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Short communication

Determination of the enthalpy of fusion of K_3TaF_8 and K_3TaOF_6

L. Kosa*, I. Macková

Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-845 36 Bratislava, Slovakia

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Abstract

The areas of the fusion and crystallization peaks of K_3TaF_8 and K_3TaOF_6 have been measured using the DSC mode of the high-temperature calorimeter (SETARAM 1800 K). On the basis of these quantities and the temperature dependence of the used calorimetric method sensitivity, the values of the enthalpy of fusion of K_3TaF_8 at temperature of fusion 1039 K: $\Delta_{\text{fus}}H_{\text{m}}(K_3TaF_8;\ 1039\ \text{K}) = (52 \pm 2)\ \text{kJ mol}^{-1}$ and of K_3TaOF_6 at temperature of fusion 1055 K: $\Delta_{\text{fus}}H_{\text{m}}(K_3TaOF_6;\ 1055\ \text{K}) = (62 \pm 3)\ \text{kJ mol}^{-1}$ have been determined.

Keywords: K_3TaF_8; K_3TaOF_6; Enthalpy of fusion; High-temperature calorimeter

1. Introduction

The compounds K_3TaF_8 and K_3TaOF_6 are formed in the ternary system K_2TaF_7–KF–Ta_2O_5 that was investigated together with its binary subsystems by several authors. However, no calorimetric data of these title compounds have been reported so far.

The K_2TaF_7–KF system was studied in Refs. [1–4]. In this system, the congruently fused compound K_3TaF_8 with dystectic melting point at 1049 K [1,3] or at 1053 K [4] was reported.

The authors of Refs. [2,5,6] studied a part of the ternary K_2TaF_7–KF–Ta_2O_5 system. The field of the primary crystallization of K_3TaOF_6, besides the fields of KF, K_3TaF_8 and K_2TaF_7 was described. The fusion temperature of K_3TaOF_6 at 1079 K is referred in Ref. [6]. In Ref. [7] the temperature of phase transition and the temperature of fusion of K_3TaOF_6 are given to be (310 ± 10) and (1090 ± 10) K, respectively. The crystallographic characteristics of K_3TaOF_6 and the line positions in its X-ray diffraction pattern can be found in Ref. [8].

The aim of this work was to determine the enthalpy of fusion of K_3TaF_8 and K_3TaOF_6 on the high-temperature calorimeter, SETARAM HTC 1800 K as the value of this quantity for these compounds has not been determined experimentally, yet.

2. Experimental

K_2TaF_7, KF and Ta_2O_5 have been used as the starting compounds for the preparation of K_3TaF_8 and K_3TaOF_6. K_2TaF_7 (minimum 99 wt.%) and Ta_2O_5 (minimum 99.5 wt.%) were prepared at the Institute of Chemistry and Technology of Rare Elements and Minerals, RAS, Apatite (Russia). Their purity was verified by the X-ray diffraction analysis. The purity of KF (Fluka) was 99.5 wt.%. All three compounds were dried in vacuum at temperature about 453 K and kept in a dry box.

K_3TaF_8 was prepared by heating of equimolar mixture of K_2TaF_7 and KF at 1173 K. The mixture was weighed in a dry box into a specially arranged platinum crucible with a lid (both from $Pt_{90}Rh_{10}$ material) sealed to it by platinum. The small hole for loading of the sample into the crucible was closed by platinum wire and soldered using gold. The tightness of the crucible was tested by repeated weighing after its heating at temperature 1173 K (at this temperature the sample was melted) during 3 h. The purity of K_3TaF_8 was verified only after calorimetric measurements by X-ray powder diffraction analysis. As the diffraction patterns of K_3TaF_8 are not available in the PDF-2/2003 database, its presence in the prepared sample was deduced only from comparison of the X-ray diffraction pattern of the sample with those of the initial K_2TaF_7 and KF components. In the powder record neither patterns of KF nor patterns of K_2TaF_7 were detected. Only the pattern that does not belong to any relevant compound in the PDF-2 database was observed.

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* Corresponding author.
E-mail address: uachkosa@savba.sk (L. Kosa).

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The sample of K_3TaOF_6 was synthesized on the basis of the stoichiometric equation [6,7,9]

$$3K_2TaF_7 + Ta_2O_5 + 9KF = 5K_3TaOF_6 \qquad (A)$$

by heating the mixture of the initial compounds at temperature of 1173 K during 30 min in an open Pt crucible under Ar atmosphere. Its X-ray powder pattern showed the line positions which are coincident with the line positions in the X-ray powder pattern of the K_3TaOF_6 given in the database. The sample of K_3TaOF_6 was dried at 523 K and sealed into the specially arranged Pt crucible, described above. The tightness of the crucible was verified by weighing after its heating at 1173 K for 3 h. No mass changes were observed.

The enthalpies of fusion of K_3TaF_8 and K_3TaOF_6 were determined using the high-temperature calorimeter, the SETARAM HTC 1800 K, working in DSC mode. In this mode, the temperature and the temperature difference between two crucibles of the calorimetric cell were recorded at a constant rate of the temperature change. The measurements were carried out at the rate of 1 K min^{-1}. The experimental data processing is based on the assumptions discussed in Ref. [10].

Note: Neither cited authors nor our effort provided suitable single crystals to determine the exact structures of the title compounds.

3. Results and discussion

From the measured data on the curves of time dependence of the temperature difference between the crucibles with the studied (X) and reference substances, the areas of the fusion and crystallization peaks were evaluated ($A_{\mathrm{fus}}(\mathrm{X})$ and $A_{\mathrm{cryst}}(\mathrm{X})$, respectively) (X is K_3TaF_8 or K_3TaOF_6). The values of arithmetic means (symbol Φ) of these quantities (from five measurements) and the errors of their determination are presented in Table 1.

The errors of arithmetic means of these quantities were calculated considering the Student distribution on the reliability level $(1-\alpha) = 0.95$.

The measured numeric value of the peak area of phase change of the pertinent substance depends on the specific enthalpy of phase change (Δh), on the mass of the sample (m) as well as on the temperature of the phase change. Using the symbol "trans" as the common symbol for fusion and crystallization we can express the relation between the individual quantities in the form

$$\frac{A_{\mathrm{trans},\Phi}(\mathrm{X})}{m(\mathrm{X})} = \varepsilon_{\mathrm{trans}}\,\Delta_{\mathrm{trans}}h(\mathrm{X}) \qquad (1)$$

The coefficient of proportionality $\varepsilon_{\mathrm{trans}}$, i.e. the sensitivity of the calorimetric method, is a function of the temperature. At the pertinent process this coefficient represents the ratio of the peak area (expressed in K s) and the heat effect (expressed in J). The temperature dependence of $\varepsilon_{\mathrm{trans}}$ was determined in our earlier work [11] in the interval of 607–1342 K:

$$\varepsilon_{\mathrm{trans}}/(\mathrm{K\,s\,J^{-1}}) = (14.156 \pm 0.190) - (7.881\times10^{-3} \pm 1.79\times10^{-4})T/\mathrm{K} \qquad (2)$$

The negative sign of the coefficient at T expresses the decrease of the calorimeter sensitivity with the increasing temperature.

The "mean temperatures" (T_Φ) of the fusion and crystallization peaks of K_3TaF_8 and K_3TaOF_6 as well as the pertinent values of ε calculated according to Eq. (2) are summarized in Table 1. This table presents also the values of the change of specific enthalpy of fusion and crystallization of K_3TaF_8 and K_3TaOF_6 ($m(K_3TaF_8) = 0.2476$ g and $m(K_3TaOF_6) = 0.2516$ g) calculated according to Eq. (1).

The errors of determination of the specific enthalpy of fusion and crystallization of K_3TaF_8 and K_3TaOF_6 were calculated from the errors of determination of the arithmetic mean of peak areas of fusion and crystallization and from $\sigma(\varepsilon)$, using Gauss' law of errors propagation.

The values of the specific enthalpy of fusion and crystallization of K_3TaF_8 correspond to each other. The mean value of the temperature of the beginning of fusion from the five measurements was determined at 1039 K (it differs from the mean temperature of the peak of 1052 K). Analogously, the values of the specific enthalpy of fusion and crystallization of K_3TaOF_6 correspond to each other, as well. The mean value of the temperature of the beginning of fusion was determined at 1055 K.

The values of molar enthalpy of fusion of K_3TaF_8 and K_3TaOF_6 at temperatures of fusion are

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_3TaF_8;\ 1039\,\mathrm{K}) = (52 \pm 2)\,\mathrm{kJ\,mol^{-1}} \qquad (3)$$

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_3TaOF_6;\ 1055\,\mathrm{K}) = (62 \pm 3)\,\mathrm{kJ\,mol^{-1}} \qquad (4)$$

The temperature dependence of the specific enthalpy of fusion and crystallization of K_3TaF_8, and K_3TaOF_6 was omitted. The calculated value of the temperature change of specific enthalpy of fusion of K_3TaF_8 was 1.01 J g^{-1} (using Kirchhoff's law for calculation of change of specific enthalpy of fusion on temperature and Neumann–Kopp's rule for calculation of heat capacities of crystalline K_3TaF_8 and its melt using the heat capacities of KF and K_2TaF_7 taken from [12,13]). This value is considerably lower than the value of the error of determination of the specific enthalpy of fusion of K_3TaF_8 given in Table 1. Analogous

Table 1
The values of arithmetic means of peak areas of K_3TaF_8 and K_3TaOF_6 fusion (crystallization), the values of "mean temperatures" of the peaks of these processes as well as the calculated values of ε and of the change of the specific enthalpy of K_3TaF_8 and K_3TaOF_6 fusion (crystallization)

Sample (X)	Process	$A_\Phi(\mathrm{X})/(\mathrm{K\,s})$	$T_\Phi/(\mathrm{K})$	$\varepsilon/(\mathrm{K\,s\,J^{-1}})$	$\Delta h(\mathrm{X})/(\mathrm{J\,g^{-1}})$
K_3TaF_8	Fus	165 ± 6	1052	5.86 ± 0.03	114 ± 4
	Cryst	−174 ± 5	1036	5.99 ± 0.03	−117 ± 3
K_3TaOF_6	Fus	205 ± 11	1068	5.74 ± 0.03	142 ± 8
	Cryst	−218 ± 5	1056	5.83 ± 0.03	−149 ± 4

calculation for K_3TaOF_6 could not be made because its heat capacities are unknown.

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