

Synthesis, thermal behavior and thermodynamic data of hafnium selenite tetraaqua complex dihydrate

Ginka Baikusheva-Dimitrova, Svetlana Genieva, Romyana Yankova

Assen Zlatarov University, Burgas, Bulgaria

Abstract

Data are reported about the hydrothermal synthesis, thermal behavior and the thermodynamic properties of hafnium selenite tetraaqua complex dihydrate. The compound was subjected to infrared spectroscopic analysis and the experimental data were compared to the theoretically calculated ones by the density functional theory (DFT) and analogous experimental data on zirconium selenite. By thermal decomposition, the hydrate water is released up to 110°C, above which temperature the tetraaqua complex of the hafnium selenite remains stable up to 240°C. The anhydrous hafnium selenite decomposes in the temperature interval 580–700°C, probably forming dihafnyl selenite $\text{Hf}_2\text{O}_3(\text{SeO}_3)$. Using the experimental data from the differential scanning calorimetric analysis (DSC) the specific heat capacities ($C_{p,m}$) and the thermodynamic properties ($\Delta_T^T S_m^\circ$, $\Delta_T^T H_m^\circ$, $-\Delta_T^T G_m^\circ/T$) of the initial phase and the phases formed after the thermal decomposition of the compound synthesized were calculated. The temperature dependencies of their molar heat capacities were determined by regression analysis.

Keywords: Hafnium selenite, Thermal behavior, Heat capacity, Thermodynamic properties.

1. Introduction

Among the compounds of the elements belonging to group IVB (Ti, Zr, Hf), the least studied ones are these of hafnium. Due to the lanthanide contraction, zirconium and hafnium have almost the same atomic and ionic radii which results in a strong analogy of their chemical behavior. Many hafnium compounds are used in various fields of industry. Ceramics based on hafnium (carbides, borides, nitrides) have unique properties, e.g. extremely high hardness and melting temperature, high electric and heat conductivity and high chemical stability, so they can be used as materials for manufacturing high temperature structural applications including engines, supersonic vehicles, plasma arc electrodes, cutting instruments and high temperature elements for furnaces [1]. Some hafnium compounds have specific catalytic activities;

others are important components for production of optical glass with special characteristics suitable for optoelectronics, nuclear technology and medicine [2]. So far as the structure, properties and the thermal stability are concerned, the chalcogenite compounds of hafnium (sulfites, selenites and tellurites) are not thoroughly studied. There are few data on the preparation of hafnium selenites. White crystalline substance with composition $\text{Hf}(\text{SeO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ has been obtained at room temperature in presence of 10-fold excess of selenous acid while anhydrous $\text{Hf}(\text{SeO}_3)_2$ was prepared by prolonged keeping of the main selenite in the native solution at 80–90°C [2]. Using hydrothermal synthesis, light violet crystalline phase was obtained and determined to be tetraaqua complex of hafnium selenite dihydrate $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$. The thermogravimetric analysis showed two-stage dehydration of the complex accompanied by release of two molecules of crystallization water and four coordinated water molecules. Geometric optimization of the $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]$ molecule in gaseous phase was made by the density functional theory (DFT) and the values of some thermodynamic parameters were calculated [3]. The standard thermodynamic functions entropy (S_m°), heat capacity ($C_{p,m}^\circ$) and enthalpy (ΔH_m°), for the title compound were obtained using DFT/B3LYP method with 6-31G(d) basis set and LANL2DZ for hafnium on the basis of vibrational analysis and statistical thermodynamics [4].

Knowing the thermodynamic properties specific molar heat capacity ($C_{p,m}$), enthalpy ($\Delta_T^T H_m^\circ$), entropy ($\Delta_T^T S_m^\circ$) and Gibbs energy ($-\Delta_T^T G_m^\circ/T$) are of crucial importance for the studies on the possibilities for application of the newly synthesized compounds. The specific heat capacities and the thermodynamic properties of all the phases formed by the dehydration and decomposition of the tetraaqua complex of hafnium sulfate $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ were calculated using experimental data from the DSC and, furthermore, the temperature

dependencies of their molar heat capacities were determined by regression analysis [5].

There are no data in the available literature on the specific molar heat capacities and the thermodynamic properties of hafnium selenite. The thermodynamic parameters calculated for this compound were compared to the theoretically calculated ones by DFT.

2. Materials and Methods

The tetraqua complex of hafnium selenite dihydrate $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ was obtained from hafnium dioxide and selenic acid by hydrothermal synthesis at temperature of 250°C. To confirm its composition, the FTIR spectrum was registered on a Bruker Tensor 27 FT-IR spectrometer in the 4000 – 400 cm^{-1} range, with the samples embedded in KBr.

The thermogravimetric analysis was carried out on an apparatus STA 449 F3 JUPITER (Netzsch) with recording the TG-DTG/DSC curves at heating rate of 10°C min^{-1} , from room temperature to 850°C in air flow (20 $\text{cm}^3 \text{min}^{-1}$). The DSC curve showed three endothermic effects, two of which are due to the dehydration of the complex and one – to the decomposition of the anhydrous $\text{Hf}(\text{SeO}_3)_2$.

The statistical problems provide an estimation of the relationship between two or more variables and determine the type and shape of the dependence. The correlation describes the strength of the relationship while the regression – its type. The regression analysis estimates the values of a variable describing certain entity on the basis of knowing the values of another value of the same entity and it is widely used technique for analysis of experimental data [6,7].

The experimental results obtained for the specific heat capacity of the compound studied were processed by the least squares method [8–12]. Using regression analysis, the coefficients a , b and c were determined in the polynomial:

$$C_p = a + bT + cT^2, \quad (1)$$

Aiming to find the minimum of the function $C_{p,m}$:

$$C_{p,m} = f(T, a, b, c) \quad (2)$$

After finding the coefficients in Eq. (1), its adequacy is checked by comparing the predicted values with the experimentally determined ones [9]. The correctness of the model is estimated by the coefficient of linear regression R^2 , which is obtained by analysis of the scattering of the specific heat

capacity ($C_{p,m}$) around its average value [9,10]. When R^2 approximates unity, the model adequately describes the relationship but if its values are lower the regression model does not describe properly the effect of temperature on the specific heat capacity [8,12].

After calculating the temperature dependence of the specific molar heat capacity at constant pressure in wide temperature interval, the values of the thermodynamic properties entropy, enthalpy and Gibbs free energy can be found. To calculate ΔS_T° ($\Delta S_{298}^\circ = f(T)$) the following equation is used:

$$\Delta S_T^\circ = \Delta S_{298}^\circ + \int_{298}^T \frac{C_p}{T} dT \quad (3)$$

The value of the change of the temperature dependence of the enthalpy is calculated by the equation:

$$\Delta H_T^\circ - \Delta H_{298}^\circ = \int_{298}^T C_p dT, \quad (4)$$

and that of the Gibbs free energy ΔG_T° :

$$\Delta G_T^\circ = \Delta H_{298}^\circ + \int_{298}^T (a + bT + cT^2) dT - T \cdot \left(\Delta S_{298}^\circ + \int_{298}^T \frac{(a + bT + cT^2)}{T} dT \right) \quad (5)$$

The same approach was used for the determination of the thermodynamic properties of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ [5,13] and some tellurites of Cu(II), Hg(II) [14] and rare earth elements [15,16].

The studies on the specific molar heat capacity allows calculating the thermodynamic properties in wide temperature interval [10,11]. At low temperatures, this temperature dependence is closely related to the crystalline structure of solid substances. Besides investigating the possibilities for application of hafnium compounds, the data on the specific molar heat capacity provide possibilities to study the processes of arrangement which, for example, determine the magnetic, segnetoelectric and superconducting properties, as well as the formation of point defects in the crystals.

3. Results and discussion

The experimental IR spectrum of the tetraqua complex of hafnium selenite dihydrate $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ was compared to the

theoretically calculated one by DFT and the one of zirconium selenite obtained in [17].

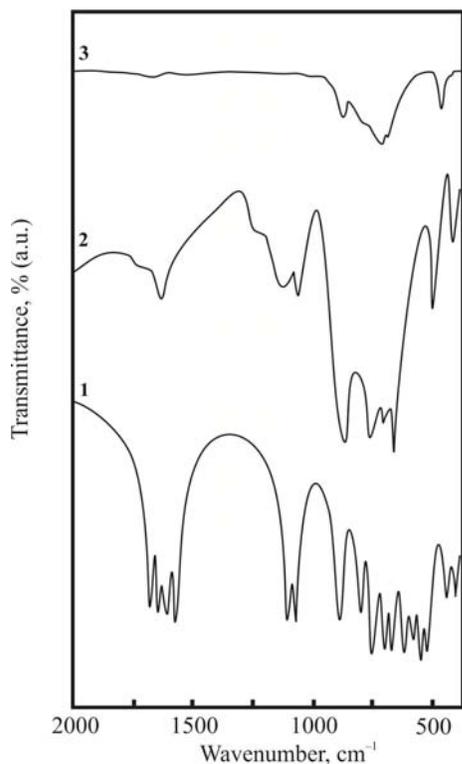


Fig. 1. Theoretically calculated (1) [3] and experimental (2) FTIR spectra of the hafnium selenite obtained and spectrum of zirconium selenite (3), obtained in [17] in the range 400–2000 cm^{-1} .

In the range 400 – 1000 cm^{-1} , similar absorption bands were observed in all the three spectra attributed to the stretching vibrations of Se–O in SeO_3^{2-} anions. The band at 1630 cm^{-1} observed in the experimental spectrum of the selenite complex can be attributed to the water molecules in-plane bending vibration. In the range studied, no characteristic bands were observed for absorptions by the Hf–O bond. The theoretically computed values for Hf–O stretching vibrations are observed at 363, 321 and 301 cm^{-1} [3].

3.1. Thermal behavior and heat capacity

The experimental data obtained from the thermogravimetric analysis of the tetraaqua complex of hafnium selenite prepared under the conditions of hydrothermal synthesis are shown in Fig. 2.

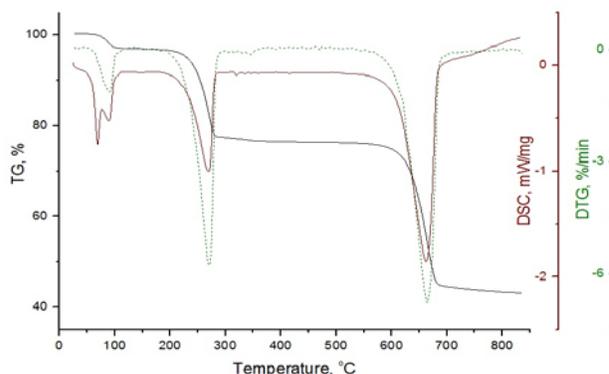


Fig. 2. TG/DTG/DSC curves of dehydration and decomposition of $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$.

The total mass loss calculated from the TG curve in Fig. 2 corresponds to the stoichiometric composition of the compound obtained – hafnium diselenite with six molecules of water. Two of the water molecules are released in the temperature interval 80–110°C. The release of the other four molecules was observed at higher temperatures (240–300°C) which means that they take part in the coordinated structure together with the hafnium ion. The anhydrous hafnium selenite $\text{Hf}(\text{SeO}_3)_2$ is stable up to 580°C and above this temperature it begins to decompose. The X-ray analysis of the product of selenite decomposition showed that hafnium dioxide did not form at the final temperature of the analysis. The residue of the decomposition of the anhydrous hafnium selenite was probably dihafnyl selenite $\text{Hf}_2\text{O}_3(\text{SeO}_3)$ which would decompose to hafnium dioxide at higher temperature [18].

The thermogravimetric analysis of the complex synthesized showed a total of three stages of dehydration and decomposition:

- (I) $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O} \rightarrow \text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4 + \text{H}_2\text{O}$
- (II) $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \rightarrow \text{Hf}(\text{SeO}_3)_2 + 4\text{H}_2\text{O}$
- (III) $2\text{Hf}(\text{SeO}_3)_2 \rightarrow \text{Hf}_2\text{O}_3(\text{SeO}_3) + 3\text{SeO}_2$

The experimental data on the specific molar heat capacity ($C_{p,m}$) of the initial complex $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ and the two phases formed during its dehydration $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]$ and $\text{Hf}(\text{SeO}_3)_2$ in the temperature interval 45 – 660°C are presented in Table 1.

Table 1. Experimental data on the $C_{p,m}$ of $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]$ and $\text{Hf}(\text{SeO}_3)_2$

T, K	$C_{p,m}, \text{J K}^{-1} \text{mol}^{-1}$ $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$	T, K	$C_{p,m}, \text{J K}^{-1} \text{mol}^{-1}$ $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]$	T, K	$C_{p,m}, \text{J K}^{-1} \text{mol}^{-1}$ $\text{Hf}(\text{SeO}_3)_2$
318	306.78	465	299.68	860	481.21
320	323.66	470	325.98	865	541.83
322	348.55	474	351.83	870	612.86
324	383.01	478	382.06	875	705.30
326	430.14	482	420.37	880	828.75
328	492.60	486	469.21	885	986.54
330	570.32	490	545.17	890	1186.79
332	669.13	494	629.85	895	1468.04
334	825.38	498	694.88	900	1822.65
336	1103.64	502	799.08	905	2217.39
338	1537.32	506	930.43	910	2644.11
339	1792.59	510	1087.98	915	3096.04
340	2043.30	514	1273.90	921	3642.28
341	2254.70	518	1489.88	927	4193.01
342	2389.18	523	1806.90	934	4653.72

The experimental values from Table 1 were processed by the method of linear regression and empiric equations were derived for each phase with coefficients a , b and c according to eq. (1). Using the method of Koumok [10], the standard molar entropy ΔS_{298}° and enthalpy ΔH_{298}° were calculated for the three compounds and they are presented in Table 2.

Table 2. Standard molar entropy ΔS_{298}° and standard molar enthalpy ΔH_{298}° of the hafnium compounds

Compound	$\Delta S_{298}^{\circ}, \text{J K}^{-1} \text{mol}^{-1}$	$\Delta H_{298}^{\circ}, \text{J mol}^{-1}$
$[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$	1316.7	3620.4
$[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]$	938.7	3049.4
$\text{Hf}(\text{SeO}_3)_2$	182.7	1907.4

Fig. 3 shows graphically the dependencies of the experimental values of the specific heat capacity (C_p) on the temperature and the empiric equations derived for the three phases – the initial complex $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ and the two phases formed after its dehydration $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]$ and $\text{Hf}(\text{SeO}_3)_2$.

The dependencies between the experimentally determined values and those obtained by regression analysis are shown in Fig. 4.

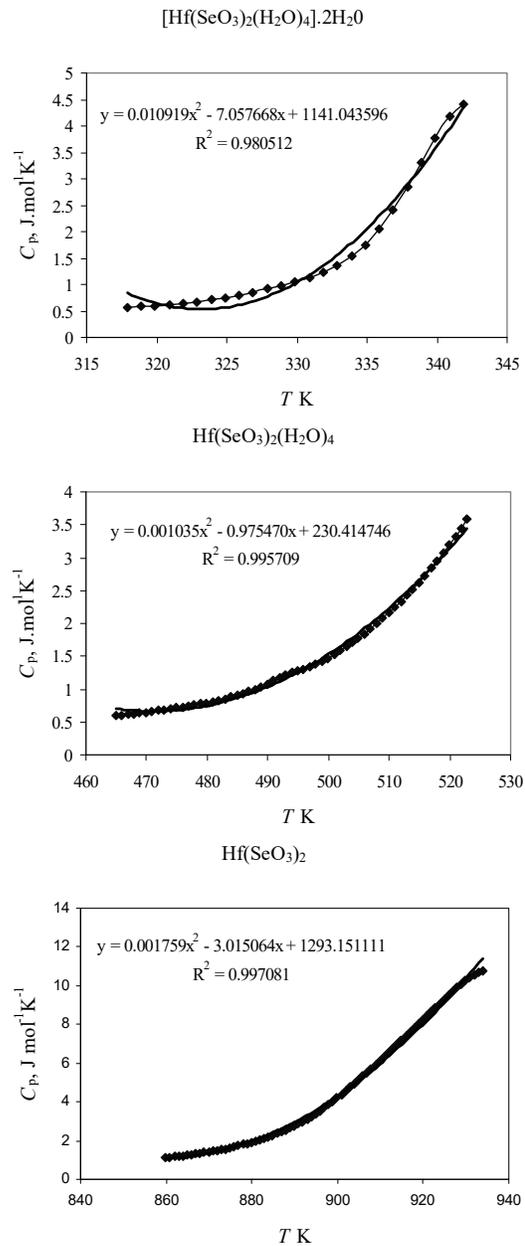


Fig. 3. Dependence of the experimental values of C_p on the temperature for $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]$ and $\text{Hf}(\text{SeO}_3)_2$.

As can be seen from Fig. 4, the dependencies of the experimentally determined specific heat molar capacities and the calculated ones have values of R^2 close to unity which means that the calculation approach used was precise and adequate. On this basis, it is possible to calculate the values of C_p at temperatures for which there are no experimental data.

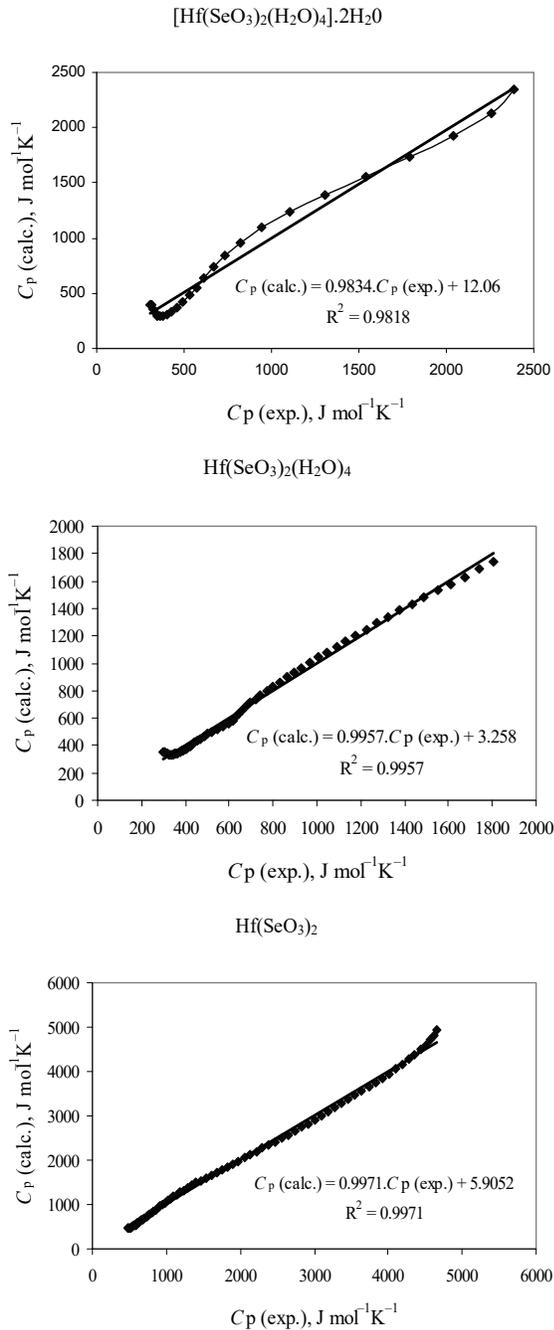


Fig. 4. Dependence between the measured molar heat capacity of $[Hf(SeO_3)_2(H_2O)_4] \cdot 2H_2O$, $[Hf(SeO_3)_2(H_2O)_4]$ and $Hf(SeO_3)_2$ and these calculated by regression analysis.

The values of the specific molar heat capacities calculated by Eq. (1) allows finding the temperature dependencies of the change of entropy ($\Delta_{T'}^T S_m^\circ$),

enthalpy ($\Delta_{T'}^T H_m^\circ$) and Gibbs energy ($-\Delta_{T'}^T G_m^\circ / T$) using the following equations:

$$\Delta_{T'}^T S_m^\circ = \Delta_0^T S_m^\circ + \int_{T'}^T (C_{p,m} / T) dT \quad (6)$$

$$\Delta_{T'}^T H_m^\circ = \Delta_0^T H_m^\circ + \int_{T'}^T C_{p,m} dT \quad (7)$$

$$(-\Delta_{T'}^T G_m^\circ / T) = \Delta_{T'}^T S_m^\circ - \Delta_{T'}^T H_m^\circ / T \quad (8)$$

The results obtained from the calculation of the thermodynamic functions for the initial complex $[Hf(SeO_3)_2(H_2O)_4] \cdot 2H_2O$ are shown in Table 3 and for the two phases formed after its dehydration in Tables 4 and 5.

The studies on the physicochemical properties of hafnium compounds is of substantial interest since the thermodynamic functions enthalpy, entropy and Gibbs free energy are directly related to the strength of the chemical bonds. The thermodynamic parameters found for $[Hf(SeO_3)_2(H_2O)_4] \cdot 2H_2O$ are important for calculations of certain chemical reaction. The thermodynamic information comprises data on the aggregate and phase states of the complex in the temperature interval of interest, the phase transitions, enthalpy entropy of its formation.

From scientific point of view, the studies on the physicochemical properties of hafnium compounds is interesting due to the fact that the entropy, enthalpy and the free energy of Gibbs are directly related to the strength of the chemical bonds in these compounds. The thermodynamic parameters found for these compounds are important for the calculations made for certain chemical reaction in which one or another chemical compound takes part. The thermodynamic information includes data on their aggregate and phase states in the temperature interval of interest, the enthalpy and entropy of formation, as well as phase transitions of the compounds studied.

4. Conclusion

Data on the hydrothermal synthesis, thermal behavior and thermodynamic properties of hafnium selenite tetraaqua complex dihydrate obtained were discussed.

Table 3. Molar thermodynamic functions of $[\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$

T, K	$C_{p,m},$ $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T S_m^o),$ $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T H_m^o),$ J mol^{-1}	$(-\Delta_T^T G_m^o/T),$ $\text{J K}^{-1} \text{mol}^{-1}$
318	404.23	1344.94	12596.47	1316.70
320	353.06	1340.69	11294.43	1292.71
322	298.51	1338.71	10705.75	1294.69
324	291.16	1339.84	11113.61	1293.54
326	331.01	1344.87	12801.23	1288.53
328	418.06	1354.61	16051.81	1278.79
330	552.31	1369.83	21148.55	1263.57
332	733.76	1391.29	28374.66	1242.11
334	962.42	1419.71	38013.34	1213.69
336	1238.27	1455.82	50347.79	1177.58
338	1561.33	1500.31	65661.22	1133.09
339	1740.55	1525.92	74523.55	1107.48
340	1931.58	1553.89	84236.83	1079.51
341	2134.41	1584.29	94836.45	1049.11
342	2349.04	1617.20	106357.82	1016.20

Table 4. Molar thermodynamic functions of $\text{Hf}(\text{SeO}_3)_2(\text{H}_2\text{O})_4$

T, K	$C_{p,m},$ $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T S_m^o),$ $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T H_m^o),$ J mol^{-1}	$(-\Delta_T^T G_m^o/T),$ $\text{J K}^{-1} \text{mol}^{-1}$
465	354.61	1065.89	62176.00	811.51
470	335.44	1061.30	60656.55	816.10
474	338.90	1064.38	62606.84	813.02
478	359.08	1073.75	67588.47	803.65
482	395.96	1089.67	75801.98	787.73
486	449.56	1112.40	87447.90	765.00
490	519.87	1142.17	102726.76	735.23
494	606.89	1179.22	121839.12	698.18
498	710.62	1223.78	144985.49	653.62
502	831.06	1276.06	172366.43	601.34
506	968.21	1336.29	204182.46	541.11
510	1122.08	1404.66	240634.12	472.74
514	1292.66	1481.37	281921.94	396.03
518	1479.94	1566.63	328246.48	310.77
523	1737.55	1685.50	393540.52	191.90

Table 5. Molar thermodynamic functions of Hf(SeO₃)₂

T, K	$C_{p,m},$ $J K^{-1} mol^{-1}$	$(\Delta_T^T, S_m^o),$ $J K^{-1} mol^{-1}$	$(\Delta_T^T, H_m^o),$ $J mol^{-1}$	$(-\Delta_T^T, G_m^o/T),$ $J K^{-1} mol^{-1}$
860	463.14	485.26	262070.36	318.14
865	503.40	512.56	287201.73	281.42
870	581.68	565.01	334474.71	251.93
875	697.98	642.82	404457.63	221.30
880	852.31	746.20	497726.84	183.78
885	1044.66	875.38	614846.68	154.97
890	1275.03	1030.54	756389.49	143.45
895	1543.43	1211.90	922925.63	180.47
900	1849.84	1419.65	1115025.42	189.49
905	2194.29	1653.55	1333259.21	173.51
910	2576.75	1915.10	1578197.34	168.53
915	2997.24	2203.17	1850410.16	152.55
921	3552.01	2584.70	2213871.18	136.57
927	4268.45	3079.60	2689901.81	123.59
934	4941.83	3546.83	3143620.31	119.61

The coefficients in the polynomial dependence of $C_p = f(T)$ were calculated by processing the experimental data obtained from the TG/DTG/DSC analysis. Based on these data and using the standard entropy of the initial compounds, the temperature dependencies of the change of entropy (Δ_T^T, S_m^o), enthalpy (Δ_T^T, H_m^o) and Gibbs function ($-\Delta_T^T, G_m^o/T$) were determined. The thermodynamic data obtained and the analysis of the synthesis conditions will be useful both for preparation of materials with desired thermal characteristics and in studies on the possibilities for application of these compounds.

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