Thermochimica Acta, 87 (1985) 377–380
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

LOW-TEMPERATURE ANOMALIES OF HEAT CAPACITY OF SOME AMMONIUM HEXAFLUOROMETALLATES(III)

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(Received 14 December 1984)

Many ammonium hexafluorometallates, $(NH_4)_3MF_6$, have cryolite-type structures [1]. Some possess polymorphism properties and in the majority of cases transitions between different crystal modifications of the compounds take place below room temperature: 248 K for $(NH_4)_3GaF_6$ [2,3], 264 K for $(NH_4)_3FeF_6$ and 217 K for $(NH_4)_3AlF_6$ [4]. (The authors of ref. 5 revealed two transitions of $(NH_4)_3AlF_6$, at 193.0 and 220.79 K.)

All these compounds have a cubic structure at room temperature. Unlike the above compounds, $(NH_4)_3InF_6$ exists as a tetragonal modification at room temperature [1] and its transition into a high-temperature cubic form takes place at 355 K [2].

Thermodynamic characteristics of the majority of ammonium hexafluorometallates are practically nonexistent. The only data known are measurements of the low-temperature heat capacity of $(NH_4)_3AlF_6$ [5] and $(NH_4)_3FeF_6$ [6].

The aim of this paper is to study the heat capacity of some ammonium hexafluorometallates(III), $(NH_4)_3MF_6$ (where M = Al, Ga, In, Fe), in the region of their phase transitions.

METHODS

The $(NH_4)_3MF_6$ (M = Al, Ga, In, Fe) compounds were synthesized according to ref. 7 by interaction of metal(III) bromides with ammonium fluoride in "absolute" methanol. The metal(III) bromides were also prepared in methanol by the action of bromine on the corresponding pure metals.

Results of the chemical analysis of the compounds on ammonium and metal content are given in Table 1. Ammonium was determined acidimetrically and metal by gravimetric analysis as an oxide.

Heat capacity measurements were conducted by means of a triple heat bridge (THB) method within the 150–320 K temperature range. The apparatus was as described earlier [8]. The error in heat capacity determination did not exceed 3%. We used pressed polycrystal samples of the compounds.

0040-6031/85/$03.30

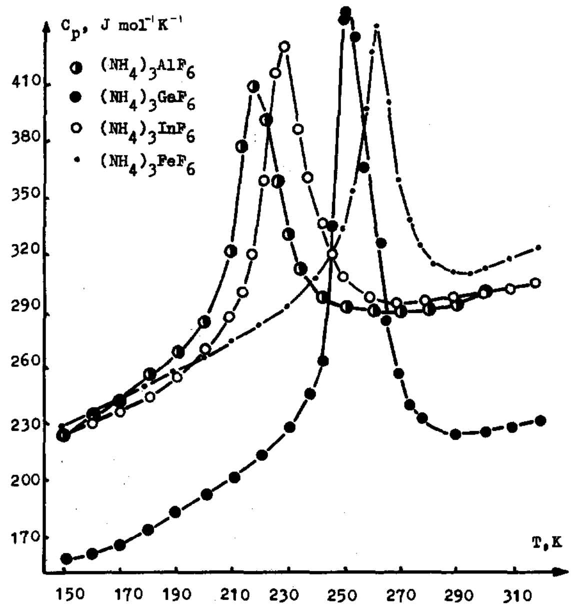

Fig. 1. Heat capacity of $(NH_4)_3MF_6$ (M = Al, Ga, In, Fe) compounds.

Before measurement the samples were cooled to about 90 K. The heating rate was 2.2 K min^{-1}. Copper (99.95% purity) was used as a reference. Values of copper heat capacity were taken from refs. 9 and 10. (For the calculations we accepted the following molecular weights: 195.0876, 237.8261, 282.9291 and 223.9531 for Al, Ga, In and Fe compounds, respectively, and the conversions 1 cal = 4.184 J.)

RESULTS AND DISCUSSION

Experimental results on heat capacity determination are shown in Fig. 1.

As is seen from Fig. 1, for each $(NH_4)_3MF_6$ compound within the temperature range studied we found one anomaly of heat capacity with

TABLE 1

Results of chemical analysis of $(NH_4)_3MF_6$ (M = Al, Ga, In, Fe) compounds

Compound	Ammonium content (%)		Metal content (%)	
	calc.	exp.	calc.	exp.
$(NH_4)_3AlF_6$	27.74	27.77	13.83	13.81
$(NH_4)_3GaF_6$	22.75	22.80	29.32	29.78
$(NH_4)_3InF_6$	19.13	19.44	40.58	40.32
$(NH_4)_3FeF_6$	24.16	24.12	24.94	24.86

maxima at 218 ± 2, 251 ± 2, 230 ± 2 and 261 ± 2 K for M = Al, Ga, In and Fe, respectively. Repeated measurements on the same samples showed that in all cases these anomalies were reversible. Temperatures of heat capacity maxima for gallium, aluminium and iron compounds satisfactorily agree with the temperatures of polymorphic phase transitions known from the literature [2–4,6]. Thus, the heat-capacity anomalous behaviour of these compounds is evidently due to a transition from low-temperature into high-temperature cubic modifications.

As mentioned above, the temperature of $(NH_4)_3InF_6$ phase transition is 355 K according to ref. 2. However, we recorded the heat capacity anomaly at 230 ± 2 K. The absence of a sample mass decrease during several of the experiments with the same sample, as well as the reversibility of the revealed transition suggest that this is due to an ammonium hexafluoroindate(III) phase transition proceeding, which was not known before. Thus, one can assume that $(NH_4)_3InF_6$ exists not in two, as it was considered earlier, but in three polymorphic modifications and its transition into a low-temperature phase occurs below room temperature as in the case of similar aluminium, gallium and iron compounds.

The enthalpy values of these transitions, ΔH (kJ mol^{-1}), were estimated by integration of the heat capacity dependence on temperature in the region of the corresponding phase transition: $\Delta H((NH_4)_3AlF_6) \approx 2.1$, $\Delta H((NH_4)_3GaF_6) \approx 4.5$, $\Delta H((NH_4)_3InF_6) \approx 4.0$, $\Delta H((NH_4)_3FeF_6) \approx 2.1$ kJ mol^{-1}.

Unlike the data of ref. 5, we did not reveal a transition at about 193 K for the $(NH_4)_3AlF_6$ compound. There is some discrepancy between our data on the heat capacities of $(NH_4)_3AlF_6$ and $(NH_4)_3FeF_6$ and those measured by means of adiabatic calorimetry [5,6]. In our opinion the above discrepancy may be due to different methods of sample preparation. The authors [5,6] used synthesis techniques based on fluoride aqueous solutions which, as was observed by the authors themselves [5,6], in a number of cases led to a deviation from a stoichiometric composition of the compounds synthesized.

Note that our ΔH values obtained for aluminium and iron compounds are somewhat lower than those given in refs. 5 and 6, which can be explained by the difficulties of accurately determining the temperatures at the beginning and end of the transitions from the heat capacity data.

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