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R. G. GREBENSHCHIKOV and N. A. TOROPOV

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R. G. GREBENSHCHIKOV and N. A. TOROPOV

PHASE DIAGRAM OF THE SYSTEM BaO–SiO_2 IN THE REGION OF ELEVATED SILICA CONTENT

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The system BaO–SiO_2, studied as early as 1922 by P. Eskola ([1]), is important for silicate technology. At present it has entered, without changes, into many ternary systems: Li_2O, CaO, B_2O_3, Al_2O_3/SiO_2–BaO ([2], [3]). Contradictions in the proposed versions of the equilibrium relations of the components in the $Ba_2Si_3O_8$–$BaSi_2O_5$ region of the barium oxide–silica system required further study of this region. Among systems $Me^{2+}O$–SiO_2, only in the case of BaO–SiO_2 have compounds of the stoichiometry $2MeO \cdot 3SiO_2$ and $MeO \cdot 2SiO_2$ been found: dibarium trisilicate $Ba_2Si_3O_8$ (B_2S_3) and barium disilicate $BaSi_2O_5$ (BS_2). On the basis of a crystal-optical study, P. Eskola represented the solid-phase relations of the components in the B_2S_3–BS_2 region as involving the formation of continuous solid solutions. Simultaneously with our study of the B_2S_3–BS_2 region, an analogous investigation by R. Roth and E. Levin ([4]) refuted the existence of solid solutions; instead, in this interval two new compounds were found: $5BaO \cdot 8SiO_2$ (B_5S_8)—congruently melting, and $3BaO \cdot 5SiO_2$ (B_3S_5)—incongruently melting, with closely similar refractive-index values.

The solution of the question of the nature of the phases in the B_2S_3–BS_2 region was facilitated by our obtaining a number of data on the structures of $BaSiO_3$, $Ba_2Si_3O_8$, and $BaSi_2O_5$ ([5]-[8]). In our work ([8]), on the basis of X-ray, spectroscopic, and crystallochemical investigations of BS, B_2S_3, and BS_2, it was shown that the structures of B_2S_3 and BS_2 can be derived by condensation of the chains $[Si_2O_6]^{4-}_{\infty}$—an element of the structure of barium metasilicate: 1) into triple chains (ribbons) with an anionic radical $3 \times [Si_2O_6]^{4-}_{\infty} - 2O = [Si_6O_{16}]^{8-}_{\infty}$ —for B_2S_3* and 2) into layers with the radical $[Si_4O_{10}]^{4-}$—for BS_2 (sanbornite). In the lattices of BS, B_2S_3, and BS_2 one of the parameters, 4.6 kX, corresponding to the repeat period of the metasilicate chain $[Si_2O_6]^{4-}_{\infty}$, remains unchanged upon condensation of the chains in the structures of B_2S_3 and BS_2.

For constructing the BaO–SiO_2 diagram in the composition interval from 58 to 67 mol.% SiO_2, B_2S_3 and BS_2 were synthesized from starting $BaCO_3$ (analytical grade) and amorphous silica (chemically pure) by repeated firing (not fewer

Figure 1

Figure 1: Figure 1

than three times) at 1400° (the holding time at the maximum temperature was 5-6 hr), with intermediate grinding. The homogeneity of the finished fired products B_2S_3 and BS_2 was checked in each case microscopically. Compositions corresponding to the proposed compounds B_5S_8 and B_3S_5 were obtained in two ways: from starting $BaCO_3$ and amorphous silica, and from the finished B_2S_3 and BS_2. The identity of each of these products, obtained by different—by methods that confirmed this, by X-ray diffraction and crystal-optical methods. In the concentration range studied, six compositions were prepared from the starting materials BS_2 and $BaCO_3$:

$$Ba_2Si_4O_{10} + 2/15,\ 4/15,\ 6/15,\ 8/15,\ 10/15 \text{ (corresponds to } B_2S_3)$$

and 12/15 mol.% BaO. These compositions were fired twice, with intermediate grinding, at temperatures close to the onset of melting of the samples.

Characterization of the phase composition of the samples was carried out by X-ray structural and crystal-optical analysis. All samples were recorded in VRS-3 cameras using MoK_α radiation and on an ionization apparatus in the temperature range 20—1400° using CuK_α radiation. The optical study was carried out in monochromatic light of the sodium *D*-line.

Fig. 1. Dependence of the refractive index of barium silicates on composition in the range 58.5—66.67 mol.% SiO_2. **1** —solid lines —our data; **2** —points *a* —data (^{1}); **3** —points *b* correspond to the refractive indices of B_5S_8 and B_3S_5 according to (^{4}).

The solid-phase equilibrium data for annealed samples (under normal conditions) in the concentration range from $\simeq$ 58.5 to 66.67 mol.% SiO_2 are illustrated by the graph shown in Fig. 1, giving the change in refractive indices N_g^D and N_p^D as a function of their composition. For samples of composition $\simeq 58.5$ —62.5%, a smooth change in refractive index is observed from $N_g^D = 1.650$ and $N_p^D = 1.630$ to $N_g^D = 1.631$ and $N_p^D = 1.612$, respectively. Under the microscope, the phases of variable composition are represented by a homogeneous product in the form of birefringent needles with straight extinction (in some cases oblique extinction with an angle up to 5° was observed), distinct cleavage along the elongation axis of the crystallites, and (—) elongation. In samples of composition 62.5—66.67%, two phases were observed: a solid solution B_2S_3

* Needle-shaped single crystals of B_2S_3 were obtained by prolonged crystallization from a melt. From X-ray photographs of B_2S_3 rotation about the MoKα needle axis, the identity period 4.76 kX was calculated, which corresponds to the repeat period of the silicic-acid ribbon in the B_2S_3 lattice.

Figure 2

Figure 2: Figure 2

of limiting composition with stoichiometry close to B_3S_5, and barium disilicate BS_2. Therefore, for these compositions the change in the upper refractive index is expressed by a straight line parallel to the abscissa axis, with constant $N_g^D = 1.631$, corresponding to the solid solution.

Fig. 2. Phase diagram of the BaO–SiO_2 system in the composition range 58–68 mol.% SiO_2.

The value of the lower refractive index in this concentration range also retains the constant value $N_p^D = 1.596$, corresponding to BS_2. A sharp change in birefringence (Fig. 1) at the composition boundary 62.5% was also observed by P. Eskola; however, he did not interpret it as being associated with the appearance of two phases in this range.

The phase diagram of the BaO–SiO_2 system shown in Fig. 2 const-

constructed chiefly on the basis of a comprehensive study of the relationships of the components in the solid phase. The use of classical methods of physicochemical analysis, based on study of the character of the liquidus curve (its breaks), in the present case could not be considered justified for the following reasons: the close melting temperatures of B_2S_3 (1447°) and BS_2 (1420°) and the narrow range of variation of SiO_2 concentrations in the presence of phases of variable composition, with their inevitable structural zonality, complicated the experiment and could not guarantee the attainment of equilibrium crystallization of phases from the melt over short intervals of time. The latter was a necessary condition for maintaining the constancy of the composition of the samples. Therefore the firing of the samples was carried out in the subsolidus region at temperatures close to the boundary lines of the solidus.

In the investigated interval of the system, the maximum on the liquidus curve at 1447° corresponds to the compound B_2S_3. The region of phases of variable composition formed on the basis of B_2S_3 extends from $\simeq 58.5$ to 62.5 mol. %. Annealing of B_2S_3 samples with an elevated BaO content in the composition range $\simeq 58.5$–60.0 mol. % SiO_2 at 1300° lowers the solubility of BaO in B_2S_3, which is shown on the diagram by the slope of the solubility boundary of BaO. The solubility of BS_2 in B_2S_3 is limited to 62.5 mol. % SiO_2. Two polymorphic modifications were found for barium disilicate: the low-temperature form β-BS_2, stable under normal conditions and identical with the natural mineral sanbornite; at 1350° β-BS_2 transforms into the high-temperature form α-BS_2, stable up to 1420° (melting). On the diagram the boundary line at 1350° separates the stability fields of β- and α-BS_2. The solubility of BaO in α-BS_2 increases with increasing temperature, reaching a limit at the temperature of the peritectic reaction (1425°). In the low-temperature form β-BS_2, BaO is practically insoluble.

Schematic X-ray powder patterns

Figure 3: Schematic X-ray powder patterns

Simultaneous holding at 1415°, i.e., somewhat below the melting of barium disilicate, of samples BS_2 and $B_2S_4 + 2/15,\ 4/15,\ \ldots\ 12/15$ mol. % BaO (previously fired twice) was not accompanied by their melting, whereas raising the temperature by $\simeq 10°$ caused considerable melting of BS_2, $B_2S_4 + 2/15$ mol. % BaO (65.2 mol. % SiO_2), and $B_2S_4 + 4/15$ mol. % BaO (63.8 mol. % SiO_2), and only slight melting of the sample $B_2S_4 + 6/15$ mol. % BaO (62.45 mol. % SiO_2). The melting of the indicated samples, proceeding from the established equilibrium in the solid phase, can be associated only with the peritectic reaction $B_2S_{3\,\mathrm{tr}} \rightleftarrows BS_{2\,\mathrm{tr}} + \mathrm{liq.}$, to which the boundary line at 1425° corresponds on the diagram.

It should be noted that a certain uncertainty in the question of the structure of the phases of variable composition B_2S_3 does not at present make it possible to assert unambiguously the continuity of the change in composition of B_2S_3 in the interval $\simeq 58.5$–62.5%. The similarity of the crystal structure of B_2S_3 and its solid solutions follows from the similarity of the X-ray diffraction patterns shown in Fig. 3. At the same time, the differing change in interplanar spacings of identical reflections is caused by different changes in the three parameters of the rhombic solid solutions of B_2S_3 as a function of composition. X-ray ionization powder patterns of the solid solutions of B_2S_3 and BS_2 show a considerable difference between them.

The formation of the numerous group of barium silicates and, in particular, B_2S_3—the sole representative of such stoichiometry among the silicates of alkali and alkaline-earth metals—is explained by the pronounced tendency toward condensation of silico-oxygen anions with change in the ratio $BaO : SiO_2$ in barium silicates. In this connection it is possible that the phases of variable composition formed on the basis of B_2S_3 may represent products of further condensation of the ribbons $[Si_6O_{16}]^{8-}_{\infty}$ and chains $[Si_2O_6]^{4-}_{\infty}$. For example, the anionic radicals of compositions corresponding to the stoichiometry of the assumed compounds B_5S_8 and B_3S_5 may be represented as condensations: 1) $[Si_6O_{16}]^{8-}_{\infty} + [Si_2O_6]^{4-}_{\infty} - O = [Si_8O_{21}]^{10-}_{\infty}$—for B_5S_8 and 2) $[Si_6O_{16}]^{8-}_{\infty} + 2[Si_2O_6]^{4-}_{\infty} - 2O = [Si_{10}O_{26}]^{12-}_{\infty}$—for B_3S_5. Such

the character of the complication of the anionic radicals suggests condensation of chains and ribbons in one layer, but other modes are also possible.

The noted break in solubility in the region B_2S_3—BS_2, with the formation of a narrow range of phases of variable composition, is caused by the attainment, for the ribbon structure, of the condensation limit equal to 5 metasilicate chains

Fig. 3. Schematic representation of X-ray powder ionization diagrams recorded with CuKα radiation. Compositions: *a* $-B_2S_3$ with addition of 5 wt.% BaO, $-B_2S_3$, $-B_5S_8$, $-B_3S_5$, $-\beta$-BS_2 (sanbornite)

chains (composition B_3S_5). Consequently, phases of composition B_2S_3, B_5S_8, B_3S_5 may be regarded not only as members of one series of solid solutions, but also as distinct products of condensation of metasilicate chains. The high hardness of the B_2S_3—BS_2 silicates (of the order of 6-7), together with low coefficients of thermal expansion, will make it possible on their basis to obtain, for example in the BaO—Al_2O_3—SiO_2 system, new glass-crystalline materials opaque to γ-radiation.

Institute of Silicate Chemistry
Academy of Sciences of the USSR

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