\gamma$-Ca_2SiO_4 solid solution; **a**—γ-Ca_2SiO_4; —60% Ca_2SiO_4 + 40% Ca_2GeO_4; —57.5% Ca_2SiO_4 + 42.5% Ca_2GeO_4; **, ,** —low-temperature Ca_2GeO_4 solid solution; —55% Ca_2SiO_4 + 45% Ca_2GeO_4; —40% Ca_2SiO_4 + 60% Ca_2GeO_4; —low-temperature Ca_2GeO_4.

a uniform increase in the refractive indices from $n_p = 1.644$ and $n_g = 1.652$ to $n_p = 1.676$ and $n_g = 1.680$; then, after a sharp increase in birefringence, a uniform increase in n_p and n_g is again observed, from values of 1.674 and 1.692 to 1.700 and 1.734, respectively.

These data are in complete agreement with the data of X-ray phase analysis. Fig. 2 presents X-ray patterns of several compositions in the Ca_2SiO_4–Ca_2GeO_4 system. For compositions containing Ca_2GeO_4 in the range from 0 to 42.5%, the X-ray pattern of γ-Ca_2SiO_4 is retained, whereas compositions with a higher Ca_2GeO_4 content show the X-ray pattern of low-temperature Ca_2GeO_4. Because the values of the interplanar spacings for γ-Ca_2SiO_4 and low-temperature Ca_2GeO_4 are close, the transition from one crystalline form to the other is not so visually apparent, but it is quite definite, as can be seen from the sharp change in intensities of the strongest lines and from a certain general change in the character of the X-ray patterns. In the transition from γ-Ca_2SiO_4 to low-temperature Ca_2GeO_4, a uniform shift of the lines toward smaller angles is

Differential thermal curves of solid solutions in the Ca_2SiO_4–Ca_2GeO_4 system

Figure 3: Differential thermal curves of solid solutions in the Ca_2SiO_4–Ca_2GeO_4 system

observed.

Thus, on the basis of microscopic and X-ray phase analyses, the existence of two types of solid solutions has been established in the low-temperature part of the system: one solid solution based on γ-Ca_2SiO_4 within the range of Ca_2GeO_4 content from 0 to 42.5%, and a second solid solution based on low-temperature Ca_2GeO_4 when its content is from 43.75 to 100%.

High-temperature phase equilibrium was studied by means of high-temperature X-ray photography, a high-temperature microscope, and thermal analysis. The data of differential thermal analysis are presented in Fig. 3. Samples containing from 0 to 38% Ca_2GeO_4 show on the thermograms two endothermic effects, which correspond to the transition of the γ-Ca_2SiO_4 solid solution into the high-temperature α'- and α-modifications.

The region of the γ-Ca_2SiO_4 solid solution between 38.0 and 42.5% passes, on heating, directly into the α-solid solution, bypassing the α'-form. On the thermograms of samples for this part of the system, one large endothermic effect is observed.

Samples of the low-temperature Ca_2GeO_4 solid solution show one endothermic effect, corresponding to the polymorphic transformation into the high-temperature α-form of the solid solution. The characterization of the phase composition in the high-temperature part of the diagram is confirmed by high-temperature X-ray photography data.

On the basis of the data obtained, a phase diagram of the Ca_2SiO_4–Ca_2GeO_4 system was constructed, presented in Fig. 4. In the low-temperature part of the diagram there exist two solid solutions: a γ-Ca_2SiO_4 solid solution from 0 to 42.5% and a low-temperature Ca_2GeO_4 solid solution from 43.75 to 100% Ca_2GeO_4. We were unable to establish a two-phase region within the investigated compositions, although the gap between neighboring compositions of the two solid solutions was 1.25 mole %. Apparently, this region exists in a very narrow concentration interval. On the diagram this region is indicated by dashed lines.

The boundary curves between the different polymorphic forms of the solid solutions were constructed from the temperatures of the endothermic minima corresponding to the respective polymorphic transformations.

Fig. 3. Differential thermal curves of solid solutions in the Ca_2SiO_4–Ca_2GeO_4 system

The positions of the lower boundary curves were not determined, and they

Fig. 4. Phase diagram of the system Ca_2SiO_4—Ca_2GeO_4. a—compositions investigated, b—temperatures of endothermic minima, c—high-temperature X-ray photography

Figure 4: Fig. 4. Phase diagram of the system Ca_2SiO_4—Ca_2GeO_4. a—compositions investigated, b—temperatures of endothermic minima, c—high-temperature X-ray photography

are drawn hypothetically. The solubility of Ca_2GeO_4 in the α'-Ca_2SiO_4 solid solution is $\simeq 37\%$. In the high-temperature part of the diagram, a single-phase solid-solution region is realized between α-Ca_2SiO_4 and α-Ca_2GeO_4.

On cooling, both during annealing and during quenching in air, the high-temperature forms of the solid solutions transform into the low-temperature γ-Ca_2SiO_4 and Ca_2GaO_4 solid solutions. High-temperature X-ray photography made it possible to establish that, on cooling, samples with a small content of Ca_2GeO_4 (up to 15%) pass through a metastable-

···the β-Ca_2SiO_4 form of the solid solution, whereas for specimens with a higher content of Ca_2GeO_4 (up to 42.5%) the α'-Ca_2SiO_4 form of the solid solution becomes metastable.

The slope of the liquidus curve was determined from the melting temperatures of several compositions relative to the melting temperatures of the initial Ca_2SiO_4 and Ca_2GeO_4, using a high-temperature microscope. The design of the latter and the procedure for working with it are described in (9). Since direct measurement of the temperature was not carried out, the liquidus curve is drawn as a dashed line. The melting temperature of Ca_2GeO_4 is $1900 \pm 30°$.

Fig. 4. Phase diagram of the system Ca_2SiO_4—Ca_2GeO_4.
a—compositions investigated, *b*—temperatures of endothermic minima, *c*—high-temperature X-ray photography.

As a result of the study of solid solutions between Ca_2SiO_4 and Ca_2GeO_4, a phase diagram of the system Ca_2SiO_4—Ca_2GeO_4 was constructed, in which the existence of four stable and one metastable forms of solid solutions was established.

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