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Abstract

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CRYSTALLINE PHASES OF THE SYSTEM BARIUM OXIDE–GERMANIUM DIOXIDE

Like fluoroberyllates, which in the light of V. M. Goldschmidt' s concepts are crystallochemical models of silicates, germanates likewise show a similarity of crystalline structure to silicates. However, in contrast to fluoroberyllates, germanates and silicates, owing to the closeness of their principal physical properties, form broad series of isomorphous mixtures with one another. Solid solutions based on germanates and silicates are an example of isomorphous substitutions in the anionic part of the lattice (^1, ^2).

Table 1

Compounds	BaO, wt. % theor.	BaO, wt. % exper.	GeO_2, wt. % theor.	GeO_2, wt. % exper.
$3BaO \cdot GeO_2$	81.11	80.11	18.89	19.89
$2BaO \cdot GeO_2$	74.57	73.73	25.43	26.27
$BaO \cdot GeO_2$	59.45	58.18	40.55	41.82
$BaO \cdot 4GeO_2$	26.82	26.84	73.18	73.16

The system $BaO{-}GeO_2$ may to a certain extent be regarded as an analog of the $MeO{-}SiO_2$ systems, where Me^{2+}–Ca, Sr, Ba. Therefore the study of germanates is of definite interest for silicate technology and, in particular, for the chemistry of cements and other mineral binders. At present the literature contains only fragmentary information on the syntheses and investigations of the properties of barium germanates (^{3}-6). In order to fill this existing gap, we studied the conditions of synthesis and the principal properties of germanates in the system $BaO{-}GeO_2$.

For the preparation of barium germanates the reagents used were: $BaCO_3$ (analytical grade) and GeO_2 (chemically pure grade). Samples of barium germanates, pressed in the form of tablets, were subjected to repeated firing with intermediate grinding. In all, eight compositions with different $BaO : GeO_2$ ratios were studied: 4 : 1, 3 : 1, 2 : 1, 3 : 2, 2 : 3, 1 : 2, 1 : 3, and 1 : 4. The firing temperature of samples with BaO : GeO_2 ratios of 4 : 1, 3 : 1, and 2 : 1 was raised to 1450° with a holding time of about 3 hr. Compositions with BaO : GeO_2 ratios of 3 : 2 and 2 : 3 were fired at 1200°, the 1 : 2 composition at 1150°, and the 1 : 3 and 1 : 4 compositions at 1250° and 1350°, respectively.

Table 2

Compounds	Density, g/cm^3	Refractive indices N_p	Refractive indices N_g	Refractive indices $N_g - N_p$
$3BaO \cdot GeO_2$	5.79	1.90	1.91	0.01
$2BaO \cdot GeO_2$	5.71	1.83	1.87	0.04
$BaO \cdot GeO_2$	4.73	1.678	1.726	0.048
$BaO \cdot 4GeO_2$	5.09	1.780	1.805	0.025
Quartz—GeO_2	4.28	1.705	1.724	0.019
Rutile—GeO_2	6.28	1.945	1.985	0.04

According to X-ray (at ordinary and high temperatures), crystallo-optical in immersion high-refractive-index phosphorus liquids, and differential-thermal analyses, four individual compounds of the following composition were found in the system BaO—GeO_2: $3BaO \cdot GeO_2$, $2BaO \cdot GeO_2$, $BaO \cdot GeO_2$, and $BaO \cdot 4GeO_2$. Tribarium germanate is a new chemical compound, about which there is no information in the literature. Table 1 gives the results of chemical analysis of the barium germanates; Table 2 gives the light refraction, measured with an accuracy of \$±\$0.005, and the densities of the barium germanates, determined in outgassed kerosene at 25°.

In the homologous series of barium germanates (see Table 2), the density and refractive index, beginning with the highly basic compound $3BaO \cdot GeO_2$, decrease to the metagermanate $BaO \cdot GeO_2$ and then increase again in the tetragermanate $BaO \cdot 4GeO_2$; in this, the minimum values of density and refractive index, which occur for $BaGeO_3$, correspond to the maximum birefringence of the metagermanate. Such an "anomalous" change in properties in the homologous series of barium germanates is most probably explained by the presence in $BaGe_4O_9$—the crystallochemical analogue of benitoite $BaTiSi_3O_9$—of octahedral coordination for 1/4 of the formal germanium content in the tetragermanate. This leads to densification of the $BaGe_4O_9$ structure and, correspondingly, to an increase in its density and refractive index as compared with the metagermanate. In the

Fig. 1. Thermogram of tribarium germanate $3BaO \cdot GeO_2$

Figure 1: Fig. 1. Thermogram of tribarium germanate $3BaO \cdot GeO_2$

Fig. 2. X-ray powder patterns of $3BaO \cdot GeO_2$ and of zeolite $BaO \cdot 3.5GeO_2 \cdot nH_2O$, taken with CuK$\alpha$ radiation at various temperatures

Figure 2: Fig. 2. X-ray powder patterns of $3BaO \cdot GeO_2$ and of zeolite $BaO \cdot 3.5GeO_2 \cdot nH_2O$, taken with CuK$\alpha$ radiation at various temperatures

germanates Ba_3GeO_5, Ba_2GeO_4, and $BaGeO_3$, the germanium cations occur only in tetrahedral coordination.

Fig. 1. Thermogram of tribarium germanate $3BaO \cdot GeO_2$

According to X-ray and thermal investigations, Ba_3GeO_5 is stable in the solid state in the temperature interval 20–1500°. The thermogram of Ba_3GeO_5, as is evident from Fig. 1, indicates the presence of modification transformations; this is also confirmed by X-ray patterns of tribarium germanate taken in the temperature range from room temperature to 1300°, see Fig. 2. On quenching, the high-temperature forms of Ba_3GeO_5 without addition of mineralizers are practically not preserved; the specimens disintegrate. The complexity of the scheme of modification transformations of Ba_3GeO_5 requires an independent study of its P–T diagram, of the structures of the polymorphic varieties, and also of the influence of mineralizers on the stabilization of the individual forms of Ba_3GeO_5.

Fig. 2. X-ray powder patterns of $3BaO \cdot GeO_2$ and of zeolite $BaO \cdot 3.5GeO_2 \cdot nH_2O$, taken with CuK$\alpha$ radiation at various temperatures

Barium orthogermanate Ba_2GeO_4, according to X-ray and thermal investigations, shows no modification transformations up to 1300°.

Barium metagermanate $BaGeO_3$ crystallizes in two polymorphic varieties: pyroxenoid–with a chain germanate-oxygen radical, and pseudowollastonite–with a ring radical ([3],[6]). In our investigation, in synthesis in the solid phase, chain $BaGeO_3$ was obtained; it showed no modification transformations up to 1100°.

In contrast to the BaO—SiO_2 system ([7],[8]), in which the individual compounds $2BaO \cdot 3SiO_2$ and $BaO_2 \cdot 2SiO_2$ exist, in the BaO—GeO_2 system no germanates with a similar stoichiometric composition were found. At the same time, in the BaO—GeO_2 system $BaO \cdot 4GeO_2$ was obtained, which has no stoichiometric analogue in the silicate system. Barium tetragermanate shows no polymorphism up to its melting point, 1390°.

In accordance with the procedure described in work ([9]), we synthesized a barium-germanate zeolite of composition $BaO \cdot 3.5GeO_2 \cdot nH_2O$, which in the pro-

during heating undergoes a series of endothermic structural transformations caused by dehydration of the zeolite. At a temperature of about 700° barium

Fig. 3

Figure 3: Fig. 3

tetragermanate is formed from the dehydrated product of zeolite composition; in this case the reaction proceeds with a very large exothermic effect. Fig. 2 gives X-ray powder photographs of the zeolite obtained during its heating; the X-ray photograph at 760° corresponds to $BaO \cdot 4GeO_2$—the final member of the modification series of transformations of the zeolite.

Fig. 3. X-ray powder line diagrams of crystalline phases of the BaO—GeO_2 system:
$3BaO \cdot GeO_2$, $2BaO \cdot GeO_2$, $BaO \cdot GeO_2$, and $BaO \cdot 4GeO_2$.

For a more complete characterization of the synthesized germanates, Fig. 3 gives X-ray powder line diagrams (with values of interplanar spacings) of the low-temperature form Ba_3GeO_5, Ba_2GeO_5, chain $BaGeO_3$, and $BaGe_4O_9$.

In conclusion, we note that among the synthesized germanates the triebarium germanate Ba_3GeO_5 is of the greatest interest—a crystal-chemical analogue of the principal product of cement clinker, Ca_3SiO_5. Investigation of the structure of the polymorphic varieties of Ba_3GeO_5 and of its hydraulic activity is of great importance for solving many problems in the physical chemistry of cement silicates.

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