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Abstract

Full Text

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STUDY OF THE SYSTEM BeF_2–ZrF_4

In connection with the study of the ternary system KF–BeF_2–ZrF_4, we undertook a study of the corresponding binary systems. The present paper reports the results of an investigation of the BeF_2–ZrF_4 system. We found no data in the literature on this system. According to literature data, the isomorphous zirconium fluorides ThF_4 and UF_4 (1) and (2) form systems of the eutectic type with beryllium fluoride. No compounds have been found in them. The eutectic points are located very close to beryllium fluoride: at 2 mole % ThF_4 and 0.5 mole % UF_4, which indicates the comparatively low solubility of beryllium fluoride in melts of these fluorides. The eutectic temperatures are, respectively, 525-530° and 537°.

There are also a number of papers in the literature (3-5) which indicate that zirconium fluoride forms binary compounds of various composition with fluorides of divalent metals (Mg, Ba, Zn, Cd, Ni). All the compounds indicated were obtained only from aqueous solutions and were isolated in the form of crystalline hydrates.

Fig. 1. Phase diagram of the BeF_2–ZrF_4 system

Thermal analysis of the BeF_2–ZrF_4 system was carried out by us on a Kurnakov FPK-59 pyrometer. The alloy under investigation was placed in a platinum crucible with a tightly fitted lid, which had a pocket for the thermocouple. To avoid loss of zirconium fluoride as a result of evaporation, the alloys were introduced into a furnace preheated somewhat above the melting temperature of the alloy. Analyses for the total oxides of zirconium and beryllium showed no significant deviations from the initial compositions.

For alloys with a content from 0 to 80 mole % BeF_2, cooling curves were recorded. Alloys with a higher content of beryllium fluoride

were obtained in the form of glass; therefore, only the heating curves after annealing the alloys were recorded for them.

For preparing the alloys, mixtures of $(NH_4)_2BeF_4$ and $(NH_4)_3ZrF_7$ were taken

X-ray patterns of BeF2—ZrF4 alloys

Figure 2: X-ray patterns of BeF2—ZrF4 alloys

in calculated amounts, and ammonium fluoride was driven off in a stream of CO_2. To avoid melting of the double fluorides during distillation, most of the ammonium fluoride was driven off at 300°; then the temperature was gradually raised to 500–550°, and the final removal of NH_4F from the alloys was carried out. Annealing of the alloys was performed in nickel crucibles sealed in ampoules, at a residual argon pressure of 100-120 mm Hg. Argon was used to suppress sublimation of zirconium fluoride. The annealing temperature was 380–400°, and the time was 30 h.

X-ray studies of the alloys were carried out with Fe radiation in RKD-57 cameras. Alloys with a high BeF_2 content were photographed in capillaries made of Pyrex glass; nonhygroscopic alloys were photographed on glass whiskers. The film loading was asymmetric. The data from thermal and X-ray phase analysis of the BeF_2—ZrF_4 system are presented in Figs. 1 and 2.

Fig. 2. Comparison of reflection angles and line intensities in X-ray patterns of alloys of the BeF_2—ZrF_4 system. *a*—annealing at 400°, *b*—annealing at 550°.

On the heating curves of zirconium fluoride obtained by decomposition of $(NH_4)_3ZrF_7$ at 550°, endothermic effects were found at 612, 690, and 903°. The effect at 612° is absent from the thermograms of zirconium fluoride obtained by decomposition of $(NH_4)_3ZrF_7$ at temperatures above 600°. This effect cannot be attributed to a phase transformation of ZrF_4, since the X-ray patterns of ZrF_4 obtained at 550 and 650° proved to be identical.

Nor can it be assumed that the last traces of ammonium fluoride are removed at this temperature, since according to the data of work (6) this occurs at 410°. Probably, at 612° a second-order transformation of ZrF_4 occurs.

The effect at 690° is reversible and corresponds, as already reported in work (7), to the $\alpha \rightleftarrows \beta$ transformation of ZrF_4. At 903° zirconium fluoride melts. Single crystals of ZrF_4 that had grown under the lid of a platinum crucible were photographed. The photographs were taken in an RKOP camera with Cu radiation. The study showed that the crystals belong to the monoclinic modification described by Schulz (8).

Beryllium fluoride was obtained by the method described in work (9). It was obtained in a quartz-like form. In this same form it was also found in alloys annealed at 400°.

On the heating curve of BeF_2, effects were found at 220, 575, and 793°. The effect at 220° corresponds to the $\alpha \rightleftarrows \beta$ transformation of quartz-like BeF_2; 575° corresponds to melting of this modification. In work (10) it was found that after melting at 580°, BeF_2 solidifies again, passing into a high-temperature modification, which melts at about 800°. Endothermic-effect at 793° probably also corresponds to the final melting of beryllium fluoride.

As already noted in (11), in melts of BeF_2 and ZrF_4 a new modification of BeF_2 was found, which we indexed in a rhombic body-centered cell with the parameters: $a = 10.01 \pm 0.01$ kX, $b = 13.07 \pm 0.02$ kX, $c = 16.27 \pm 0.01$ kX.

Special experiments showed that the rhombic modification of BeF_2 is formed in the presence of very small amounts of zirconium fluoride and that the crucible material (the experiments were carried out in nickel and platinum crucibles) has no effect on its formation.

To determine the stability region of the rhombic modification of BeF_2, we annealed it, first at 550° for 150 hours, and then at 380–400°. After annealing at 380–400° this modification transformed into the quartz-like form of BeF_2.

In the study of the $NaF{-}BeF_2$ system (12), a transition at 420–450° of an then unknown modification of BeF_2 into the quartz-like form was found. Therefore we may regard 420° as the lower boundary of existence of the rhombic modification. The upper boundary, corresponding to the transition of BeF_2 into a more high-temperature form, probably analogous to cristobalite, according to the data of (12) lies at 680°. We marked the upper boundary of existence of rhombic BeF_2 on the diagram by a dashed line (Fig. 1).

By thermal and X-ray phase analysis in the $BeF_2{-}ZrF_4$ system, one incongruently melting compound of composition $BeZrF_6$ was found. The temperature of the peritectic reaction of its formation lies at 712°. The eutectic between this compound and beryllium fluoride lies at a temperature of 578° and 80 mol. % BeF_2.

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named after M. V. Lomonosov

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