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Phases of the K_2TaF_7–TaF_5 binary system

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Abstract The phase equilibria in the K_2TaF_7–TaF_5 binary system were determined up to $x_{TaF_5} = 0.5$ by means of differential scanning calorimetry. XRD diffraction analysis of solidified mixtures was performed. Besides the K_2TaF_7 and $KTaF_6$ phases, the presence of a third phase was observed, as well. It was suggested that the last phase melts incongruently.

Keywords Differential scanning calorimetry; Phase equilibrium; Tantalum.

Introduction

In the binary KF–TaF_5 system the formation of several related compounds, $KTaF_6$, K_2TaF_7, and K_3TaF_8, was reported.

The structure of $KTaF_6$ was described by *Bode* and *Döhren* [1]. The isolated $\{TaF_6\}$ complex anions were identified as having a distorted bi-pyramid geometry. *Range* [2] denoted the high-temperature modification as α-$KTaF_6$, room temperature modification as β-$KTaF_6$ and low-temperature modification as γ-$KTaF_6$. The melting point of $KTaF_6$, $t_m = 512$°C, was published for the first time by *Zui Bin-Sin et al.* [3].

The structure of K_2TaF_7 was investigated for the first time by *Hoard* [4] and it consists of K^+ cations and isolated $\{TaF_7\}$ complex anions. The polyhedron $\{TaF_7\}$ is defined as a trigonal prism with 6 fluorine atoms at its vertices. The seventh fluorine atom is situated above the centre of the rectangular face of prism. Almost the same results were reported by *English et al.* [5] and *Torardi et al.* [6]. A reversible phase transition at about 200°C was reported by *Agulyansky et al.* [7]. The structure of the β-phase at 236°C was reported by *Langer et al.* [8].

The structure of K_3TaF_8 compound was discussed by *Kuznetzov et al.* [9] based on the similarities with the structure of K_3NbF_8 studied previously [10, 11]. Surprisingly, even although this compound was mention in literature many times [3, 12–16] no relevant data on its structure were given. K_3TaF_8 is a congruently melting compound; however the reported temperature of melting differs in the range 776–780°C [3, 12, 14, 17].

The phase diagram of KF–K_2TaF_7, also considering the formation of K_3TaF_8, was studied relatively often [3, 12–16] and critically revised by *Boca et al.* [17]. The later authors concluded that K_2TaF_7 melts incongruently at the temperature $t_p = 743$°C.

The phase diagram of the K_2TaF_7–TaF_5 system has not been reported so far while the phase diagrams of the NbF_5–MF (M = Li, Na, and K) [11] and NbF_5–MF (M = Cs and Rb) [18] system were reported.

In the present work the phase diagram of the K_2TaF_7–TaF_5 binary system was investigated up to $x_{TaF_5} = 0.50$ by means of differential scanning calorimetry. The aim was to spread the knowledge on phase equilibria in the more acidic region towards to TaF_5 of the general system KF–TaF_5.

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Results and discussion

Temperatures of particular thermal effects for certain compositions are summarised in Table 1.

Table 1 Temperatures of endothermic effects in the K_2TaF_7–TaF_5 binary system

$x_{K_2TaF_7}$	x_{TaF_5}	t/°C				
1	0	215		692	737	778
0.9648	0.0352	215	477	692	736	761
0.9337	0.0663	215	477	690	734	744
0.927	0.073	215	476	692		728
0.8999	0.1001	214	469	690		708
0.8487	0.1513	213	461			678
0.8005	0.1995	213	473			660
0.7481	0.2519	213	464			638
0.6995	0.3005	212	465			601
0.6494	0.3506	208	468			582
0.5994	0.4006		464			510
0.55	0.45		461			490
0.50	0.5					512

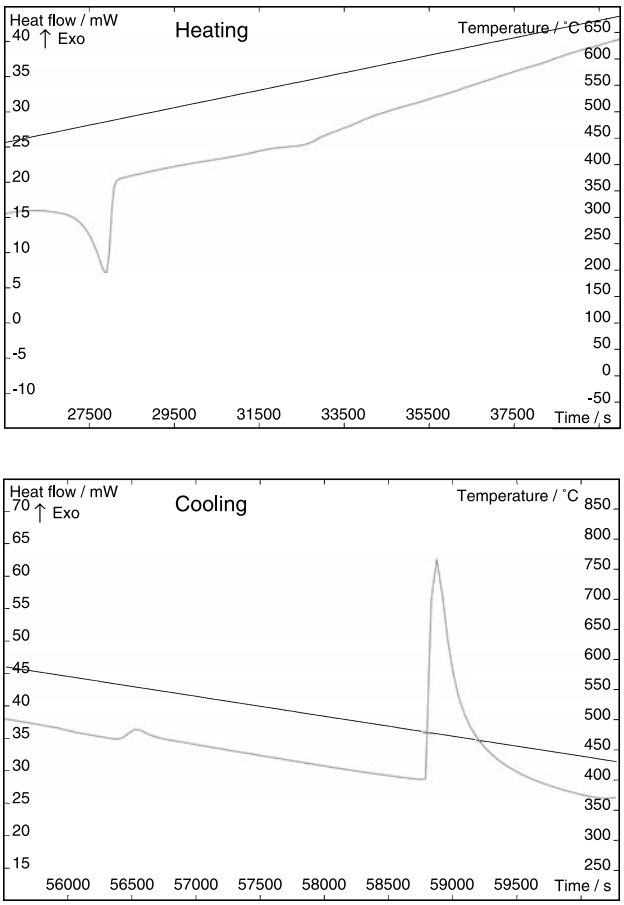

Fig. 1 Heating and cooling part of representative DSC curve for the K_2TaF_7–TaF_5 ($x_{TaF_5} = 0.3506$)

A representative DSC curve is shown on Fig. 1.

Two endothermic effects were observed for the K_2TaF_7–TaF_5 system in the composition range $x_{TaF_5} = 0.1513 - 0.45$ on the heating curve as well as two corresponding exothermic effects on the cooling part in the temperature range 680–450°C. The first one is attributed to the primary crystallisation and the second one to eutectic crystallisation. For the sample $KTaF_6$ ($x_{TaF_5} = 0.50$) only one thermal effect was observed corresponding to the melting of pure compound. Reported melting point of $KTaF_6$ is 512°C [3] which corresponds to our observation.

The most complicated part of the system is the K_2TaF_7-rich side. Complications arise from the fact that K_2TaF_7 does not melt congruently. As reported previously thermal effects at $t = 743$ and 691°C are connected with the incongruent melting of K_2TaF_7 and solid-solid phase transition of K_2TaF_7, respectively [17, 19]. Comparing the enthalpies of corresponding thermal effects, the highest value of enthalpy (15.9 kJ mol^{-1}) was achieved for the thermal effect at $t = 737$°C. Comparable but lower value (10.3 kJ mol^{-1}) had the thermal effect at $t = 778$°C. The lowest enthalpy (1.8 kJ mol^{-1}) was achieved for $t = 692$°C. Effects connected with melting of pure K_2TaF_7 are present on phase diagram up to $x_{TaF_5} = 0.8999$.

The eutectic temperature was evaluated to the value $t = 469$°C. Composition of eutectic point lies close to the $x_{K_2TaF_7} = 0.55$, however the exact value could not be calculated due to the lack of experimen-

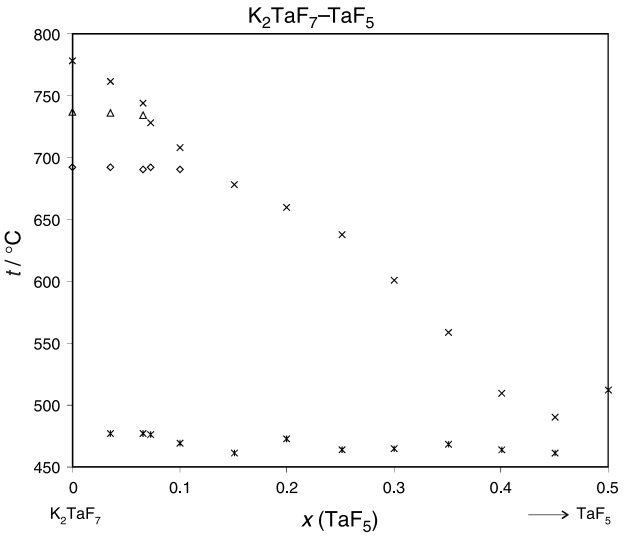

Fig. 2 Temperatures of thermal effects in the K_2TaF_7–TaF_5 binary system in the temperature range (450–800) °C

tal data. In principle, this calculation can be provided for example by the Tamman method using at least five points of composition and enthalpy data. However, in our case only two experimental points are available on the right side.

Temperatures of all observed thermal effects in the investigated binary system are shown in Fig. 2.

These points clearly show the outlines of the phase diagram, even if it was not optimised due to the lack of thermodynamic data of all presented phases (see below).

For identification of the present phases, XRD analysis of the solidified samples was performed. XRD diffraction patterns of selected samples comprising all important regions of the binary system are shown in Fig. 3.

For pure K_2TaF_7 the presence of only one phase was observed (PDF No. 2/84-1255) after ''recrystallisation''. On the other side of the phase diagram the presence of pure $KTaF_6$ was observed (PDF No. 2/51-1743) as was expected. In the region between these two boundary compounds the presence of two phases can be expected for a binary system in any point. In fact, in the concentration range of $x_{TaF_5} = 0.0663 - 0.45$ in the solidified mixtures three phases were observed, K_2TaF_7, $KTaF_6$, and a new phase which could not be identified comparing with the international X-ray diffraction database (PDF-2).

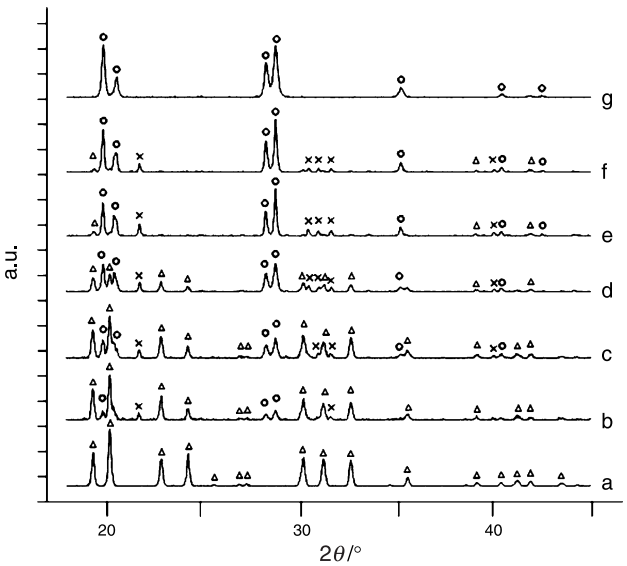

Fig. 3 XRD diffraction patterns of the solidified K_2TaF_7–TaF_5 mixtures; Δ – K_2TaF_7, ○ – $KTaF_6$, × – new phase; a – K_2TaF_7, b – $x_{TaF_5} = 0.0663$, c – $x_{TaF_5} = 0.20$, d – $x_{TaF_5} = 0.35$, e – $x_{TaF_5} = 0.40$, f – $x_{TaF_5} = 0.45$, g – $x_{TaF_5} = 0.50$

With the increasing content of TaF_5, intensity of K_2TaF_7 XRD diffraction patterns decreases and intensity of the $KTaF_6$ XRD diffraction patterns increases. Maximum intensity of new phase appeared in the concentration range $x_{TaF_5} = 0.35 - 0.40$. The presence of the last phase together with the shape of the phase diagram indicate that this phase melts incongruently, however there is no explanation as to why all three phases are present in the mentioned concentration region.

Experimental

For preparation of samples, the following chemicals were used: K_2TaF_7 (prepared at the Institute of Chemistry and Technology of Rare Elements and Minerals, RAS, Apatity-Russia; min. 99.5%) and TaF_5 (AlfaAesar, 99.9%). K_2TaF_7 was dried in vacuum at 130°C for 24 h. Handling of all salts was done in a glove box under dry argon atmosphere (Messer, 99.99%).

The thermal effects in the K_2TaF_7–TaF_5 system were determined by means of differential scanning calorimetry using a Setaram DSC 121. The experimental device was calibrated by the so-called ''*Joule* effect''. Calibration was performed by measurements of temperatures and enthalpies of phase transitions of standard substances (indium, tin, lead, silicon). Each sample, approximately 200 mg in mass was placed into the standard inconel crucible. Each experiment consisted of at least two heating and cooling cycles. Experimental thermograms were recorded at different rates (1–5°C/min) in the temperature range 30–820°C. Constant flow of argon was adjusted during each experiment. Temperature monitoring and data processing were computer-operated. For temperature and enthalpy determination the Setaram Setsoft software was used to process experimental thermograms. Temperatures indicated in the Table 1 were obtained from the experiments with the heating rate 1°C/min.

After DSC experiments the samples were opened and the present phases were identified by XRD analysis by a Stoe Stadi P transmission diffractometer equipped with a curved Ge (111) monochromator placed in the primary beam and a linear PSD. In order to achieve a better resolution the CoK_α radiation was used. The records were taken in the 2θ range 7–70° at room temperature, each for two hours.

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