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THERMAL PROPERTIES OF HAFNIUM(IV) AND ZIRCONIUM(IV) β-DIKETONATES

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Five volatile hafnium(IV) and zirconium(IV) β-diketonates: hafnium(IV) acetylacetonate, hafnium(IV) trifluoroacetylacetonate, hafnium(IV) pivaloyltrifluoroacetonate, hafnium(IV) 2,2,6,6-tetramethylheptane-3,5-dionate and zirconium(IV) 2,2,6,6-tetramethylheptane-3,5-dionate were obtained, purified and identified. Thermal behavior of solid compounds was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) in helium atmosphere and in vacuum. DSC method was also used for definition of thermodynamic characteristics of melting processes. Using the static method with quartz membrane zero-manometer and the flow method the temperature dependencies of saturated vapor pressure for hafnium(IV) complexes was obtained. The standard thermodynamic characteristics ΔH^0_T and ΔS^0_T of sublimation and evaporation processes were calculated from the temperature dependences of saturated vapor pressure.

Keywords: *β-diketonates, DSC, hafnium(IV), TG, thermodynamic characteristics, vapor pressure, zirconium(IV)*

Introduction

Attention to hafnium(IV) and zirconium(IV) β-diketonates is due to their intense application in MOCVD processes aimed at obtaining oxide films. Specific properties of hafnium dioxide and zirconium dioxide, such as their high dielectric constant and reasonable band gap [1–6], make them promising candidates to replacing silicon dioxide commonly used as a dielectric in microelectronics. The problem of controlling the deposition processes of film materials, however, is often solved on the basis of limited information on the precursor used [7]. For hafnium(IV) β-diketonates available information normally involves a structural study [8–12], data of the thermogravimetry and differential thermal analysis are sometimes used [9, 13–16], and there are practically no researches on the vapor pressure. At present the saturated vapour pressure data for hafnium(IV) acetylacetonate and hafnium(IV) 2,2,6,6-tetramethylheptane-3,5-dionate have been published in [16, 17]. It is extremely important, therefore, to obtain detailed information on the set of thermal properties of the initial compounds, which could form the basis for choosing the precursor and for optimizing the film-deposition regimes. The major part of the data on the thermal behavior of zirconium(IV) β-diketonates was published by us in [18, 19].

In this work, we investigated the follow volatile hafnium(IV) and zirconium(IV) β-diketonates: hafnium(IV) acetylacetonate $Hf(acac)_4$, hafnium(IV) trifluoroacetylacetonate $Hf(tfac)_4$, hafnium(IV) pivaloyltrifluoroacetonate $Hf(ptac)_4$, hafnium(IV) 2,2,6,6-tetramethylheptane-3,5-dionate $Hf(thd)_4$ and zirconium(IV) 2,2,6,6-tetramethylheptane-3,5-dionate $Zr(thd)_4$. The temperature dependence of saturated vapour pressure and thermodynamic characteristics of melting and vaporization processes were obtained for these compounds.

Experimental

The compounds were synthesized, purified and identified as described in [10–12, 20]. The compounds, not containing fluorine, were obtained by the interaction of water and alcohol solutions of metal chloride with β-diketones under heating with the subsequent addition of NaOH up to pH 5–6. The fluorinated chelates were synthesized under reflux in inert solvents. The complexes were purified by means of zone sublimation in a vacuum gradient furnace at p=1 Pa and T=393–473 K. The yield of the resulting compounds was 60–95%. Obtained compounds were identified by means of elemental analysis, IR and NMR spectroscopy, mass spectrometry, X-ray diffraction [10–12, 20, 21].

Thermogravimetric measurements were carried out in helium atmosphere using a Netzsch STA 449C Jupiter thermoanalytical equipment (flux

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rate – 30 cm^3 min^{-1}; heating rate – 5 K min^{-1}; temperature interval – 25–450°C; sample mass – 9–21 mg).

Calorimetric measurements were performed using a Setaram DSC 111 scanning calorimeter (heating rate – 0.5–1.0 K min^{-1}; sample mass – 13–25 mg) for definition of thermodynamic characteristics of melting process (*m.p.*, $\Delta_{\text{melt}}H^0_{\text{m.p.}}$). The errors in the heat effect measurements estimated from calibration experiments (C_6H_5COOH, In) were less than 1.5%. Five calorimetric experiments were performed for each investigated compounds. During the measurements the investigated substance was contained in evacuated glass ampoule.

The vapour pressure of $Hf(thd)_4$, $Hf(ptac)_4$, $Hf(tfac)_4$ was measured by the static method using a quartz membrane zero-manometer [22]. The error of the pressure measurement was 40 Pa. The error of the temperature measurement estimated from calibration against mercury, naphthalene and argon did not exceed 0.5 K. The scheme and the main characteristics of the experimental unit are described in detail in [23]. The investigated compound was loaded into the membrane zero-manometer and after evacuation it was sealed. Pressure measurements were recorded after reaching the equilibrium at a given temperature. The time of equilibrium establishment was 15–20 min. For each of investigated compounds from two to four series of measurements were performed with sample masses of 3–20 mg and different volumes of membrane vessels (V=0.012–0.071 L). Data analysis on saturated vapour shows that under the examined conditions the pressure does depend on initial concentrations, thus, at vaporization processes of these compounds the equilibriums are monovariant.

Measurement of the saturated vapour density above complexes $Hf(acac)_4$, $Hf(tfac)_4$, $Hf(ptac)_4$, $Hf(thd)_4$ was carried out using the flow method in the atmosphere of an inert carrier gas (helium). The experimental procedure was described in detail elsewhere [24]. The relative error of the method did not exceed ±5%. Calculation of the partial pressure of vapour taking into account the data on the molecular composition of the gas phase determined from the mass spectrometric investigation was performed using equation:

$$p=p_{\text{total}}n/(n+N)$$

where n is the amount of transferred substance, moles, N is the amount of the carrier gas, moles, p_{total} is total pressure in the system.

Processing of experimental data on saturated vapor pressure was performed by the method of least squares using the objective function recommended in [25]. Data are presented as the equation $\ln(p/p_0)=B-A/(T, \text{K})$, where $A=\Delta H^0_T/R$ and $B=\Delta S^0_T/R$, p_0=1 atm=760 Torr=$1.013\cdot10^5$ Pa, R is absolute gas

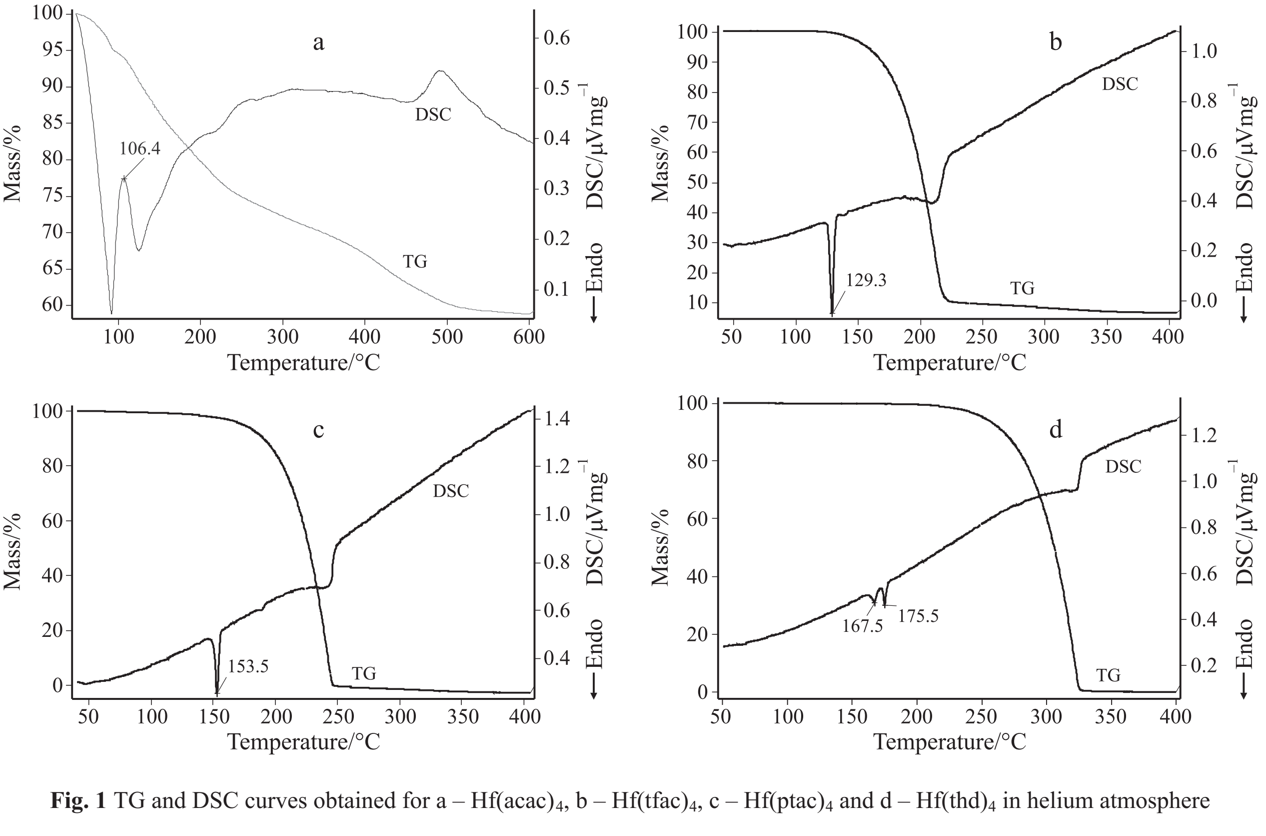

Fig. 1 TG and DSC curves obtained for a – $Hf(acac)_4$, b – $Hf(tfac)_4$, c – $Hf(ptac)_4$ and d – $Hf(thd)_4$ in helium atmosphere

constant. Calculation also took into account p and T measurements, as well as the limiting errors of pressure Δp and temperature ΔT measurements.

Results and discussion

Figure 1 shows the TG and DSC curves obtained in helium atmosphere for hafnium(IV) compounds. We succeeded in detecting the decomposition point only for Hf(acac)$_4$ complex; it is equal to 106°C (Fig. 1a). We failed to detect the decomposition temperature for Hf(thd)$_4$, Hf(ptac)$_4$, Hf(tfac)$_4$ because all three compounds are thermally stable and almost completely pass to the gas phase. A conventional range of thermal stability for the compounds looks like follows: Hf(acac)$_4$<Hf(tfac)$_4$<Hf(ptac)$_4$≈Hf(thd)$_4$, so, the most stable chelates are β-diketonate ones with *tert*-butyl substituents. The estimated volatility sequence (for 20% mass loss) is Hf(thd)$_4$<Hf(ptac)$_4$< Hf(tfac)$_4$.

Calorimetric measurements were performed in the temperature ranges of 378–408 K for Hf(tfac)$_4$, 398–433 K for Hf(ptac)$_4$, 418–633 K for Hf(thd)$_4$ and 418–633 K for Zr(thd)$_4$. The thermodynamic characteristics of the melting processes are summarized in Table 1. The samples of Hf(tfac)$_4$ and Hf(ptac)$_4$ exhibited an only phase transition (melting) over the temperature range studied. The nontrivial thermal behavior of Hf(thd)$_4$ and Zr(thd)$_4$ should be noted. These compounds melted at the enough high temperatures of 630±1 and 614±1 K with low values of enthalpy $\Delta_{\text{melt}}H^0_{630}$=5.4±0.8 kJ mol^{-1} and $\Delta_{\text{melt}}H^0_{614}$=5.7±0.3 kJ mol^{-1} relatively. The melting processes, however, are preceded by two endothermic effects. They formed a doublet for Hf(thd)$_4$ at T=433±1 and 446±1 K with the common value of enthalpy $\Delta_{\text{trans}}H^0$=15.8±1.0 kJ mol^{-1}, for Zr(thd)$_4$ – at T=438±0.5 and 446±0.5 K with $\Delta_{\text{trans}}H^0$= 11.57±0.25 kJ mol^{-1}. They are likely to correspond to solid-phase transitions because no melting was observed for the samples at these temperatures. Temperature values for these reversible solid-phase transitions correspond to the values obtained by means of DTA in [16].

For hafnium(IV) compounds, measurements of saturated vapour pressure were carried out using the static method and the flow method.

Measurement of vapour pressure of hafnium(IV) compounds with 2,2,6,6-tetramethylheptane-3,5-dione, pivaloyltrifluoroacetone and trifluoroacetylacetone in the saturated-unsaturated vapour mode according to the static procedure allowed calculating the mean molecular mass of the gas phase on the basis of the known weighed portion of the substance and the volume of the gas chamber. Obtained mean values – Hf(thd)$_4$= 934±24 g mol^{-1}, Hf(ptac)$_4$=1050±90 g mol^{-1}, Hf(tfac)$_4$= 814±24 g mol^{-1} – correspond to the molecular mass of the monomer – Hf(thd)$_4$=911.5 g mol^{-1}, Hf(ptac)$_4$= 959.1 g mol^{-1}, Hf(tfac)$_4$=790.8 g mol^{-1}. This fact was evidence of the absence of other molecular forms in the gas phase to within the accuracy specified above. These data agreed with results of our previous mass spectrometer study [21].

The data on the dependence of saturated vapour pressure of the compounds on temperature obtained using the flow method and the static method are shown in Fig. 2. Using these dependencies we calculated standard thermodynamic characteristics of enthalpy and entropy of sublimation and evaporation (Table 2). For Hf(thd)$_4$, Hf(ptac)$_4$ and Hf(tfac)$_4$, the

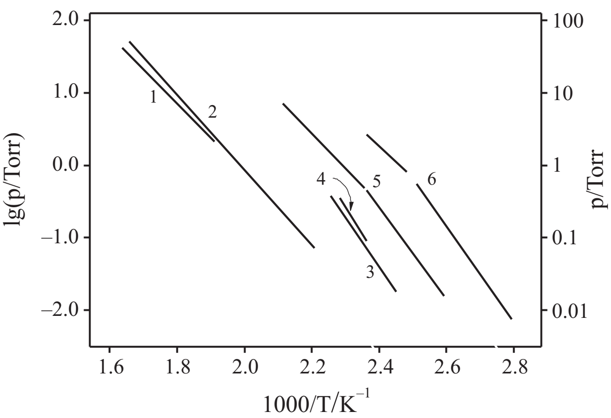

Fig. 2 Temperature dependences of the saturated vapour pressure for hafnium(IV) compounds: 1 – Hf(thd)$_4$ (lit.); 2 – Hf(thd)$_4$ (membr.+flow); 3 – Hf(acac)$_4$ (flow); 4 – Hf(acac)$_4$ (lit.); 5 – Hf(ptac)$_4$ (membr.+flow); 6 – Hf(tfac)$_4$ (membr.+flow)

Table 1 Melting points (*m.p.*) and enthalpies ($\Delta_{\text{melt}}H^0_{\text{m.p.}}$) for Hf(ptac)$_4$, Hf(tfac)$_4$, Hf(thd)$_4$ and Zr(thd)$_4$

Compound	Method			
	Calorimetry		Tensimetry	
	m.p./K	$\Delta_{\text{melt}}H^0_{\text{m.p.}}$/kJ mol^{-1}	*m.p.*/K	$\Delta_{\text{melt}}H^0_{\text{m.p.}}$/kJ mol^{-1}
Hf(tfac)$_4$	398±1	40.1±0.9	401±2	43.3±2.7
Hf(ptac)$_4$	420±1	31.0±1.0	423±2	30.3±0.9
Hf(thd)$_4$	630±1	5.4±0.8		
Zr(thd)$_4$	614±1	5.7±0.3		

Table 2 Temperature dependences of the saturated vapor pressure, enthalpy ($\Delta H^0_{T_{mean}}$) and entropy ($\Delta S^0_{T_{mean}}$) of evaporation and sublimation of hafnium(IV) complexes, normalized to the mean temperature in the examined interval

Compounds	Method	Process	Number of points	Temperature range/K	$\ln(p/p_0)\pm2\sigma=B-A/(T, \mathrm{K})$			$\Delta H^0_{T_{mean}}$/ kJ mol^{-1}	$\Delta S^0_{T_{mean}}$/ J mol^{-1}K^{-1}
					A	*B*	σ^2		
Hf(acac)$_4$	flow	subl.	8	408–443	15700	27.8	$532600/T^2-2500/T+2.9$	130.4±6.1	231±14
	[22]	subl.	3	423–438	16650	30.4		139±16	253±30
Hf(tfac)$_4$	[a]co-processing data	subl.	23	358–398	15210	31.0	$49300/T^2-254/T+0.326$	126.5±1.8	257.5±4.7
		evap.	13	403–423	10010	18.0	$61600/T^2-298/T+0.361$	83.2±2.0	149.5±5.0
Hf(ptac)$_4$	[a]co-processing data	subl.	39	386–423	14610	27.1	$9880/T^2-47.2/T+0,056$	121.5±0.8	225.3±2.0
		evap.	24	424–472	10960	18.5	$1230/T^2-5.28/T+0.006$	91.2±0.3	153.7±0.6
Hf(dpm)$_4$	[a]co-processing data	subl.	67	453–603	11930	17.1	$8280/T^2-30.2/T+0.028$	99.1±0.8	141.8±1.4
	[21]	subl.	–	523–611	10800	14.8		89.8±1.5	122.8±2.7

p_0=1 atm=760 Torr=1.013 ·10^5 Pa, [a] – co-processing data obtained by flow and static methods

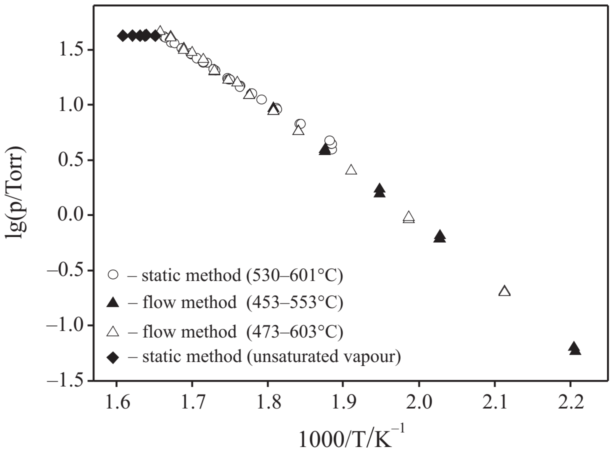

Fig. 3 Temperature dependences of the saturated vapour pressure for $Hf(thd)_4$

joint statistical processing of the experimental data obtained using two different methods (static method and flow method) was carried out.

Figure 3 shows the data on the dependence of $Hf(thd)_4$ saturated vapour pressure on temperature, obtained with the flow method (experiment included two sets of runs) and with the static method within a broad temperature range 180–340°C. One can see that saturated vapour pressure values obtained using different methods coincide with a good accuracy. Together with the data on the measurements of the pressure of unsaturated vapour of the compounds, the results thus obtained provide evidence of the high thermal stability of this complex. The co-processing data gives the equation: $\lg p=10.4–5250/T$ (temperature interval 453–603 K).

Based on the data for evaporation and sublimation processes for $Hf(ptac)_4$ and $Hf(tfac)_4$, the thermodynamic characteristics of melting of the examined compounds were calculated (Table 1). The results of calculation are in good agreement with calorimetric investigation.

In order to arrange the compounds in the volatility series, we used temperature values at the $p–T$ curves of the compounds at the same saturated vapour pressure value (p=67 Pa), changing in the following sequence: $Hf(thd)_4$ – 488 K, $Hf(acac)_4$ – 446 K, $Hf(ptac)_4$ – 424 K, $Hf(tfac)_4$ – 397 K. So, the volatility series for these compounds looks like follows: $Hf(dpm)_4<Hf(acac)_4<Hf(ptac)_4<Hf(tfac)_4$ and coincides with the qualitative volatility series composed on the basis of TG curves for hafnium(IV) β-diketonates. One can see in the data presented that the introduction of trifluoromethyl group into β-diketonates increases the volatility of the compound, which is a usual fact for this class of chelates [26].

A good coincidence between our data on saturated vapour pressure with the literature data for $Hf(acac)_4$ [17] should be stressed. For $Hf(thd)_4$, our data somewhat differ from those reported in literature [16]. However, experimental procedure and the processing of the results on saturated vapour pressure were not presented in [16].

Conclusions

Five complexes of hafnium(IV) and zirconium(IV) with different β-diketones are synthesized: hafnium(IV) acetylacetonate $Hf(acac)_4$, hafnium(IV) trifluoroacetylacetonate $Hf(tfac)_4$, hafnium(IV) pivaloyltrifluoroacetonate $Hf(ptac)_4$, hafnium(IV) 2,2,6,6-tetramethylheptane-3,5-dionate $Hf(thd)_4$, zirconium(IV) 2,2,6,6-tetramethylheptane-3,5-dionate $Zr(thd)_4$. The results reported in the present work have allowed determination of the thermodynamic characteristics of melting, evaporation and sublimation for these compounds. Investigated thermal properties showed that the chelates are volatile and thermostable compounds within a wide temperature range.

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