PHYSICAL METHODS OF INVESTIGATION

Thermal Behavior of Ammonium-Containing Titanium and Germanium Fluoride Complexes $(NH_4)_4Li_2(AF_6)_3$ and NH_4NaAF_6 (A = Ge or Ti)

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Abstract—The compounds $(NH_4)_4Li_2A_3F_{18}$ and NH_4NaAF_6 (A = Ge or Ti) were studied thermogravimetrically. These fluoro complexes are thermolyzed in the range 230–450°C. Measurements on a differential scanning microcalorimeter revealed reversible phase transitions in NH_4NaAF_6 at $T_1 = 126$ °C and $T_2 = 111$ °C.

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In [1], we described ammonium-containing complexes of germanium and titanium fluorides $(NH_4)_4Li_2A_3F_{18}$ and NH_4NaAF_6 (A = Ge or Ti). The structural study of (NH₄)₄Li₂(GeF₆)₃ [2] showed that the structural motif of this compound had not been encountered in mixed-cation hexafluoro complexes. The crystal structure of $(NH_4)_4Li_2(GeF_6)_3$ can conventionally be divided into alternating NH₄LiGeF₆ and $(NH_4)_2$ GeF₆ layers. The coordination polyhedra around Ge(1) and Ge(2) atoms are octahedra with fluorine atoms in their vertexes; the coordination polyhedron around a lithium atom is a tetrahedron. Layers lying parallel to plane (100) and built of tetranuclear fragments are distinguished in the three-dimensional framework of the $(NH_4)_4Li_2(GeF_6)_3$ crystal structure. These fragments are built of two Ge(1) octahedra and two Li tetrahedra, which share corners. Ge(2) octahedra link layers into a continuous framework. Ammonium cations reside in channels that penetrate the crystal architecture.

We described the NH₄NaTiF₆ structure in [3]. This compound crystallizes in an NH₄NaTiF₆-type orthorhombic structure with the following unit cell parameters: a = 8.034 Å, b = 12.953 Å, c = 10.755 Å [4]. NaRbSnF₆ crystals have a continuous three-dimensional framework built of pairs of edge-sharing distorted NaF₆⁻ and TiF₆⁻; octahedra; pairs are linked via polyhedral corners into zigzag ribbons running along the direction [100]. Interstices are occupied by ammonium cations, which additionally link architecture elements via hydrogen bonds N–H…F.

Coordination compounds of complex composition typically experience complex chemical and structural

transformations during heating. Each compound follows its own route, and it is difficult to predict the transformation character. This work describes the thermal stability and the mechanism of thermal transformations in the compounds studied.

EXPERIMENTAL

A Paulik-Paulik-Erdey derivatograph was used to study the thermal behavior of ammonium complexes of germanium fluoride and titanium fluoride in labyrinth platinum crucibles in air at a heating rate of 10 K/min. Alumina calcined at 1000°C was the reference. The temperature measurement accuracy was $\pm 3^{\circ}$ C K. The sample size was 200 mg. The TG error was ± 1 mg.

All X-ray diffraction patterns of intermediates and final products were recorded on a DRON-2 diffractometer (graphite monochromator, CuK_{α} radiation), High-temperature experiments were carried out on an Advance D8 diffractometer (CuK_{α} radiation).

Calorimetric measurements were carried out on a DSM-2M differential scanning calorimeter at $60-210^{\circ}$ C in heating and cooling modes at a rate of ± 8 K/min. Heating/cooling cycles were repeated several times to improve the ruggedness of the results. Samples were fine powders ground with an agate mortar. Sample sizes were 0.13–0.16 g.

IR absorption spectra were recorded on an IFS Equinox 55S instrument ($350-4000 \text{ cm}^{-1}$; wavenumber accuracy, $\pm 0.5 \text{ cm}^{-1}$). Test samples were prepared by a routine procedure: they were finely ground with an agate mortar and spread as Nujol mull onto KBr substrates.



Fig. 1. DTA and TG curves for ammonium titanium fluoride and germanium fluoride complexes: (a) $(NH_4)_4Li_2(GeF_6)_3$, (b) NH_4NaGeF_6 , (c) $(NH_4)_4Li_2(TiF_6)_3$, and (d) NH_4NaTiF_6 .

RESULTS AND DISCUSSION

Data on the thermal stability of the complexes $(NH_4)_4Li_2Ge(Ti)_3F_{18}$ and $NH_4NaGe(Ti)F_6$ were obtained from thermal analysis (Fig. 1) and X-ray diffraction analysis of thermolysis products.

The thermal curves for an $(NH_4)_4Li_2Ge_3F_{18}$ sample (Fig. 1a) show a considerable endotherm (390–435°C), which is accompanied by a substantial weight loss and associated with removal of four NH_4F molecules and, in part, GeF_4 . X-ray powder diffraction shows β -Li₂GeF₆ in the sample calcined to 435°C. As temperature rises, β -Li₂GeF₆ degrades to LiF and GeF₄. GeF₄ partially hydrolyzes to GeO₂. The $(NH_4)_4Li_2Ge_3F_{18}$ thermolysis can be represented by the scheme

$$(\mathrm{NH}_{4})_{4}\mathrm{Li}_{2}\mathrm{Ge}_{3}\mathrm{F}_{18} \longrightarrow 4\mathrm{NH}_{4}\mathrm{F}\uparrow + 2\mathrm{Ge}\mathrm{F}_{4}\uparrow + \mathrm{Li}_{2}\mathrm{Ge}\mathrm{F}_{6},$$
$$\mathrm{Li}_{2}\mathrm{Ge}\mathrm{F}_{6} \longrightarrow 2\mathrm{Li}\mathrm{F} + \mathrm{Ge}\mathrm{F}_{4},$$
$$\mathrm{Ge}\mathrm{F}_{4} \longrightarrow \mathrm{GeO}_{2} + 4\mathrm{H}\mathrm{F}\uparrow.$$

According to this scheme, a weight loss of 60.5 wt % corresponds to removal of $4NH_4F$ and $2GeF_4$. The weight loss derived from the TG curve is 56.4 wt %, which is slightly lower than the calculated value. This disagreement can arise from small hydrolysis of GeF_4 to GeO_2 , which precipitates onto the walls of the crucible.

In the thermal curve for NH_4NaGeF_6 (Fig. 1b), there is an endotherm at 340-420°C with the attendant weight loss exceeding removal of one NH₄F molecule. The sample calcined to 420°C has X-ray diffraction reflections from Na₂GeF₆ and an unknown phase. We carried out IR spectroscopic analysis in order to identify this phase. The IR absorption spectrum contains a strong band with a peak at 610 cm⁻¹; we assigned it to the stretching vibrations of the hexafluoride ion GeF_6^{2-} in the compound Na₂GeF₆ [5, 6]. A broad band in the region 800-1000 cm⁻¹ and a band at 3250-3300 cm⁻¹ imply the existence, along with Na_2GeF_6 , of a phase containing an OH group. According to [6], the spectral manifestations of M-OH groups are in the aforementioned regions. From the above, we infer the following scheme of NH₄NaGeF₆ degradation:

 $2NH_4NaGeF_6 \longrightarrow 2NH_4F^{\uparrow} + GeF_4 + Na_2GeF_6,$ GeF_4 + 2H_2O \longrightarrow Ge(OH)_2F_2 + 2HF^{\uparrow}.

According to this scheme, removal of NH_4F and HF is 25.1%, which virtually coincides with the weight loss derived from the TG curve in the range 320–420°C. In the sample calcined to 560°C, X-ray diffraction reflections from Na_2GeF_6 and several reflections from an unknown phase are observed. The final products (at 760°C) are Na_2GeF_6 and tetragonal GeO₂.

thermal curves for NH₄NaTiF₆ The and $(NH_4)_4Li_2Ti_3F_{18}$ (Figs. 1c, 1d) show that ammonium fluorotitanate complexes are stable up to 230–250°C. Prior to thermolysis, the thermal curve for NH₄NaTiF₆ shows an endotherm, which is not accompanied by weight low and is due to reversible polymorphic transition. The X-ray diffraction pattern for the product of NH_4NaTiF_6 heated to 150°C and then cooled to room temperature coincides with that of the starting compound. To prove the existence of a high-temperature NH₄NaTiF₆ phase, we recorded X-ray diffraction patterns of a sample at 130–150°C. The table contains X-ray diffraction data for the β -NH₄NaTiF₆ phase and, as a reference, our previous data for the starting compound [1, 2]. The X-ray diffraction pattern for β -NH₄NaTiF₆ slightly differs from that for the starting compound. The unit cell parameters of β -NH₄NaTiF₆ were determined by indexing its powder pattern by iteration with reference to the unit cell parameters of the starting NH₄NaTiF₆, found from a single-crystal experiment, with the doubled parameter *a* (table).

The phase transition in NH₄NaTiF₆ was studied by DSC in more detail. Figures 2 and 3 display the results of two sets of calorimetric measurements on NH₄NaTiF₆ in the range 60–210°C. As a result of the first heating, two anomalies with peaks at $T_1 = 143 \pm 2$ °C and $T_2 = 124 \pm 2$ °C are found on the DSM signal versus temperature curve (Fig. 2a). The thermal anomaly observed in DTA–TG measurements corresponds to an intermediate temperature; most likely, averaging occurred because of the lower temperature resolution of DTA compared to DSC. A temperature hysteresis is found upon cooling, corresponding to the DSM signal peaks (Fig. 2b): $\delta T_1 = 17$, and $\delta T_2 = 13^{\circ}$ C. Repeated thermocycling shows considerably lower temperatures of thermal anomalies: $T_1 = 126 \pm 2^{\circ}$ C, and $T_2 = 111 \pm 2^{\circ}$ C (Fig. 3). These temperatures remain unchanged in further experiments: for the third heating, $T_1 = 126 \pm 2^{\circ}$ C and $T_2 = 110 \pm 2^{\circ}$ C. Most likely, annealing occurred during the first heating.

The reproducibility of the thermal anomalies in thermocycling implies that NH₄NaTiF₆ consecutively experiences two enantiotropic transitions. The great values of T_1 and T_2 hysteresis argue in favor of firstorder transitions. The peak heights of the DSM signal at T_1 and T_2 are redistributed as a result of annealing, which is made clear by the comparison of the panels of Fig. 2: the heat capacity anomaly at T_1 considerably increases, whereas that at T_2 decreases. In order to gain quantitative data on thermal features, we converted the DSM signal to the excess (anomalous) heat capacity ΔC_p , which is associated with the enthalpy and entropy changes, by the procedure used in [7]. At the first stage, the systematic contribution was subtracted (the dashed line in Fig. 2). These data were used to calculate the enthalpy and entropy changes in phase transitions. However, we failed to resolve the excess heat capacity contributions from individual phase transitions; we only calculated the overall enthalpy change $\Sigma \Delta H_i$ = $\Delta C_p dt$. This quantity is 3.3 ± 0.45 kJ/mol for the first

heating, 3.1 ± 0.45 kJ/mol for the second heating, and 2.6 ± 0.45 kJ/mol for the third one. The average entropy change determined by integrating the $(\Delta C_p/T)(T)$ function is $\Sigma \Delta S_i = 7.2$ J/(mol K). A weight loss of 0.7% was found when the sample was weighed after the experiment was over. Thus, the decrease in the enthalpy as a result of three heating cannot be associated with weight loss. Quite likely, thermocycling can cause blurring of the anomalies associated with phase transitions, which made it difficult to determine the integration boundaries and changed ΔH .

Next (Fig. 1d), NH₄NaTiF₆ thermolysis in the range 230–450°C is accompanied by a set of endotherms of complex shapes with more considerable weight loss than resulted from removal of an NH₄F molecule. This is because the test fluorotitanates below 450°C under an undried air atmosphere thermally dissociate to NH₄F and TiF₄; the latter at these temperatures in the presence of atmospheric moisture partially hydrolyzes to TiO₂ (anatase) and partially leaves, because the TiF₄ sublimation temperature is 285.5°C [8]. Above 450°C, TiF₄ hydrolyzes further to yield oxytitanate and oxyfluorotitanate products as shown by its TG curve. X-ray powder diffraction shows these products in the residues obtained at 450–950°C. In an NH₄NaTiF₆ sample calcined to 450°C, we observed reflections of TiOF₂ and



Fig. 2. DSM signal vs. temperature for the compound NH_4NaTiF_6 recorded during (a) first heating, (b) cooling, and (c) second heating. The dashed line shows a systematic contribution.



Fig. 3. Excess heat capacity vs. temperature for the compound NH_4NaTiF_6 recorded during (a) first heating and (b) second heating.

m_0 obs. calc. mat m_0 obs. calc. mat β NH,MATF ₆ (Orthorbombic; $a = 16.085(5), b = 12.951(1), c = 10.825(3) Å) 5.44 5.56 021 17 2.046 2.046 614 13 5.54 5.56 021 17 2.040 2.046 623 1 5.14 5.13 1002 28 2.015 2.011 2.013 360 3 4.83 4.81 301 14 2.005 2.005 062 16 4.57 4.57 221 8 2.001 2.003 360 3 4.48 4.49 202 6 1.947 1.946 262 2 3.52 3.52 103 2 1.875 0.874 740 >1 3.42 3.42 420 12 1.815 1.846 1.847 741 25 3.23 3.26 1.26 1.846 1.847 741 25 $	1/1	d, Å				<i>d</i> , Å			
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	13	5 54	5 56	021	13	2.040	2.043	623	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	15	5 30	5.30	0021	28	2.040	2.043	550	
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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1	J.14 1.83	J.13 4 81	301	13	2.010	2.011	244	
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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2	4.02	3.52	103	$\frac{2}{2}$	1.808	0.874	740	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	>1	3.42	3.42	420	12	1.851	1.850	070	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	3.76	3.76	421	6	1.846	1.830	741	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	25	3.20	3.20	402	3	1.825	1.874	071	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	23	3.14	3.13	402	7	1.825	1.813	171	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	22	2 77	2 77	033	6	1.806	1.815	263	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2 4	2.55	2.55	611	71	1 798	1.005	831	
2 2.31 2.489 151 3 1.763 1.774 1.774 1.774 1.774 5 2.461 2.460 333 1 1.736 1.736 7.14 2 2.414 2.414 621 2 1.712 1.711 272 2 2.404 2.404 2.414 621 2 1.712 1.711 272 2 2.404 2.404 2.52 1.642 1.682 463 3 2.271 2.270 134 5 1.677 1.678 164 2 2.242 2.244 252 2 1.642 1.642 922 6 2.198 2.198 343 1 1.631 1.630 625 10 2.163 2.167 702 3 1.572 1.572 851 32 2.090 2.091 205 2 1.549 941 21 2.087 2.087 1.53	2	2.55	2.55	531	38	1.794	1.794	462	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	13	2.51	2.51	151	30	1.754	1.754	901	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5	2.461	2.460	333	1	1.705	1.705	714	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	2.401	2.400	621	2	1.730	1.750	272	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	2.414 2 404	2.414 2 404	251	2 7	1.697	1.697	902	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5	2 363	2.404	612	9	1.697	1.682	463	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3	2.303	2.302	134	5	1.677	1.678	164	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2	2.271	2.270	252	2	1.642	1.642	922	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	6	2.198	2.198	343	1	1.631	1.630	625	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	10	2.150	2.150	005	3	1.619	1.619	080	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	10	2.115	2.115	702	3	1.572	1.572	851	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	32	2.090	2.091	205	2	1.549	1.549	941	
a1.011.010441.01<	21	2.087	2.087	153	3	1.523	1.523	282	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	6	2.075	2.077	044	U	110 - 0	11020	-0-	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	NH ₄ NaTiF ₆ (Orthorhombic; $a = 8.034(2)$, $b = 12.953(3)$, $c = 10.755(3)$ Å) [3]								
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	9	6.51	6.47	200	6	1.881	1.882	024	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	47	5.54	5.54	210	5	1.868	1.865	540	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	36	5.37	5.38	020	8	1.851	1.850	700	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	100	4.56	4.56	211	5	1.817	1.817	541	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	27	4.46	4.47	021	8	1.794	1.793	060	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	73	4.00	4.00	310	4	1.778	1.778	711	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	6	3.41	3.41	202	4	1.749	1.749	720	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	45	3.24	3.24	400	5	1.707	1.707	404	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	40	3.13	3.14	230	9	1.692	1.692	542	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	9	2.55	2.55	113	5	1.680	1.680	603	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	13	2.484	2.483	240	9	1.637	1.637	452	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	10	2.460	2.464	501	4	1.590	1.590	015	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5	2.401	2.402	511	4	1.566	1.568	353	
4 2.235 2.235 042 4 1.484 1.487 812 6 2.193 2.195 341 4 1.459 1.459 154 8 2.110 2.113 242 4 1.432 1.432 254 11 2.040 2.041 250 5 1.362 1.362 372 31 2.008 2.009 004 3 1.339 1.339 006 5 1.888 1.889 214	8	2.357	2.358	123	5	1.523	1.523	650	
62.1932.19534141.4591.45915482.1102.11324241.4321.432254112.0402.04125051.3621.362372312.0082.00900431.3391.33900651.8881.889214	4	2.235	2.235	042	4	1.484	1.487	812	
82.1102.11324241.4321.432254112.0402.04125051.3621.362372312.0082.00900431.3391.33900651.8881.889214	6	2.193	2.195	341	4	1.459	1.459	154	
112.0402.04125051.3621.362372312.0082.00900431.3391.33900651.8881.889214 </td <td>8</td> <td>2.110</td> <td>2.113</td> <td>242</td> <td>4</td> <td>1.432</td> <td>1.432</td> <td>254</td>	8	2.110	2.113	242	4	1.432	1.432	254	
31 2.008 2.009 004 3 1.339 1.339 006 5 1.888 1.889 214 3 1.339 006	11	2.040	2.041	250	5	1.362	1.362	372	
5 1.888 1.889 214	31	2.008	2.009	004	3	1.339	1.339	006	
	5	1.888	1.889	214					

X-ray diffraction data for $\alpha\text{-}NH_4NaTiF_6$ and $\beta\text{-}NH_4NaTiF_6$

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Na₂TiF₆ along with those of titania; at 575°C, the amount of Na₂TiF₆ decreases and a sodium salt of tervalent titanium (Na₅Ti₃F₁₄) appears. We failed to identify several reflections, but at 650°C the unknown phase disappears and reflections from TiO₂ (anatase), Na₂TiF₆ (minor amounts), and Na₅Ti₃F₁₄ exist. Above 750°C, TiO₂ (anatase), TiO₂ (rutile), and Na₅Ti₃F₁₄ are produced. Tervalent titanium appears in the thermolysis products because NH₄F manifests the reducing properties of ammonia: at 167°C, it decomposes to HF and NH₃ [9], and the latter above 400°C dissociates to N₂ and H₂, creating a reducing atmosphere. Because labyrinth crucibles were used, the processes studied occurred under the own vapor atmosphere, i.e., in a reducing atmosphere.

The X-ray diffraction pattern of the $(NH_4)_4Li_2Ti_3F_{18}$ calcined to 450°C shows reflections belonging to Li_2TiF_6 , TiO₂ (anatase), and TiOF₂. At 850°C, TiO₂ (rutile) and LiF are produced.

Having compared the thermal stabilities of ammonium fluorotitanate complexes and their fluorogermanate analogues, we inferred that the fluorogermanates are more thermally stable.

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