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Abstract

Full Text

Chemistry

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STUDY OF THE SYSTEM KF–ZrF_4

Zirconium fluoride forms double salts of complex composition with alkali-metal fluorides. Thus, in the system NaF–ZrF_4, studied by Barton et al. (⁀1), two congruently melting compounds, Na_3ZrF_7 and $Na_7Zr_6F_{31}$, were found; three compounds melting incongruently–$Na_5Zr_2F_{13}$, Na_2ZrF_6, and $Na_3Zr_4F_{19}$; and one compound–$Na_3Zr_2F_{11}$–existing only in the solid state.

According to the literature data, KF and ZrF_4 form the compounds: K_3ZrF_7, K_2ZrF_6, and $KZrF_5$. The fusibility diagram of the system KF–ZrF_4 (up to 65% ZrF_4) was investigated in works (^{2},3), apparently by the visual-polythermal method, since in work (⁀2) the phase fields below the solidus line are not indicated on the diagram of this system. In work (⁀3) there are likewise no indications of transformations in this system in the solid state.

In the present work we carried out differential thermal analysis and an X-ray phase study of the system KF–ZrF_4. According to the data of work (⁀4), zirconium fluoride undergoes a polymorphic transformation at $405 \pm 5°$. Schulze (⁀5) determined the parameters of the low-temperature monoclinic modification of ZrF_4: $a = 9.46$ Å; $b = 9.87$ Å, $c = 7.64$ Å; $\beta = 94°30'$. According to Barton' s determination (⁀1), ZrF_4 melts at 912°. Sense et al. (⁀6) determined the dependence of the vapor pressure of ZrF_4 on temperature; according to their data, the sublimation temperature of ZrF_4 is 903°.

Starting substances. For the study of the system we obtained potassium fluoride by dehydrating $KF \cdot 2H_2O$; zirconium fluoride was prepared from $(NH_4)_3ZrF_7$ by distilling off ammonium fluoride in a stream of CO_2. The synthesis of $(NH_4)_3ZrF_7$ was carried out by the method described in work (⁀7).

For the preparation of melts containing less than 33.3% ZrF_4, we used potassium fluoride and the available preparation K_2ZrF_6. Melts containing more than 33.3% ZrF_4 were prepared by fusing calculated amounts of K_2ZrF_6 and $(NH_4)_3ZrF_7$ in a stream of CO_2. Because of the volatility of ZrF_4, melts with a content of it greater than 75% were not studied. The results of analyses of the starting preparations and the melts obtained for potassium, zirconium, and fluorine agreed well with the calculated values. The errors of determination did not exceed 0.2–0.25%.

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Fig. 1. System KF–ZrF4. Phase fields diagram

Figure 1: Fig. 1. System KF–ZrF4. Phase fields diagram

Thermal and X-ray phase analysis of the system KF–ZrF$_4$. Differential thermal analysis was carried out on an N. S. Kurnakov pyrometer using a platinum-platinum-rhodium thermocouple. Aluminum oxide served as the standard. Melts for thermal analysis were taken in an amount of 0.5 g. For melts containing up to 33.3% ZrF$_4$, cooling and heating curves were recorded. For melts with a ZrF$_4$ content greater than 33.3%, only cooling curves were recorded, since during slow heating of the melts their composition changed noticeably. In order to reduce the loss of ZrF$_4$, the melts were placed in a furnace preheated to a temperature slightly exceeding the melting temperature of the melt, and then after several minutes the furnace was switched off and the cooling curve was recorded. The temperatures were noted from the beginning of the effect on the differential curve.

For the X-ray investigation, the alloys were ground and, with the aid of zapon lacquer, applied to a Pyrex whisker. Potassium fluoride and alloys with a high content of it were photographed in sealed capillaries made of Pyrex glass. X-ray patterns were recorded in RKD-57 cameras using Fe radiation.

In view of the fact that a number of effects connected with its transformations were detected on the heating curves of K_2ZrF_6, we recorded X-ray patterns of K_2ZrF_6 at 260 and 340° in a Unicam camera (8) on a BSVLT tube with a copper anode. At a higher temperature it was impossible to carry out the recording because of the interaction of K_2ZrF_6 with quartz.*

The phase diagram of the system $KF–ZrF_4$, constructed by us on the basis of thermal and X-ray phase analysis, is presented in Figs. 1 and 2.

The zirconium fluoride synthesized by us was a monoclinic modification, described in (5). On its heating curve, endothermic effects at 612 and 685°, corresponding to transformations in the solid state, were found; on repeated heating the effect at 612° was absent.

In view of the strong volatility of ZrF_4 on heating, beginning at 880° a strong deviation of the differential curve is noted on the thermogram. The endothermic effect corresponding to the melting of ZrF_4 is found at $903 \pm 5°$. If a closed platinum crucible with ZrF_4 is placed in a furnace preheated to 930-940° and then, after switching off the furnace, the cooling curve is recorded, then the effect of solidification of ZrF_4 is observed at $903 \pm 5°$; on further cooling a polymorphic transformation occurs at 685°. Potassium fluoride, according to our data, melts at 850°. In the system

Fig. 1. System $KF–ZrF_4$. Phase fields: **1** –KF+ liq.; **2** –K_3ZrF_7+ liq.; **3** –$K_5Zr_2F_{13}$+ liq.; **4** –solid solution + liq.; **5** –δ-K_2ZrF_6+ liq.; **6** –γ-K_2ZrF_6+ liq.; **7** –γ-$KZrF_5$+ liq.; **8** –δ-K_2ZrF_6+ liq.; **9** –α-ZrF_4+ liq.; **10** –KF +

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Fig. 2. Line diagrams of compounds in the KF–ZrF_4 system

Figure 2: Fig. 2. Line diagrams of compounds in the KF–ZrF_4 system

K_3ZrF_7; **11** –$K_3ZrF_7 + K_5Zr_2F_{13}$; **12** –solid solution; **13** –solid solution +δ-K_2ZrF_6; **14** –solid solution +γ-K_2ZrF_6; **15** –solid solution +α-K_2ZrF_6; **16** –γ-$K_2ZrF_6+\gamma$-$KZrF_5$; **17** –γ-$K_2ZrF_6+\beta$-$KZrF_5$; **18** –γ-$K_2ZrF_6+\alpha$-$KZrF_5$; **19** –γ-$K_2ZrF_6+K_7Zr_6F_{31}$; **20** –α-$K_2ZrF_6+\beta$-$K_3Zr_2F_{11}$; **21** –γ-$K_2ZrF_6+\alpha$-$K_3Zr_2F_{11}$; **22** –α-$K_2ZrF_6+\alpha$-$K_3Zr_2F_{11}$; **23** –β-$K_3Zr_2F_{11}+K_7Zr_6F_{31}$; **24** –$\alpha$-$K_3Zr_2F_{11}+K_7Zr_6F_{31}$; **25** –$\alpha$-$KZrF_5+K_7Zr_6F_{31}$; **26** –$\alpha$-$KZrF_5+\alpha$-$ZrF_4$; **27** –$\beta$-$KZrF_5+\alpha$-$ZrF_4$; **28** –$\gamma$-$KZrF_5+\alpha$-$ZrF_4$.

* When the present work had been completed, a paper (9) appeared in print on the thermal stability and polymorphism of K_2ZrF_6.

In the KF–ZrF_4 system the following compounds were found: K_3ZrF_7, $K_5Zr_2F_{13}$, K_2ZrF_6, $K_3Zr_2F_{11}$, $K_7Zr_6F_{31}$, $KZrF_5$. The fluorozirconates K_3ZrF_7 and $KZrF_5$ melt congruently at temperatures of 923 and 455°, respectively. The fluorozirconates $K_5Zr_2F_{13}$ and K_2ZrF_6 are formed by peritectic reactions:

$$\mathrm{K_3ZrF_7} + \text{melt}\ (\mathrm{KF}, \mathrm{ZrF_4}) \overset{848^\circ}{\rightleftarrows} \mathrm{K_5Zr_2F_{13}},$$

$$\mathrm{K_3ZrF_7} + \text{melt}\ (\mathrm{KF}, \mathrm{ZrF_4}) \overset{585^\circ}{\rightleftarrows} \mathrm{K_2ZrF_6}.$$

The fluorozirconates $K_3Zr_2F_{11}$ and $K_7Zr_6F_{31}$ exist only in the solid state below 327 and 380°, respectively. The eutectic between KF and K_3ZrF_7 lies at 760° and 13% ZrF_4; between K_3ZrF_7 and $KZrF_5$ at 430° and 47% ZrF_4, and between $KZrF_5$ and ZrF_4 at 440° and 60% ZrF_4.

Fig. 2. Line diagrams of compounds in the KF–ZrF_4 system

Several modifications were found for the fluorozirconate K_2ZrF_6 (Fig. 3). The transformations of K_2ZrF_6 may be represented by the scheme:

$$\alpha\text{-}\mathrm{K_2ZrF_6} \xrightarrow{240^\circ} \beta\text{-}\mathrm{K_2ZrF_6} \xleftarrow[130^\circ]{} \gamma\text{-}\mathrm{K_2ZrF_6} \xrightarrow{298^\circ}$$

$$\gamma\text{-}\mathrm{K_2ZrF_6} \overset{445^\circ}{\rightleftarrows} \delta\text{-}\mathrm{K_2ZrF_6} \overset{585^\circ}{\rightleftarrows} \text{liquid} + \mathrm{K_3ZrF_7}.$$

The fluorozirconate $KZrF_5$ undergoes polymorphic transformations at 400 and 424°. The fluorozirconate of composition $K_3Zr_2F_{11}$ undergoes a polymorphic transformation at 313°. K_3ZrF_7 has one modification, crystallizing in a face-centered cubic lattice

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Fig. 3. Line diagrams of the α, β, γ modifications of K_2ZrF_6

Figure 3: Fig. 3. Line diagrams of the α, β, γ modifications of K_2ZrF_6

Fig. 3. Line diagrams of the α, β, γ modifications of K_2ZrF_6

$$a = 8.966 \pm 0.003 \text{ kX}$$

and forms a solid solution with K_2ZrF_6 (in the region 73–75% KF).

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named after M. V. Lomonosov

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