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INVESTIGATION OF THE PHASE DIAGRAM OF THE SYSTEM RbF–BeF$_2$ AND ITS RELATION TO THE SYSTEM BaO–SiO$_2$

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Among fluoride systems of the type Me^+F–BeF$_2$, where Me^+ is an alkali element, phase diagrams have been constructed only for two systems: LiF–BeF$_2$ ([1],[2]) and NaF–BeF$_2$ ([3]-[5]), which, in the light of Goldschmidt' s concepts, may be regarded as weakened fluoride "models" of the silicate systems Mg(Zn)O–SiO$_2$ and CaO–SiO$_2$, respectively.

In order to fill the gap—the absence of a fluoride "model" of the BaO–SiO$_2$ system—it was of interest to investigate the previously unstudied RbF–BeF$_2$ system with respect to its chemical compounds and phase diagram.

To construct the phase diagram of the RbF–BeF$_2$ system, differential-thermal, X-ray phase, and crystal-optical methods of investigation were used. Twenty-five different compositions of the system were subjected to thermal investigation; after each experiment they were examined under a microscope in polarized light in immersion preparations* in order to determine the phase composition of the samples from the refractive indices of the individual substances. Some mixtures (15; 40; 46.5; 60; 75 mol.% BeF$_2$ and several additional compositions) were investigated radiographically for additional control of their phase composition. The RbF–BeF$_2$ system, shown in Fig. 1, consists of four separate eutectic systems; in the thermal investigation of these, the end members of these partial systems served as the starting substances. The exception is the RbBe$_2$F$_5$–BeF$_2$ system, where BeF$_2$ was introduced into the starting mixtures in the form of the salt $(NH_4)_2BeF_4$**, which decomposed in the range 220-380° into BeF$_2$ and gaseous NH_4F.

The starting substances used in obtaining rubidium fluoroberyllates were Rb_2CO_3 (chemically pure) and $(NH_4)_2BeF_4$. Three compounds were found in the system: Rb_2BeF_4, $RbBeF_3$, and $RbBe_2F_5$. Rb_2BeF_4 was first obtained by Makerji ([6]); the existence of $RbBeF_3$ is indicated by Novoselova and Simanov ([7]); no data on $RbBe_2F_5$ are available in the literature. We synthesized Rb_2BeF_4 from an aqueous solution of equimolecular amounts of Rb_2CO_3 and $(NH_4)_2BeF_4$; $RbBeF_3$ and $RbBe_2F_5$ were prepared by sintering Rb_2BeF_4 and $RbBeF_3$—each separately—with $(NH_4)_2BeF_4$ in a molar ratio of 1 : 1 in both cases. RbF was obtained from Rb_2CO_3 by displacement of CO$_2$ with hydroflu-

Fig. 1. Phase diagram of the RbF—BeF_2 system: 1 —temperatures of thermal effects on heating thermograms, 2 —temperatures of thermal effects on cooling thermograms

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oric acid. Questions concerning the study of the polymorphism, structure, and crystal-optical properties of Rb_2BeF_4 and $RbBeF_3$ as fluoroberyllate "models" of Ba_2SiO_4 and $BaSiO_3$, respectively, are considered in detail in our works ([8],[9]). The individuality of rubidium ortho-, meta-, and difluoroberyllates was confirmed by us through measurement of their crystal-optical properties and by data on the interplanar spacings of the lattices of these compounds. Table 1 gives the values of the refractive indices (N_{av}), densities, and chemical analysis of $(NH_4)_2BeF_4$ and of three rubidium fluoroberyllates.

* In view of the low values of the refractive indices of the fluoroberyllates, immersion liquids were prepared from methyl alcohol ($N = 1.329$) and glycerin.

** The salt $(NH_4)_2BeF_4$ was prepared by the method of Novoselova and Averkova ([10]) from equimolecular amounts of $Be(OH)_2 \cdot (NH_4)_2CO_3$ and hydrofluoric acid.

The study of the partial eutectic system RbF—Rb_2BeF_4 presented difficulties because of the hygroscopicity and some volatility of RbF; the latter was detected by chemical analysis of a mixture of eutectic composition after thermal analysis. This apparently also explains the small scatter of points in this part of the system. The eutectic of the RbF—Rb_2BeF_4 system, formed by congruently melting RbF (m.p. 770°) and Rb_2BeF_4 (m.p. 807°),

Table 1

Content of elements in compounds (wt. %)

Elements	$(NH_4)_2BeF_4$ ($N =$ 1.397) exp.	$(NH_4)_2BeF_4$ ($N =$ 1.397) theor.	Rb_2BeF_4 (density 3.64, $N =$ 1.383) exp.	Rb_2BeF_4 (density 3.64, $N =$ 1.383) theor.	$RbBeF_3$ (density 3.03, $N =$ 1.338) exp.	$RbBeF_3$ (density 3.03, $N =$ 1.338) theor.	$RbBe_2F_5$ (density 2.81, $N =$ 1.332) exp.	$RbBe_2F_5$ (density 2.81, $N =$ 1.332) theor.
Rb^+	(NH_4^+)	(NH_4^+)	65.99	66.78	55.09	56.422	42.85	43.06
Be^{2+}	7.54	7.45	3.61	3.57	5.92	5.954	9.19	9.09
F^-	62.57	62.76	29.53	29.73	38.40	37.624	47.08	47.85
Σ	70.11	70.21	99.13	100.0	99.41	100.00	99.12	100.00

Fig. 1. Phase diagram of the RbF—BeF_2 system: 1 —temperatures of thermal effects on heating thermograms, 2 —temperatures of thermal effects on cooling thermograms

lies at 693° and has the composition 23 mol.% BeF_2 + 77 mol.% RbF. Solid-phase equilibria in the RbF—Rb_2BeF_4 system are characterized by the existence of 5 stability fields of limited solid solutions of RbF in

Rb_2BeF_4, of which there are: 1) two fields of phase stability: γ-solid solution + β-solid solution (field 6—7—8) and β-solid solution + α-solid solution (field 3—4—5), and 2) three fields of stability of γ-solid solution (field 9—6—8), β-solid solution (field 4—5—7—8), and α-solid solution (field 1—2—3—4). The necessity for the existence of the listed fields follows as a consequence of the three modifications present: γ-, β-, and α-Rb_2BeF_4, which undergo enantiotropic polymorphic transformations according to the scheme

$$\gamma \overset{528^\circ}{\rightleftarrows} \beta \overset{692^\circ}{\rightleftarrows} \alpha \overset{807^\circ}{\rightleftarrows} \text{liq.}$$

and each of which forms limited solid solutions with RbF. The exact boundaries of existence of these equilibrium fields have not been established; therefore they are shown by dotted lines. The presence of limited solid solutions of RbF in the three modifications of Rb_2BeF_4 is confirmed by the observed difference in the temperatures of the polymorphic transformations of pure Rb_2BeF_4 in comparison with its limiting solid solutions: for γ-solid solution β-solid solution, 556°, and for β-solid solution α-solid solution, 672°. In the powder pattern of the composition containing 15 mol.% BeF_2, along with lines belonging to RbF and γ-Rb_2BeF_4 solid solution, there are also sufficiently distinct lines which, in all probability, should be assigned to the β-solid-solution and α-Rb_2BeF_4 solid-solution modifications stabilized by the dissolution of RbF in them. The values N_{cp} of the different modifications of the Rb_2BeF_4 solid solution differed little from the refractive index of γ-Rb_2BeF_4, $N_{\text{cp}} = 1.383$; therefore the solubility of RbF in γ-, β-, and α-Rb_2BeF_4 was provisionally taken as not more than 10-12 wt.% RbF (at high temperatures).

The portion of the system from 33.33 to 50 mol.% BeF_2 is a eutectic phase diagram Rb_2BeF_4—$RbBeF_3$, whose eutectic has the composition 47.5 mol.% BeF_2 + 52.5 mol.% RbF and lies at 462°. $RbBeF_3$ melts congruently at 465°. In the field of separation of Rb_2BeF_4 from the melt, two dotted horizontal lines represent boundaries separating the equilibrium fields of the α and β modifications at 692°, and of β and γ at 528°. Three points corresponding to thermal effects for compositions of 37 and 40 mol.% BeF_2 at an average temperature of 632° correspond, as indicated earlier (*), to the transformation of β-Rb_2BeF_4 into the α' form, stable in the interval 632-692° in the presence of $RbBeF_3$. The absence in the RbF—Rb_2BeF_4 system of a similar transformation does not allow it to be represented in the form of corresponding equilibrium fields of the α' form in the phase diagram of the system. In the system, the existence is assumed of a compound of composition $3RbF \cdot 2BeF_2$, decomposing in the solid state at 427° into γ-Rb_2BeF_4 and α-$RbBeF_3$. It was not possible to confirm crystallographically by X-rays the individuality of the compound $3RbF \cdot 2BeF_2$; microscopically, in mixtures of the Rb_2BeF_4—$RbBeF_3$ system, the presence was detected of a small amount of a phase with a refractive-index value intermediate between N_{cp} for Rb_2BeF_4 and $RbBeF_3$. Compounds decomposing in the solid state are, in most cases, unstable; this, apparently, explains the difficulty of obtaining $3RbF \cdot 2BeF_2$ in an amount sufficient for X-ray confirmation of its chemical individuality. In one of the experiments, the thermal effect for the composition $3RbF \cdot 2BeF_2$ at 322° was caused by the β α transformation of the $RbBeF_3$ present in it. However, the reason remains unclear for the appearance of a thermal effect in $RbBe_2F_5$ at a temperature almost coinciding with the temperature of the polymorphic transformation of $RbBeF_3$. A high-temperature X-ray study of $RbBe_2F_5$ at 20, 200, and 350° did not reveal any appreciable change in its structure, apart from thermal expansion of the lattice. The horizontal line in the RbF—BeF_2 system for compositions from 40 to 66.66 mol.% BeF_2 at 316° represents the boundary of the fields of existence of the enantiotropic modifications of $RbBeF_3$, below which rhombic β-$RbBeF_3$ is stable, and above which α-$RbBeF_3$ is stable.

The RbF—BeF_2 system in the composition range from 50 to 100 mol.% BeF_2 consists of two simplest eutectic diagrams, $RbBeF_3$—$RbBe_2F_5$ and $RbBe_2F_5$—BeF_2, mixtures of whose compounds crystallize in eutectics of compositions, respectively, 58 mol.% BeF_2 + 42 mol.% RbF at 396° and 77.5 mol.% BeF_2 + 22.5 mol.% RbF at 425°. The crystals of $RbBe_2F_5$ are biaxial,

with a large angle of the optical axes, a negative (—) optical sign, and very weak birefringence. In crystals of $RbBe_2F_5$, perfect cleavage along one of the planes and a tendency toward polysynthetic twinning were found. $RbBe_2F_5$ is slightly hygroscopic, melts congruently at 462°, and has a flat melting maximum. $RbBe_2F_5$ forms limited solid solutions with BeF_2—this was established from changes in the interplanar spacings of the solid solution $RbBe_2F_5$ from a mixture of composition 70 mol.% BeF_2 in comparison with d/n of pure $RbBe_2F_5$, and also from the decrease, in $RbBe_2F_5$ solid solution, of the refractive index, which became lower than $N = 1.329$. The presence, in a mixture of composition 70 mol.% BeF_2, of an insignificant amount of a second phase, BeF_2, shows that the composition corresponding to the limiting solubility of BeF_2 in $RbBe_2F_5$ must lie between $RbBe_2F_5$ and the composition 70 mol.% BeF_2, as is also shown by the dashed line in the diagram. In the field of the partial diagram $RbBe_2F_5$—BeF_2, below the eutectic temperature, in equilibrium with $RbBe_2F_5$ solid solution there is a quartz-like modification of BeF_2, possessing extremely low birefringence.

BeF_2 gradually softens on heating, remaining rather viscous; in addition, it is prone to supercooling. Therefore determining the character and temperature of melting of BeF_2 presents great experimental difficulties. Kirkina, Novoselova, and Simanov (11) note that BeF_2 begins to melt at 545° and finally melts at about 740°, but the authors do not indicate the character of its melting. In constructing the phase diagram of the RbF—BeF_2 system, in view of the uncertainty of the melting of BeF_2, we do not bring the liquidus of its separation from the melt up to the temperature ordinate characterizing the thermal behavior of BeF_2.

Comparison of the "model" systems RbF—BeF_2 and BaO—SiO_2 and their phase diagrams shows that compounds similar in stoichiometry of composition, in character of melting (congruent), and in structure are realized in the systems. The phase diagrams of both systems have similar liquidus curves in the composition interval from RbF to $RbBeF_3$ in the fluoride system and from BaO to $BaSiO_3$ in the silicate system. However, the solid-phase equilibria in the RbF—BeF_2 system are more complex than in BaO—SiO_2. The presence of polymorphism in Rb_2BeF_4 and $RbBeF_3$, i.e., in the fluoride "models" of Ba_2SiO_4 and $BaSiO_3$, may serve as a basis for searches for polymorphism also in barium silicates, the existence of which could have remained unnoticed because of the difficulty of attaining equilibrium states in silicate systems. The existence in the BaO—SiO_2 system ([12]) of the compound $2BaO \cdot 3SiO_2$, which forms continuous solid solutions with $BaSi_2O_5$, and the absence of a compound analogous in formula in the RbF—BeF_2 system requires verification of the individuality of the compound $2BaO \cdot 3SiO_2$. It is possible that $2BaO \cdot 3SiO_2$ represents a case of a limiting solid solution of $BaSiO_3$ in $BaSi_2O_5$—of composition close in stoichiometry to $2BaO \cdot 3SiO_2$.

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