CRYSTALLOGRAPHY

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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE STRUCTURE OF BARIUM SILICATES

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The structure of crystals of metasilicates and metagermanates of alkaline-earth metals MXO_3 has been investigated by many authors; however, only some of the structures have been fully deciphered. In a considerable number of cases, judgments on the structure of these crystals and on the structure of complex anions were based on determinations of lattice parameters and comparison with known structures (see, for example, ([1])). We have shown the possibility of studying the structure of complex anions in silicates and germanates by means of their vibrational spectra. In this way the spectra of pyroxenes ([2]), wollastonite, and calcium metagermanate ([3]) were interpreted; the existence of ring anions $[Si_3O_9]^{6-}$ in pseudowollastonite ([4]) and strontium metasilicate was proved; and the presence of two modifications of strontium metagermanate with structures similar to wollastonite ([3]) and pseudowollastonite ([4]) was found.

Fig. 1. Infrared spectrum of the high-temperature form of barium metasilicate $Ba_2(Si_2O_6)$; pressed in KBr; 3.5 mg of substance per 2 g KBr, $d = 25$ mm

The crystal structure of barium metasilicate $BaSiO_3$ (high-temperature form) differs from the structure of other metasilicates $MSiO_3$ and has not yet been established by x-ray methods. We investigated the infrared absorption spectrum of the high-temperature form of $BaSiO_3$ in order to elucidate the structure of the silicon-oxygen anion. The spectrum shown in Fig. 1 reveals a similarity to the spectra of pyroxenes (or lithium and sodium metasilicates) ([2]), but differs from the spectra of silicates with ring anions ([4]). Along with a group of bands in the region 1100–800 cm^{-1}, corresponding to antisymmetric valence vibrations of SiOSi and vibrations of the groups O^-SiO^-, in the frequency interval 750–600 cm^{-1}, characteristic of symmetric vibrations of SiOSi ([2–4]), two bands of medium intensity are observed*. This may be regarded as an indication of the existence of silicon-oxygen chains containing two tetrahedra in the identity

Fig. 2

Figure 2: Fig. 2

period $[(SiO_3)_2]_\infty$.

Fig. 2. *a*–chain $[Si_2O_6]_\infty$ in barium metasilicate; *b*–chain $[Si_3O_8]_\infty$ (after Ito ([6])); *c*–ribbon $[Si_6O_{16}]_\infty$ (derived from the wollastonite chain); *d*–ribbon $[Si_6O_{16}]_\infty$ (derived from the chain of barium metasilicate or from the layer in sanbornite ([5]))

* The terms "symmetric" and "antisymmetric" vibrations refer to the symmetry of the corresponding vibrations of the isolated group SiOSi or O^-SiO^-.

(For the assignment of frequencies see Table 1.) Similar suggestions on the structure of the high-temperature form of $BaSiO_3$ were made by Liebau on the basis of consideration of lattice parameters ([1]). The identity period of this chain is about 4.6 Å, which coincides with the value of the identity period in the X-ray-studied structure of the layered barium silicate sanbornite, $Ba_2(Si_4O_{10})$ ([5]). One may think that the layer in sanbornite is the product of condensation of the chains $[Si_2O_6]_\infty$ existing in barium metasilicate, just as a flat hexagonal net of the talc type is formed upon condensation of pyroxene chains. In Fig. 2a the proposed configuration of the chain in $BaSiO_3$ is shown; its only symmetry element is the screw axis $\overline{C}_2$ (the factor group of the one-dimensional space group is isomorphic to C_2).

Table 1

Frequencies of bands in the infrared spectra of barium silicates

$Ba_2(Si_2O_6)$	$Ba_2(Si_2O_6)$	$Ba_4(Si_8O_{10})$	$Ba_4(Si_8O_{10})$
Assignment of frequencies, chain $[Si_2O_6]_\infty$, factor group C_2	Frequencies, cm^{-1}	Frequencies, cm^{-1}	Assignment of frequencies (sheet $[Si_6O_{10}]_\infty$)
$\nu'_{as}(SiOSi)$ (B)$\nu_{as}(SiOSi)$ (A)$\nu'_{as}(O{-}SiO{-})$ (B)$\nu_{as}(O{-}SiO{-})$ (A)$\nu'_s(O{-}SiO{-})$ (B)$\nu_s(O{-}SiO{-})$ (A)	10381010990974891	111210551020[2]986935896	$\nu_{as}(SiOSi)\nu_{as}(O{-}SiO{-})\nu_s(O{-}SiO{-})\nu(SiO-$
$\nu'_s(SiOSi)$ (B)$\nu_s(SiOSi)$ (A)	740604	780 (?)755745732710634595	$\nu_s(SiOSi)$

$Ba_2(Si_2O_6)$	$Ba_2(Si_2O_6)$	$Ba_4(Si_8O_{10})$	$Ba_4(Si_8O_{10})$
$\nu(BaO)$and$\delta(SiO)$	537524508	535512504473442	$\nu(BaO)$and$\delta(SiO)$

[1] The prime mark indicates that vibrations of neighboring SiOSi (or O-SiO-) groups occur in opposite phases.
[2] The band is apparently a doublet.

In Table 2* the known structures of metasilicates and metagermanates of alkaline-earth metals are compared. It follows from this table that an increase in the ionic radius of the cation is apparently the principal factor (provided that the structures of the cation electron shells are similar) determining the transition from one structural type to another and, correspondingly, the change in the structure of the anion. It is characteristic in this connection that in metagermanates, evidently owing to the somewhat larger dimensions of the GeO_4 tetrahedra in comparison with the SiO_4 tetrahedra, there occurs, as it were, a "decrease" in the relative dimensions of the cations. Thus, $CaSiO_3$ crystallizes in two forms, whereas $CaGeO_3$ crystallizes only in one, corresponding to the low-temperature form of $CaSiO_3$. Conversely, the polymorphism of $SrGeO_3$ is analogous to the polymorphism of $CaSiO_3$, while for $SrSiO_3$ only one modification is known (with a structure of the pseudowollastonite type). Another conclusion following from consideration of Table 2 is that an increase in temperature affects the change

* From the point of view set forth, the existence of a "high-temperature" form of $BaGeO_3$ might seem somewhat unexpected. However, unlike $BaSiO_3$, the designation "high-temperature" form is essentially conventional, since this form is apparently metastable (and is obtained only with the addition of mineralizers), whereas the "low-temperature" form of $BaGeO_3$ crystallizes from the melt ([1]).

Table 2

Structure of complex anions in crystals of metasilicates and metagermanates of alkaline-earth metals

Anion structure	Compounds MXO_3, $X = Si$	Compounds MXO_3, $X = Ge$
Chain $[(XO_3)_2]_\infty$, $d \simeq 5.2$ Å	$MgSiO_3$ [1 3]	$MgGeO_3$ [2]
Chain $[(XO_3)_3]_\infty$, $d \simeq 7.3$ Å	$CaSiO_3$ (low-temperature form) [1 3]_	$CaGeO_3$ [2 3]$SrGeO_3$ (low-temperature form) [3]
Ring $[X_3O_9]^{6-}$	$CaSiO_3$ (high-temperature form) [2 3]$SrSiO_3$ [2 3]$BaSiO_3$ (low-temperature form) [2]	$SrGeO_3$ (high-temperature form) [1 3]–$BaGeO_3$ (low-temperature form) [2]

Figure 3

Figure 3: Figure 3

Anion structure	Compounds MXO_3, $X = Si$	Compounds MXO_3, $X = Ge$
Chain $[(XO_3)_2]_\infty$, $d \simeq 4.6$ Å	$BaSiO_3$ (high-temperature form) [2] [3]	$BaGeO_3$ (high-temperature form) [2]

[1] Structure established by direct X-ray structure determination.
[2] Structure proposed on the basis of the unit-cell parameters.
[3] Infrared spectrum investigated and interpreted.

of the anion structure in metasilicates in the same direction as the increase in the ionic radius of the cation. This can be explained if one takes into account that the vibrations of the relatively weakly bound M^{2+} ions are apparently more anharmonic and have a lower excitation energy than the vibrations of the Si and O atoms. Then, as the temperature is raised, it is chiefly the amplitudes of the cation vibrations that increase, which is equivalent to an increase in the "effective" radius of the cation, and a crystal structure different from that which is realized at low temperature may become energetically more favorable.*

Along with barium metasilicate, the structure of the compound of composition $2BaO \cdot 3SiO_2$, which has no analogs among the silicates of other alkaline-earth metals, is of interest. If it is assumed that all oxygen atoms take part in the formation of a complex anion, then its composition may be written as $[Si_3O_8]$. Let us attempt to consider possible forms of this anion. The complex chain (Fig. 2b), proposed by Ito for the structure of epididymite ([6]), corresponds to the formula $[Si_3O_8]_\infty$. However, the infrared spectrum of $2BaO \cdot 3SiO_2$, shown in Fig. 3, contains a large number (not fewer than 6) of bands in the frequency region of the symmetric SiOSi vibration (750—600 cm^{-1}). This cannot be reconciled with the chain $[Si_3O_8]_\infty$, which contains in a one-dimensional "unit cell" only 4 SiOSi bonds (the number of bands in the frequency region of the symmetric SiOSi vibration accordingly should not exceed 4). It is therefore expedient to consider structures with an elementary unit of doubled composition: $[Si_6O_{16}]_\infty$. Figures 2c and 2a show two possible forms of chains (ribbons) of such composition. One of them (Fig. 2c) is the result of condensation of wollastonite chains (two other types of ribbons formed from

Fig. 3. Infrared spectrum of $2BaO \cdot 3SiO_2$ ($Ba_4(Si_6O_{16})$); pellet in KBr; 5 mg of substance.

* A certain role in changing the equilibrium configuration of the anion may probably also be played by thermal excitation of low-frequency deformations of the SiOSi angles and of rotational rocking motions relative to the Si—O bonds.

wollastonite chains, described by N. V. Belov and co-workers in the structures of ksonotlite ([7]) and epididymite ([8]). The ribbon shown in Fig. 2e, "cut out" from the infinite layer in the structure of sanbornite $Ba_2(Si_4O_{10})$, may also be regarded as the result of condensation of three chains of barium metasilicate. For both models the number of frequencies of the valence symmetric vibrations SiOSi is the same ([8]); therefore the number of bands in the region 750–600 cm^{-1} should not exceed 8. A choice between these two models on the basis of the infrared spectrum alone of a fine-crystalline specimen is difficult. It seems useful to take into account that, according to ([9]), in crystals of $2BaO \cdot 3SiO_2$ an identity period of 4.69 Å is observed, close to the distance ~ 4.6 Å characteristic of the crystals $Ba_2(Si_2O_6)$ and $Ba_2(Si_4O_{10})$. (The rotation X-ray photograph obtained by us for a single crystal $0.15 \times 0.15 \times 1$ mm of $2BaO \cdot 3SiO_2$, taken with Mo K_α radiation, gives, along the elongation axis of the crystal, an identity period of 4.76 Å.) Apparently only the ribbon shown in Fig. 2e can be reconciled with these data (for the ribbon in Fig. 2b a "wollastonite" identity period of ~ 7.3 Å would be characteristic). Thus it may be assumed that the structures of the complex anions in all three barium silicates $Ba_2(Si_2O_6)$, $Ba_4(Si_6O_{16})$, and $Ba_2(Si_4O_{10})$ are built on the basis of one and the same motif—chains with a period of about 4.6 Å—by condensation of such chains into ribbons and layers. It is also possible that the silicates $5BaO \cdot 8SiO_2$ and $3BaO \cdot 5SiO_2$ described in ([9]) correspond to ribbons formed, respectively, from four and five such chains: $[Si_8O_{21}]_\infty$ and $[Si_{10}O_{26}]_\infty$.

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Note: Figure translations are in progress. See original paper for figures.