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Abstract

Full Text

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CALCIUM GERMANATES AND THEIR PROPERTIES

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The periodicity of binding properties in chemical compounds of the calcium silicate type, discovered by V. A. Kind and V. F. Zhuravlev ([1]), was subsequently confirmed ([2,3]) by obtaining synthetic dicalcium germanate at 1250° by the sintering method. The same compound was also obtained by Ludekens, likewise by the sintering method, but at 1100° ([4]).

It was of interest to study dicalcium germanate in greater detail and to investigate the possibility of formation of tricalcium germanate, by analogy with the most important clinker mineral—tricalcium silicate.

For the synthesis of calcium germanates, chemically pure dried calcium carbonate and germanium dioxide were used in ratios of 2 : 1 and 3 : 1. The raw mixtures were thoroughly mixed and ground in an agate mortar until they passed completely through a 4900 mesh/cm^2 sieve.

Fig. 1. Differential heating curves of dicalcium germanate (*a*) and β-dicalcium silicate (*b*)

The mixtures were moistened with 8-10% water, pressed in the form of specimens—prisms measuring $1 \times 1 \times 3$ cm^3—and fired on platinum in a silite furnace: the mixture $2CaO \cdot GeO_2$ at $t = 1400°$, and $3CaO \cdot GeO_2$ at $t = 1500°$.

The firing of the $2CaO{\cdot}GeO_2$ mixture corresponded to the regime adopted for the synthesis of the clinker mineral—belite: gradual heating to 1400° with holding at 1400° for 3 hours. After holding, the sinter was rapidly cooled by quick immersion in water or by sharp cooling in air at 0°. The cooled sinter was ground; from it small prisms were formed, which were subjected to repeated firing. This was repeated until complete binding of lime and production of a homogeneous monomineral product. The readiness of the synthesized germanates was checked by determining free calcium oxide, for which the well-known ethyl-glycerate method was used (^{5}). The total duration of firing at 1400° was 6 hours with sharp cooling by water and 9 hours with sharp cooling by air. The synthesized C_2Ge dissolved in a 5% boric acid solution by the method of E. I. Nagerova (^{6}), as does dicalcium silicate.

The dicalcium germanate obtained was subjected to microscopic (Table 1), thermographic (Fig. 1), and X-ray investigations (Fig. 2). In addition, its binding properties were studied.

Microscopic investigations show the similarity of the crystallo-optical properties of the synthesized dicalcium germanate and β-dicalcium silicate. X-ray diffraction patterns, as well as thermograms, show···

to a fairly close agreement of the interplanar spacings in dicalcium germanate and β-dicalcium silicate.

The synthesized minerals $2CaO \cdot GeO_2$ and β-$2CaO \cdot SiO_2$ were finely ground until they passed completely through a sieve of 4900 openings/cm^2, and mixed with water to obtain a plastic paste of normal consistency. The minerals set and hardened.

When a mixture of $3CaO \cdot GeO_2$ is fired, dicalcium germanate is first formed, which then, at high temperature, combines with free lime to form tricalcium germanate. Firing was carried out in a silite furnace with a slow rise in temperature to 1500° and holding at 1500° for 4 hours. The fired product was subjected to sharp air cooling. The cooled clinker was ground, formed again into prisms, and refired. The firings were repeated 3–4 times until a homogeneous product was obtained, the phase composition of which was established with the aid of a microscope. The final product was checked for the absence of free lime.

As a result of firing at 1500° for 12–16 hours, a homogeneous monomineral product corresponding to the composition $3CaO \cdot GeO_2$ was obtained; it was a fairly dense clinker of light color with a yellowish-green tint.

The results of the microscopic study are given in Table 2, from which the similarity of the crystal-optical properties of tricalcium germanate and tricalcium silicate is evident.

A repeated firing of the tricalcium germanate obtained was carried out at 1500° with slow cooling. Microscopic examination showed that under these conditions $3CaO \cdot GeO_2$ partially decomposes into $2CaO \cdot GeO_2$ and CaO, which was confirmed by the refractive indices $n_q = 1.734$; $n_p = 1.700$. The grains of dicalcium germanate obtained had hexagonal and oval forms.

Table 1

Crystal-optical characteristics of dicalcium germanate and the γ- and β-forms of dicalcium silicate

Mineral	Formula	Color	Refractive index	Birefringence	Optical characteristic, optical sign	Habit
Dicalcium germanate, sharply cooled, $t =$ 1400°	$2CaO \cdot GeO_2$ (C_2Ge)	White with a greenish tint	$n_q = 1.734 n_p = 1.700$	0.034	Biaxial, about 80°, +	Rounded or rhombic grains
Dicalcium germanate, sharply cooled in air at $t =$ 1400°	$2CaO \cdot GeO_2$ (C_2Ge)	Light with a pinkish tint	$n_q = 1.734 n_p = 1.700$	0.034	Biaxial, about 80°, +	Rounded or rhombic grains
Dicalcium germanate, obtained by V. F. Zhuravlev, $t =$ 1250°	$2CaO \cdot GeO_2$ (C_2Ge)	White with a greenish tint	$N_q = 1.734 N_o = 1.724$	-0.010	–	Rounded grains or straight-edged prisms
Dicalcium silicate, γ-form	γ-$2CaO \cdot SiO_2$ (γ-C_2S)	Light	$N_q = 1.654 N_o = 1.642$	0.012	60°, +	Prisms
Dicalcium silicate, β-form	β-$2CaO \cdot SiO_2$ (β-C_2S)	White	$N_q = 1.735 N_p = 1.717$	0.018	Biaxial, large, +	Rounded grains or rhombic prisms

γ-C_2S

β-C_2S

C_2Ge, rapid cooling with air

C_2Ge, rapid cooling with water

Fig. 2. X-ray diffraction patterns of dicalcium germanate and γ- and β-

dicalcium silicate

X-ray investigation of the synthesized $3CaO \cdot GeO_2$, using an ionization setup (Fig. 3), confirmed the formation of a mineral close to $3CaO \cdot SiO_2$, namely $3CaO \cdot GeO_2$, with the absence of the lines of CaO and SiO_2.

C_3S

C_3Ge

Fig. 3. X-ray diffraction patterns of tricalcium germanate and tricalcium silicate

Table 2

Crystallo-optical properties of tricalcium germanate and tricalcium silicate

Mineral	Formula	Color	Refractive index	Birefringence	Optical characteristic, opt. sign	Crystal structure	Habit
Tricalcium germanate, rapidly cooled in air at 0°	$3CaO \cdot GeO_2 (C_3Ge)$	Light, with a yellowish tint	$n_q = 1.759$ $n_p = 1.754$	0.005	—		
Tricalcium silicate	$3CaO \cdot SiO_2 (C_3S)$	Light, with a yellowish tint	$N_q = 1.723$ $N_p = 1.717$	0.006	Small or 0—	Hexagonal	Hexagonal prisms

In the high-temperature thermogram of tricalcium germanate (Fig. 4) one can see an endothermic effect at 456°, which is apparently explained by the loss of hydration water by the surface of CaO grains. The effect on the curve at $t = 743°$, as also for tricalcium silicate [7], is possibly connected with the transition of forms of dicalcium germanate, which is confirmed by the presence of two deep endothermic effects at 1360 and 1454°. The effect at 1000° apparently characterizes certain transformations of tricalcium germanate. The tricalcium germanate obtained, like tricalcium silicate, dissolves completely in a 5% solution of boric acid.

The synthesized mineral $3CaO \cdot GeO_2$ was finely ground until it passed completely through a sieve of 4900 openings/cm^2, and the powder was mixed with water until a paste of normal consistency was obtained. Rapid setting and hardening were observed, with the end of setting occurring after approximately 15 min.

Fig. 4. Differential heating curves of tricalcium germanate (*a*) and tricalcium silicate (*b*)

As a result of the work carried out, the existence of tricalcium germanate—an analogue of tricalcium silicate—has been experimentally confirmed; its crystalline structure has been studied, and the presence of cementing properties in it has been established.

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