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PHASE DIAGRAM OF THE SYSTEM KF–K_2TaF_7–Ta_2O_5

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The phase diagrams of the binary system Ta_2O_5–K_2TaF_7 and the ternary system KF–Ta_2O_5–K_2TaF_7 were determined using the thermal analysis method. The system Ta_2O_5–K_2TaF_7 was measured up to 25 mol% of Ta_2O_5. Eutectic point is estimated to be at $x_{Ta_2O_5}$=0.14 and t=601°C. Crystallization of K_2TaF_7, $K_2Ta_2O_3F_6$ and a new phase was identified. The new phase shows isomorphism with $K_3Nb_2F_{11}O$. In the ternary system four nonvariant equilibria points at 3 mol% of Ta_2O_5, 72 mol% of KF and 25 mol% of K_2TaF_7 at 715(1)°C; 6 mol% of Ta_2O_5, 44 mol% of KF and 50 mol% of K_2TaF_7 at 603(2)°C; 1 mol% of Ta_2O_5, 22 mol% of KF and 77 mol% of K_2TaF_7 at 704(1)°C and 8 mol% of Ta_2O_5, 8 mol% of KF and 84 mol% of K_2TaF_7 at 580(1)°C were proposed. Crystallization fields of KF, K_2TaF_7, K_3TaF_8, K_3TaOF_6, $K_4Ta_2OF_{12}$ and $K_2Ta_2O_3F_6$ were considered.

Keywords: *K_2TaF_7, molten salts, non-variant point, phase diagram, Ta_2O_5*

Introduction

Tantalum is metal with extraordinary high resistance against the corrosion. It is used widely, in the form of metal coatings and alloys in the process industry, chemical machinery and the automotive industry. The major consumer of tantalum is the capacitor production industry. Tantalum compounds have wide application, as well. Pure oxides are used in the optical industry as additives and deposits. $LiTaO_3$ is important compound as it is produced in the form of single crystal wafer and is used for production of optoelectronic and acoustoelectronic devices and infrared sensors [1, 2].

Production of tantalum from molten salts requires knowledge of phase diagrams. Recently, the phase diagram of KF–K_2TaF_7 was reinvestigated. On K_2TaF_7 rich side the existence of two immiscible liquids was proposed [3]. This was further supported by DSC and neutron scattering experiments [4]. The phase diagram of KF–Ta_2O_5 was reinvestigated, as well [3]. Significant differences were found between previously published data. Based on these differences the demand of reinvestigation of K_2TaF_7–Ta_2O_5 and KF–Ta_2O_5-K_2TaF_7 phase diagrams aroused as legitimate task.

We are aware of only one phase diagram of the binary system K_2TaF_7–Ta_2O_5 [5]. This system was investigated up to 27.5 mol% of tantalum oxide. Reported eutectic point is at 16.5 mol% of Ta_2O_5 and 580°C.

Two reports of the partially measured ternary system can be found in literature. In the first one the eutectic point at 7 mass% (2.3 mol%) of Ta_2O_5, 30 mass% (74.5 mol%) of KF and 63 mass% (23.2 mol%) of K_2TaF_7 and 772°C was reported [6]. The alternative eutectic point was reported at 2.0 mol% of Ta_2O_5, 77.5 mol% of KF and 20.5 mol% of K_2TaF_7 and 718°C [5]. The same authors reported also peritectic point at 4.5 mol% of Ta_2O_5, 87 mol% of KF and 8.5 mol% of K_2TaF_7 and 764°C. The topology of the above phase diagram is not clear due to the uncertainty in the *X*-axis. The compound KF·K_2TaF_7 must lie in the middle of the axis when the composition is expressed in mole%.

The aim of this work was to measure parts of the phase diagram of the binary system K_2TaF_7–Ta_2O_5 and the ternary one KF–K_2TaF_7–Ta_2O_5 to verify or correct reported data similarly, as was done for KF–K_2TaF_7 and KF–Ta_2O_5 systems [3]. Another motivation in obtaining precise data for this system is its potential in electrochemical production of tantalum.

Experimental

The following chemicals were used for preparation samples: KF (Fluka, 99.5%), Ta_2O_5 and K_2TaF_7 (prepared at the Institute of Chemistry and Technology of Rare Elements and Minerals, RAS, Apatite–Russia; min. 99.5%), NaCl (Fluka, 99.9%), KCl (Merck, 99.5%). KF and K_2TaF_7 were dried under vacuum at 130°C for 24 h. Handling of all salts was done in a glove box under dry nitrogen atmosphere (Messer, 99.99%).

The temperatures of individual phase transitions were determined by means of thermal analysis method. A platinum crucible containing 10.00±0.01 g of the

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sample was placed into a resistance furnace filled by Ar atmosphere (Messer, 99.996%). The temperature was measured using Pt–PtRh10 thermocouples calibrated to the melting points of NaCl and KCl. The thermocouple was connected to 24 bits A/D converter and linked to the computer. The operating program was developed in the Lab View environment. The cooling and heating curves of the investigated mixtures were recorded at the rate of 2–3°C min^{-1}.

X-ray powder diffraction patterns of solidified samples were collected on Stoe Stadi P transmission diffractometer equipped with a curved Ge (111) monochromator placed in primary beam and a linear PSD. In order to achieve better resolution CoKα radiation was used. The records were taken in the 2θ range of 7–90° at room temperature each for 2 h.

Results and discussion

System K_2TaF_7–Ta_2O_5

The phase diagram of the system K_2TaF_7–Ta_2O_5 was investigated only up to 25 mol% of tantalum oxide due to the high temperature of primary crystallization of a crystallising phase.

Optimization of this phase diagram using a thermodynamic model is unfeasibly due to the lack of thermodynamic data as corresponding enthalpies of particular components identified by XRD experiments are not available. A schematic interpretation of the partial phase diagram of the investigated system is shown in Fig. 1.

From this figure it is evident that the investigated system represents the cross-section of reciprocal system KF–TaF_5–Ta_2O_5–K_2O. On K_2TaF_7 rich side the eutectic point is estimated to be at $x_{Ta_2O_5}=0.14$ and t=601°C based on measured data. However, the eutectic composition and eutectic temperature do not correspond to phases reported earlier [5].

From the XRD patterns of the solidified samples it follows that on K_2TaF_7 rich side the only crystallizing phases are K_2TaF_7 and $K_2Ta_2O_3F_6$, respectively, up to 14 mol% of Ta_2O_5. At this composition a new phase starts to occur. Any compound based on tantalum can be assigned to this phase from PDF-2 database. However, topology of the diffraction pattern is very close to the diffraction pattern of $K_3Nb_2F_{11}O$ [7]. Thus it can be expected that a new tantalum structural isomorph phase exists, up to now non-characterized. This statement/assumption comes from the fact that many examples of tantalum–niobium structural isomorphs can be found in the literature, e.g. $KTaF_6$–$KNbF_6$ [8, 9], K_2TaF_7–K_2NbF_7 [10], K_3TaOF_6–K_3NbOF_6 [11, 12], $CsTa_2O_5F$–$CsNb_2O_5F$ [13, 14] etc. A representative XRD record of the sample for $x_{Ta_2O_5}=0.10$ is shown in Fig. 1. Over 20 mol% of Ta_2O_5 the presence of only $K_2Ta_2O_3F_6$ phase together with the new one was observed.

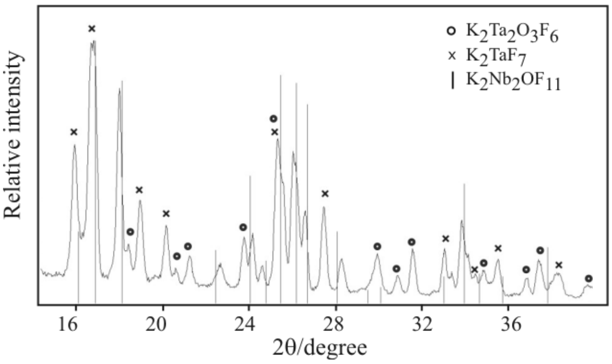

Fig. 1 A representative XRD record of the sample $x_{Ta_2O_5}=0.10$

It should be noted that high temperature region of the phase diagram up to cca. 8 mol% of Ta_2O_5 shows similar characteristics as the phase diagram of KF–K_2TaF_7 up to cca. 10 mol% of KF [3, 4]. Three thermal effects correspond to different phase transitions. The first one around 690°C corresponds to the solid-solid phase transition of K_2TaF_7. Based on DSC measurements [4] it was suggested that K_2TaF_7 possess phase transformation at 703°C. This assumption was supported by the neutron powder diffraction experiments, as two rather different patterns were recorded for K_2TaF_7 at 654 and at 710°C, respectively [4]. The thermal effect at 746°C was attributed to the incongruent decomposition of K_2TaF_7 into two immiscible melts. The third thermal effect was attributed to the mixing of two melts. This conclusion was supported by the neutron diffraction pattern taken at 749°C [4].

Based on the thermal effects observed by thermal analyses with combination of XRD data and published data from DSC, neutron diffraction experiments [4] and TA experiments [3] the schematic lines of the phase diagram were drawn (Fig. 2).

In order to estimate the ‘solubility’ of Ta_2O_5 two mixtures, K_2TaF_7+30 mol% Ta_2O_5 and K_2TaF_7+ 40 mol% of Ta_2O_5, were heated at 950°C for one h under dry nitrogen atmosphere. Both cooled powdered samples contained $K_2Ta_2O_3F_6$ and mentioned new phase (probable isomorph of $K_3Nb_2F_{11}O$). Small amount of unreacted Ta_2O_5 was detected as well for the sample containing 40 mol% Ta_2O_5.

In both mixtures significant evaporation has occurred during heating (visually approximately half of the incoming material was distributed as condensed vapours throughout apparatus, see below). The vapours have condensed on top of furnace that was cooled by water. XRD pattern of collected condensed phase revealed the presence of two phases. The first one was $K_6Ta_{10.8}O_{30}$. (It should be noted that the XRD pattern of this compound overlays with the compound

Table 1 Measured temperatures of primary crystallization, (t_{PC}), and further thermal effects, (t_1, t_2, t_3), together with crystallizing phases

$x_{Ta_2O_5}$	t_{PC}/°C	t_1/°C	t_2/°C	t_3/°C	Crystallizing phase primary/other
0	778	743	710		K_2TaF_7
0.02	762	727	694		$K_2TaF_7/K_2Ta_2O_3F_6$
0.025	754	733	691		$K_2TaF_7/K_2Ta_2O_3F_6$
0.035	734	724	690	546	$K_2TaF_7/K_2Ta_2O_3F_6$
0.05	715		692		$K_2TaF_7/K_2Ta_2O_3F_6$
0.065	708		693	575	$K_2TaF_7/K_2Ta_2O_3F_6$
0.08	687			589	$K_2TaF_7/K_2Ta_2O_3F_6$
0.1	654			599	$K_2TaF_7/K_2Ta_2O_3F_6$, new phase
0.115	644			589	$K_2TaF_7/K_2Ta_2O_3F_6$
0.13	621			591	$K_2TaF_7/K_2Ta_2O_3F_6$
0.14	601			586	$K_2TaF_7/K_2Ta_2O_3F_6$, new phase
0.15	629	603			$K_2TaF_7/K_2Ta_2O_3F_6$, new phase
0.16		596	574		$K_2TaF_7/K_2Ta_2O_3F_6$, new phase
0.175	652	589	577		$K_2TaF_7/K_2Ta_2O_3F_6$, new phase
0.18	660	584		551	$K_2TaF_7/K_2Ta_2O_3F_6$
0.19	671	597	584	561	$K_2Ta_2O_3F_6$, new phase
0.2	700	614	589	573	$K_2TaF_7/K_2Ta_2O_3F_6$, new phase
0.25	784	685	585		$K_2Ta_2O_3F_6$/new phase

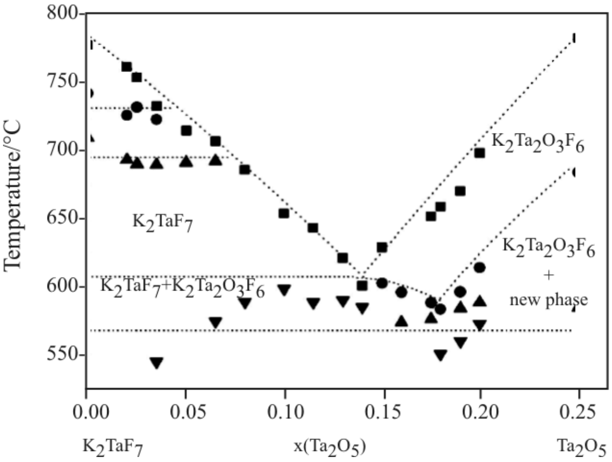

Fig. 2 The schematic phase diagram of the system K_2TaF_7–Ta_2O_5

$K_{0.4}TaO_{2.4}F_{0.6}$ ICDD 28-805.) The second identified phase could be TaF_3 or TaO_2F. Both of them are isostructural, however the presence of Ta(III) seems to be less probable thus the presence of TaO_2F seems to more reasonable.

At lower part of the furnace on the thermocouple placed just above the liquidus surface another portion of condensed vapours was reported. Measuring the cell parameters formed single crystals identified the compound $K_{12}Ta_{15.5}O_{35.5}F_{18.5}$. Consequently, the following scheme can be constructed for processes taking place in the system:

- Melting of K_2TaF_7

$$K_2TaF_7\,(s) \rightarrow 2K^+\,(l) + TaF_7^{2-}\,(l)$$

- Dissolution of Ta_2O_5

$$2K^+\,(l) + TaF_7^{2-}\,(l) + Ta_2O_5\,(s) \rightarrow$$
$$2K^+\,(l) + TaF_7^{2-}\,(l) + TaO_3^-\,(l) + TaO_2^+\,(l)$$

- Mutual reaction of ions or their dissociation and association reactions could be considered; e.g.

$$TaF_7^{2-}\,(l) + TaO_2^+\,(l) \rightarrow TaF_6^-\,(l) + TaO_2F(l \text{ or } g)$$

$$TaO_3^-\,(l) + TaF_6^-\,(l) \rightarrow Ta_2O_3F_6^{2-}\,(l)$$

and others.

- Consequent processes providing $K_2Ta_2O_3F_6$ in liquid and evolution of gaseous phases

$$2K^+\,(l) + TaF_6^-\,(l) + TaO_3^-\,(l) + TaO_2F(l) \rightarrow$$
$$K_2Ta_2O_3F_6\,(l) + TaO_2F(l \text{ or } g)\ t=950℃$$

- Next processes can be associated with further evaporation providing other phases that crystallise on different part of apparatus depending on temperature

$$K_2Ta_2O_3F_6\,(l) \rightarrow K_2Ta_2O_3F_6\,(g)$$

$$K_2TaF_7\,(l) \rightarrow K_2TaF_7\,(g)$$

$$K_2TaF_7\,(g) + K_2Ta_2O_3F_6\,(g) + TaO_2F(g) \rightarrow$$
$$xK_{12}Ta_{15.5}O_{35.5}F_{18.5}\,(s) + yK_6Ta_{10.8}O_{30}\,(s) + zTaO_2F(s)$$

Surprisingly the phase $KTaO_3$ was not identified thus the processes discussed in [3] for the binary $KF–Ta_2O_5$ probably does not take place.

System $KF–Ta_2O_5–K_2TaF_7$

Because of the limited solubility of tantalum oxide at measured temperature intervals in remaining components; the phase diagram was measured up to 8 mol% of Ta_2O_5 close to KF side and up to 20 mol% of Ta_2O_5 on K_2TaF_7 side. Moreover, the situation in the ternary system is similar as in the above binary one. It means that at this stage of knowledge it is unfeasible to calculate the phase diagram as thermodynamic data of identified phases are not accessible. However, at least a sketch of the phase diagram is shown in Fig. 3 based on measured temperatures of primary crystallization and XRD data. All temperatures of any thermal effects together with identified phases in cooled powdered samples are summarized in Table 2.

As it can be seen from Fig. 3 the crystallization field of the compound K_3TaF_8 is situated between crystallization fields of KF and K_2TaF_7 [3]. For identification of this phase own XRD record of the pure

Table 2 Measured temperatures of primary crystallization, (t_{PC}), and further thermal effects, (t_1, t_2, t_3), together with crystallizing phases

$x_{Ta_2O_5}$	$x_{K_2TaF_7}$	t_{PC}/°C	t_1/°C	t_2/°C	t_3/°C	Crystallizing phase
0.02	0.2	758	745			K_3TaOF_6
0.05	0.19	771	731	710	660	K_3TaOF_6
0.08	0.185	805	744			K_3TaOF_6
0.1	0.18	832				K_3TaOF_6
0.02	0.395	762	717			K_3TaOF_6
0.05	0.38	788				$K_3TaOF_6/K_4Ta_2OF_{12}$
0.08	0.37	775				$K_3TaOF_6/K_4Ta_2OF_{12}$
0.1	0.36	774				
0.02	0.49	751				$K_3TaOF_6/K_4Ta_2OF_{12}$
0.05	0.475	755	648			
0.08	0.46	764	746			
0.1	0.45	750	620			
0.02	0.59	737				K_3TaOF_6/K_2TaF_7
0.05	0.57	749	731	693	644	$K_3TaOF_6/K_4Ta_2OF_{12}$
0.08	0.555	745	704			
0.1	0.54	712	603			
0.02	0.785	730	714	703		K_3TaOF_6/K_2TaF_7
0.05	0.76	749	720			
0.08	0.735	699	695	598		
0.1	0.72	689	594			
0.05	0.1	826	786	774		K_3TaOF_6
0.05	0.15	838	781	756	714	
0.05	0.3	808	795	728		K_3TaOF_6
0.1	0.3	799				$K_3TaOF_6/K_4Ta_2OF_{10}$
0.05	0.4	758	752			$K_3TaOF_6/K_4Ta_2OF_{12}$
0.15	0.425	660	608	597		$K_3TaOF_6/K_2Ta_2O_3F_6/K_2TaF_7$
0.15	0.45	673	596			$K_3TaOF_6/K_2Ta_2O_3F_6/K_2TaF_7$
0.15	0.51	662	628	620	597	$K_6Ta_{6.5}O_{14.5}F_{9.5}$/ $K_3TaOF_6/K_2Ta_2O_3F_6$
0.05	0.65	815	743	726	717	
0.15	0.6	603	597			
0.05	0.85	649	617	606	599	
0.1	0.8	686	602	579		
0.15	0.75	688	668	653	619	
0.15	0.68	603	598	596		

Table 3 Non-variant equilibrium points in the ternary system

No.	T/°C	$x_{K_2TaF_7}$	x_{KF}	$x_{Ta_2O_5}$	Ref.
1	715	0.25	0.72	0.03	this work
2	603	0.50	0.44	0.06	this work
3	704	0.77	0.22	0.01	this work
4	580	0.84	0.08	0.08	this work
	718	0.205	0.775	0.02	[5]
	764	0.085	0.87	0.045	[5]
	772	0.232	0.745	0.023	[6]

K_3TaF_8 was used as any XRD pattern is accessible in the PDF-2 database. All other phases, K_3TaOF_6, $K_4Ta_2OF_{12}$ and $K_2Ta_2O_3F_6$, were identified based on the XRD records in PDF-2 database.

The four non-variant equilibrium points come from corresponding binary phase diagrams. Four non-variant equilibria in the ternary system have been proposed based on the extrapolation of the experimental data. Their coordinates are summarized in Table 3. These results are somewhat different in comparison with published data [5, 6]. The non-variant point No. 1 is closer in composition to the same point reported in [6] than in [5], however the temperature 715 corresponds better to 718°C reported in [5] in contrary to the temperature 772°C reported in [6]. The non-variant points No. 2–4 have not been presented so far. Much more serious differences in the present and reported data can be found when considering the occurrence of different phases. Existence of the compounds $K_2TaO_2F_3$ [5] or $KTaOF_4$, K_2TaO_3F [15] reported in literature seem to be highly improbable, as these compounds have never been detected by neither XRD experiments. Instead, the presence of $K_4Ta_2OF_{12}$ and $K_2Ta_2O_3F_6$ is suggested. The common features of literature and present work is the presence of K_3TaF_8 [5, 15] and K_3TaOF_6 [15] compounds.

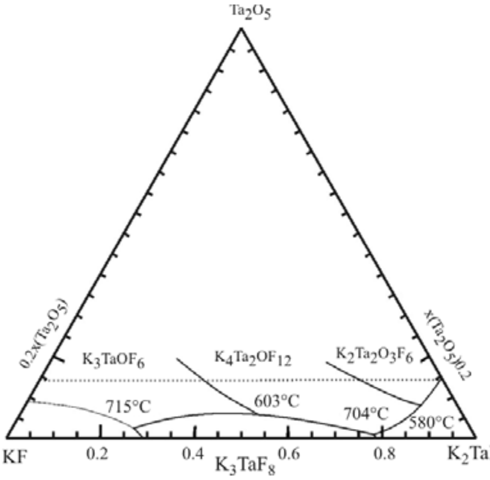

Fig 3 The schematic phase diagram of the system KF–K_2TaF_7–Ta_2O_5

Acknowledgements

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