Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. V. Novoselova, Yu. V. Orlova,

1964

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. V. Novoselova, Yu. V. Orlova,
B. P. Sobolev, L. N. Sidorov

ON THE MECHANISM OF FORMATION OF BERYLLIUM SILICATE

(Be_2SiO_4)

As shown in works ($^{1-3}$), the formation of phenakite (Be_2SiO_4) from the oxides BeO and SiO_2 does not occur without the addition of mineralizers at any temperatures. The most convenient method for obtaining phenakite, possibly imitating natural processes of mineral formation, is its synthesis by means of chemical transport reactions.

In the works of Novoselova, Sobolev, and others ($^{4-6}$), crystals of beryllium and zinc silicates and of their solid solutions were obtained by means of such reactions. The oxides BeO, ZnO, and SiO_2 were taken as the starting substances for the syntheses. Fluoroberyllates of alkali metals served as mineralizers, and, in the case of willemite, fluorozincates. The experiments were carried out in evacuated quartz ampoules. The initial mixture of reagents was placed in one end of the ampoule; the ampoule was sealed under vacuum (10^{-3} mm Hg). The ampoules were then heated in a furnace at temperatures of 1000–1200° for 5-10 hours, with the arrangement of the ampoules providing a definite temperature gradient between their ends. The crystals grew in the colder end of the ampoule. The authors assume that the transfer (transport) of silicates, in particular phenakite, is accomplished with the aid of a gas phase containing volatile compounds of beryllium, silicon, and oxygen. A hypothesis was advanced concerning the existence in the gas phase of fluorosiloxanes as a possible form of oxygen transport. However, there has been no experimental verification of these assumptions.

In order to clarify the mechanism of phenakite transfer, it is of interest to investigate not only the solid products of the reaction, but also the composition of the gas phase.

We have carried out such an investigation using the method of mass spectrometry.

The present work presents the results of a mass-spectrometric study of the gas phase. For comparison, the mass spectra of fluorosiloxanes synthesized by us are given.

Experimental Part

For carrying out the synthesis of phenakite, the procedure described in work (^{6}) was used. In addition to experiments in evacuated quartz ampoules, however, experiments were also carried out in a stream of inert gas. The starting substances were prepared as indicated in work (^{6}).

1. **Reaction in vacuum.** Preliminary experiments showed that the fluorine compounds evolved during the reaction corrode the walls of the ampoule so strongly that cracks form in them, through which air enters the ampoule. In a number of cases the ampoules broke into pieces. To protect the reactor from the ingress of air, we sealed it into a quartz jacket, which was also evacuated before the experiment.

Procedure for carrying out the synthesis. Carefully dried weighed portions of the oxides with a constant ratio $BeO : SiO_2 = 2 : 1$ (moles) and with the addition of sodium fluoroberyllate of composition Na_2BeF_4 (2-5% of the total weight of the oxides) were placed in ampoules with vacuum jackets and sealed while being evacuated to $p = 10^{-4}$ mm Hg. The ampoules were heated in a horizontal position in a tubular electric furnace equipped with two windings to create a temperature gradient. In this arrangement the weighed portions were located in the zone at the higher temperature (1000-1050°), while the part of the ampoule free from charge was at the lower temperature (800-850°). The temperature gradient was about 150°; the temperature was measured with a Pt—PtRh thermocouple; the duration of the experiment was 4-6 h. After completion of the experiment the ampoules were opened. In the colder part, crystals of phenakite had grown on the walls, which was confirmed by X-ray phase and crystal-optical analyses. Finely crystalline phenakite was also present in the oxide mass.

To investigate the gas phase, a glass trap ampoule was soldered to the quartz ampoule through a special joint; during the experiment it was cooled in a Dewar vessel with liquid nitrogen. A white solid substance, which evaporated instantaneously at room temperature, was collected in it. After completion of the reaction the cooled ampoule was sealed off and the mass spectrum of the gas obtained was recorded.

2. Carrying out the reaction in a stream of inert gas. Dry nitrogen was used as the inert gas. The charge of oxides and fluoroberyllate was placed on a Pt support in a porcelain tube. The tube was inserted horizontally into the furnace and connected by means of ground joints to a trap and drying columns. The system was checked for tightness and, before the experiment, was purged for 2-3 h with a stream of dry nitrogen while the charge was simultaneously heated to 600°. Periodically the trap and the connecting glass parts of the apparatus were heated with a burner. After complete removal of traces of moisture from the apparatus, the furnace temperature was raised and the trap was cooled. The experiments were carried out at 1000-1050° for 10-12 h. The gaseous reaction products formed were swept out of the reaction space by the nitrogen stream and, at the outlet from the furnace, condensed in the trap at −80°. The condensate collected on the bottom and walls of the trap was a white solid mass. After completion of the experiment the trap was sealed off; the condensate turned into gaseous products, and their mass-spectral analysis was carried out.

As was indicated earlier, in connection with consideration of possible forms of oxygen transport, the assumption was made that fluorosiloxanes exist in the gas phase that is formed. To test the proposed hypothesis, the composition of the gas phase formed in the $BeO—SiO_2—Na_2BeF_4$ system upon heating was investigated. For comparison, we synthesized fluorosiloxanes separately by the method of Gubo (^{7}) and studied their mass spectra.

The gas phase participating in the formation of phenakite was collected in special trap ampoules soldered to the reactor. Mass-spectral analysis of the fluorosiloxanes and of the gases taken from the reaction volume was performed on an MI-1305 instrument.

Tables 1-3 give the relative intensities of the ion currents as percentages of the intensity of the ion current $^{28}Si_2{}^{16}OF_5^+$.

Discussion of the Results

In the present work, for the first time, with the aid of mass-spectral analysis it has been possible to establish the presence of fluorosiloxanes in the gas phase formed in the $BeO—SiO_2—Na_2BeF_4$ system and to confirm the previously proposed hypothesis concerning oxygen transport in the form of fluorosiloxanes during the formation of phenakite. The presence of fluorosiloxanes explains the mechanism of formation of phenakite

from the gas phase at relatively low temperatures (800–1000°). In the mass spectrum of fluorosiloxanes, the ions $Si_2OF_6^+$, $Si_2OF_5^+$ and $SiOF_2^+$, $SiOF^+$ were found, indicating the presence in the gas phase of Si_2OF_6 and $SiOF_2$ molecules. It cannot be assumed that the $SiOF_2^+$ ion is formed only as a result of dissociative ionization of the Si_2OF_6 molecule.

Table 1

Mass spectrum of fluorosiloxanes

Experiment duration	$^{28}Si_2{}^{16}OF_6^+$	$^{28}Si_2{}^{16}OF_5^+$	$^{28}Si^{16}OF_5^+$	$^{28}Si^{16}OF^+$	$\frac{^{28}Si_2{}^{16}OF_5^+}{^{28}Si^{16}OF_5^+}$
16 h	12.5	100	175	9.0	0.57
20 h	16.0	100	80	6.0	1.25

The data presented in Tables 1, 2, and 3 show that the ratio of the intensities of the ion currents $Si_2OF_5^+$ and $SiOF_2^+$ changes sharply from experiment to experiment. This is probably associated with a change in the total pressure in the ampoule being analyzed, depending on the duration of the experiment.

Table 2

Mass spectrum of SiF_4

Experiment No.	$^{28}SiF_3^+$	$^{28}SiF_2^+$	$^{28}SiF^+$	$^{28}SiF_4^+$
1	100	1.3	4.0	2.0
2	100	0.85	3.1	1.8

A change in the total pressure leads to a change in the partial pressures of Si_2OF_6 and $SiOF_2$ in accordance with the equilibrium constant of the reaction

$$Si_2OF_6 \rightleftharpoons SiOF_2 + SiF_4.$$

In this case, the ratio of the intensities of the lines $Si_2OF_6^+$ and $Si_2OF_5^+$, as well as the lines $SiOF_2^+$ and $SiOF^+$, changes only slightly.

Thus, under the conditions of our experiments (unsaturated vapor), Si_2OF_6 and $SiOF_2$ molecules were present in the gas phase.

Carrying out the reaction in a closed system (sealed quartz ampoules) leads to the creation of heterogeneous equilibria between the gas phase and the precipitate in each temperature zone. Transfer of phenacite from the hotter zone to the colder one occurs through the gas phase by means of diffusion.

Table 3

Mass spectrum of the gas phase of the $BeO—SiO_2—Na_2BeF_4$ **system**

Experimental conditions	$^{28}Si^{16}OF_2^+$	$^{28}Si^{16}OF^+$	$^{28}Si_2{}^{16}OF_6^+$	$^{28}Si_2{}^{16}OF_5^+$	$^{28}SiF_3^+$	$^{28}SiF_2^+$	$^{28}SiF^+$	$^{28}SiF_4^+$
In a sealed ampoule	60	5.0	19	100	10 000	100	1000	24
In a sealed ampoule	107	3.0	26	100	7 140	105	1120	7.0

Experimental conditions	$^{28}Si^{16}OF_2^+$	$^{28}Si^{16}OF^+$	$^{28}Si_2{}^{16}OF_6^+$	$^{28}Si_2{}^{16}OF_5^+$	$^{28}SiF_3^+$	$^{28}SiF_2^+$	$^{28}SiF^+$	$^{28}SiF_4^+$
In a nitrogen stream	135	7.5	20	100	12 000	53	2050	24

Note. The mass spectra were recorded at an electron ionization energy of 80-100 eV.

As a result of the decomposition of gaseous complex compounds in the colder part of the ampoule, phenacite crystals are deposited, while the silicon tetrafluoride and sodium fluoride released in the process return to the reaction and interact with new portions of oxides. In this way it is possible to carry out the transfer of large amounts of phenacite.

There are indications in the literature (^{8}) of the existence, in vapors above a melt of Na_2BeF_4, of complex molecules of composition $NaBeF_3$. Thus the possibility of beryllium transfer through the gas phase in the form of fluoride complexes has been shown. In the present work, the presence of fluorosiloxanes in the gas phase in the $BeO—SiO_2—Na_2BeF_4$ system has been established.

Proceeding from this, the following mechanism for the transfer of phenakite through the gas phase may be proposed and expressed in the form of the following reaction equations:

$$2Na_2BeF_4 + SiO_2 \rightleftarrows SiF_4 + 4NaF + 2BeO, \tag{1}$$

$$SiF_4 + BeO \rightleftarrows SiOF_2 + BeF_2, \tag{2}$$

or

$$(2SiF_4 + BeO \rightleftarrows Si_2OF_6 + BeF_2),$$

$$BeF_2 + NaF \rightleftarrows NaBeF_3, \tag{3}$$

$$\frac{4SiOF_2 + 2NaBeF_3 \rightleftarrows Be_2SiO_4 + 3SiF_4 + 2NaF}{2Na_2BeF_4 + 3SiO_2 + 2BeO = 2Be_2SiO_4 + SiF_4 + 4NaF}. \tag{4}$$

The reversibility of the overall reaction was indicated in work (4). It was shown that, when the temperature is raised above 1300°, phenakite decomposes under the action of silicon tetrafluoride. The chemical analysis carried out by us of the gas collected in a trap during the decomposition reaction of phenakite by silicon tetrafluoride showed that, in the gaseous products formed, the ratio of silicon to fluorine is 1 : 2.1 (atomic), which indicates the formation of fluorosiloxanes of the general formula $(SiOF_2)_n$.

Moscow State University
named after M. V. Lomonosov

Received
11 VII 1964

REFERENCES CITED

1 R. A. Morgan, F. A. Hummel, *J. Am. Ceram. Soc.*, **32**, No. 8 (1949). 2 P. P. Budnikov, A. M. Cherepanov, *DAN*, **74**, No. 5 (1950). 3 E. N. Isupova, E. K. Keller, *ZhKh*, **5**, No. 5, 1126 (1960). 4 B. P. Sobolev, A. V. Novoselova, *Geokhimiya*, No. 1, 20 (1959). 5 B. P. Sobolev, I. P. Klyagina, *ZhKh*, **5**, No. 10, 2294 (1960). 6 A. V. Novoselova, V. N. Babin, B. P. Sobolev, *ZhKh*, **6**, No. 1, 227 (1961). 7 J. Geobeau, H. Grossrouken, *Zs. anorg. u. allgem. Chem.*, **264**, 230 (1951). 8 A. V. Novoselova, F. Sh. Muratov et al., *Vestn. Moskovsk. univ., ser. matem., mekhan., astron., fiz., khim.*, No. 6 (1958).

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