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E. I. Pogoreltsev[a,b], E. V. Bogdanov[a,c], A. V. Kartashev[a], M. S. Molokeev[a,d], I. N. Flerov[a,b], and N. M. Laptash[e]

[a]Kirensky Institute of Physics, Siberian Department of RAS, Krasnoyarsk, Russia; [b]Institute of Engineering Physics and Radioelectronic, Siberian State University, Krasnoyarsk, Russia; [c]Krasnoyarsk State Agrarian University, Krasnoyarsk, Russia; [d]Far Eastern State Transport University, Khabarovsk, Russia; [e]Institute of Chemistry, Far Eastern Department of RAS, Vladivostok, Russia

ABSTRACT

The heat capacity, thermal expansion, and T-p phase diagrams of $(NH_4)_3TiF_7$ and $(NH_4)_3SnF_7$ were studied in wide temperature and pressure ranges. The total excess entropies at successive Pa-3 ↔ P4/mnc ↔ 4/m (Ti) and single Pa-3 ↔ Pm-3m (Sn) phase transitions are close to each other and characteristic for the order–disorder processes. The Pm-3m cubic phase and direct Pa-3 ↔ Pm-3m transformation were found at high pressure in $(NH_4)_3TiF_7$. The different sign of baric coefficients for phase transition between two cubic phases in $(NH_4)_3TiF_7$ and $(NH_4)_3SnF_7$ was supposed due to nonlinear phase boundary with pressure in the latter fluoride.

Introduction

Among fluoride compounds with a crystal lattice formed by six-coordinated anionic polyhedra, the double salts with the general chemical formula $A_3MeF_7 = A_2MeF_6 \cdot AF$ stand out because of variety of their room temperature symmetry. The change of a chemical pressure generated by the decrease in the central atom size leads to the following phases in the series of ammonium fluorides: cubic Pm-$3m$, $Z = 1$ (Me: Pb) [1] and Pa-3, $Z = 8$ (Me: Sn) [2] as well as tetragonal $P4/mnc$, $Z = 8$ (Me: Ti) [3] and $P4/mbm$, $Z = 2$ (Me: Si, Ge) [4, 5]. Such a peculiarity could be considered as circumstantial evidence for the possible phase transitions in double salt fluorides under temperature and/or hydrostatic pressure variation. Moreover, the existence of the rare in occurrence transformation between two cubic phases could also be assumed completing directly or through intermediate phases. However, over a long period the physical properties of these fluorides not examined depending on the external parameters. That is the reason why the results of recent polarizing-optic and structural studies of crystals $(NH_4)_3SnF_7$ [2] and $(NH_4)_3TiF_7$ [6, 7] are of a great scientific interest. Hepta-fluorostannate having at room temperature a cubic symmetry Pa-3 was found undergoing a transformation into perovskite Pm-$3m$ cubic phase at $T_0 = 360$ K. Related titanium

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compound showed upon heating at ambient pressure the succession of phase transitions Pa-3 ($T_2 = 291$ K) $\leftrightarrow$ $P4/mnc$ ($T_1 = 360$ K) $\leftrightarrow$ $4/m$. According to the character of optical twinning as well as the analysis of observed symmetry change in the framework of group theory, a cubic phase with the Pm-$3m$ symmetry can also be assumed as a parent phase in $(NH_4)_3TiF_7$. However, the transformation $4/m \leftrightarrow Pm$-$3m$ phase was not observed experimentally, most likely because heptafluorotitanate decomposes above ~ 390 K [6, 7].

The structural analysis has revealed the completely ordered structure in the low temperature cubic phase Pa-3 of both fluorides, $(NH_4)_3SnF_7$ [2] and $(NH_4)_3TiF_7$ [6]. The appearance of fourfold axis above T_2 in tetragonal phase $P4/mnc$ of heptafluorotitanate accompanied by disordering TiF_6 octahedra. It was difficult to make any conclusion about order-disorder of NH_4 tetrahedra in this phase on the ground of X-ray experiments. However, Pm-$3m$ phase of $(NH_4)_3SnF_7$ was characterized by total disordering both octahedral SnF_6 as well as tetrahedral NH_4 groups [2]. A large entropy change ΔS, thus, would be expected to accompany order-disorder phase transitions in the fluoride double salts $(NH_4)_2MeF_6$ NH_4F. Indeed, the results of preliminary heat capacity measurements performed by differential scanning microcalorimeter (DSM) have proved this supposition [2, 7]. Rather large phase transition entropies were found in both fluorides: $(NH_4)_3SnF_7 - \Delta S_0 = 16.6$ J(mol·K)$^{-1}$; $(NH_4)_3TiF_7 - (\Delta S_1 + \Delta S_2) = (6 + 18.3) = 24.3$ J(mol·K)$^{-1}$. However, it may be safely assumed that these values are less than the actual ΔS magnitudes because the DSM-method gives, as a rule, information about entropy change except the pre-transitional heat effects, which can give a significant contribution to the total entropy change.

Strong dependence of the symmetry at ambient pressure on the central atom size suggests that a susceptibility of the $(NH_4)_2MeF_6$ NH_4F crystals to external hydrostatic pressure can also be high.

In polarizing-optic measurements on $(NH_4)_3SnF_7$ [2] and $(NH_4)_3TiF_7$ [7] a reversible cracking of crystals was observed at phase transition into Pa-3 phase which was supposed due to large jump of the unit cell volume at the transformation temperature.

Taking into account the above discussed experimental facts, in the present paper, a heat capacity, T-p phase diagrams and thermal expansion of $(NH_4)_3SnF_7$ and $(NH_4)_3TiF_7$ crystals were studied by the following experimental techniques: 1) adiabatic calorimeter of high resolution; 2) differential thermal analysis (DTA) under hydrostatic pressure, 3) X-ray powder diffractometer.

Results and discussion

Experiments were performed on samples prepared from crystals grown and given a preliminary examination in [2, 7].

The detailed studies by adiabatic calorimeter have shown two ($T_1 = 357.8 \pm 0.5$ K; $T_2 = 291.6 \pm 0.5$ K) and single ($T_0 = 356 \pm 1.0$ K) heat capacity anomalies in heptafluorotitanate and heptafluorostannate, respectively (Fig. 1), associated with phase transitions found in polarizing-optic, DSM and X-ray experiments [2, 7]. The behavior of the anomalous heat capacity $\Delta C_p(T)$ was obtained by the extraction of the lattice contribution $C_{lat}(T)$ from the total heat capacity $C_p(T)$.

The dependence $C_{lat}(T)$ was estimated by an approximation with polynomial functions of the experimental data far from the phase transition regions. As seen in Fig 1, the anomalous contribution $\Delta C_p = C_p - C_{lat}$ exists in wide temperature regions below transformations points in both fluorides. The integration of the $(\Delta C_p/T)(T)$ functions has given an information about the behavior and values of phase transition entropies (Fig. 1b and d), which were
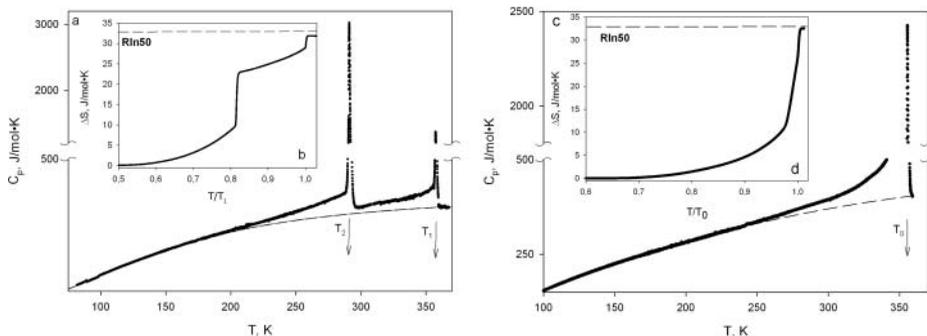
Figure 1. Heat capacity C_p and excess entropy ΔS of $(NH_4)_3TiF_7$ (a, b) and $(NH_4)_3SnF_7$ (c, d). Dashed lines indicate the lattice heat capacity C_{lat}.

found as $\Delta S_1 = 9.2 \pm 0.6$ J/(mol·K), $\Delta S_2 = 22.7 \pm 1.6$ J/(mol·K) for $(NH_4)_3TiF_7$ and $\Delta S_0 = 32.5 \pm 3.0$ J/(mol·K) for $(NH_4)_3SnF_7$. The relations between jumps of entropy at phase transition points and total entropy values $\delta S_1/\Delta S_1 = 0.33$, $\delta S_2/\Delta S_2 = 0.57$; $\delta S_0/\Delta S_0 = 0.62$ show that in accordance with the supposition above pre-transitional heat effects significantly contribute to the ΔS_i magnitudes, which exceed entropies determined by DSM [2, 7].

Very large values of the total phase transition entropies, Rln48 for NH$_4$)$_3$TiF$_7$ and Rln50 for $(NH_4)_3SnF_7$, point to significant structural distortions in both fluorides resulted from ordering processes. This is in agreement with the results of structural analysis exhibiting that octahedral MeF$_6$ and tetrahedral NH$_4$ groups are disordered completely in Pm-$3m$ phase, partially in $P4/mnc$ and $4/m$ phases, and totally ordered in Pa-3 phase of both fluorides under investigations [2, 6].

Information about the temperature behavior of the cell volume V_{cell} was obtained using the X-ray powder diffraction data collected in a wide temperature range. For heptafluorotitanate, we were able to examine the $V_{cell}(T)$ dependence only near Pa-$3 \leftrightarrow P4/mnc$ phase transition. Figure 2 depicts a sharp increase of V_{cell} at phase transition points: $\delta V_2/V = 0.4\%$ in $(NH_4)_3TiF_7$ and $\delta V_0/V = 1.35\%$ in $(NH_4)_3SnF_7$. Large values of the volume and entropy jumps point to the fact that both fluorides undergo transformations of the strong first order.

In accordance with the results of the calorimetric data analysis, the total entropy change at successive transitions Pa-$3 \leftrightarrow P4/mnc \leftrightarrow 4/m$ in titanium fluoride is close to the value of
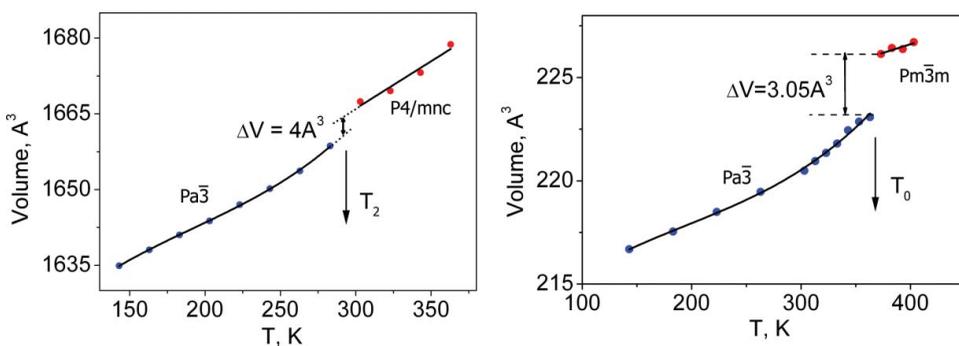
Figure 2. Temperature dependences of the cell volume at T_2 in $(NH_4)_3TiF_7$ (a) and at T_0 in $(NH_4)_3SnF_7$ (b).

entropy related to direct transformation between two cubic phases $Pa\text{-}3 \leftrightarrow Pm\text{-}3m$ in hepta-fluorostannate. It means that the plausible $4/m \leftrightarrow Pm\text{-}3m$ transition in the former compound should be accompanied by small entropy change. Because such a transformation was not observed in $(NH_4)_3TiF_7$ at ambient pressure due to the decomposition of crystal at about 390 K [7], it was hoped to detect it at high pressure. In order to check this hypothesis and to construct a phase diagram in wide regions of temperature and pressure, we performed the study of the susceptibility of phase transition temperatures to hydrostatic pressure using DTA installation with a high sensitive Ge–Cu thermocouple.

The results of DTA-measurements on $(NH_4)_3TiF_7$ are presented in the pressure-temperature phase diagram (Fig. 3a). Two DTA-anomalies associated with successive $Pa\text{-}3$ (T_2) $\leftrightarrow$ $P4/mnc$ (T_1) $\leftrightarrow$ $4/m$ phase transitions were recorded at ambient pressure. Both phase boundaries are linear with the following baric coefficients $dT_2/dp = 18$ K/GPa and $dT_1/dp = -42$ K/GPa. A sharp change of the slope of the boundary between $4/m$ and $P4/mnc$ phases at rather low pressure, where dT/dp ranges from -42 to -164 K/GPa, testifies that the triple-point exists at $T_{trp1} = 345.5$ K and $p_{trp1} = 0.125$ GPa. Taking into account the assuming of cubic parent phase with $m3m$ point group in $(NH_4)_3TiF_7$ [7] and the cubic symmetry $Pm\text{-}3m$ at room temperature in $(NH_4)_3PbF_7$ [1], one can suppose that the third boundary at triple-point 1 (dashed line in Fig. 3a) divides phases $4/m$ and $Pm\text{-}3m$.

The relations for entropy and volume jumps around the triple-point 1 are $\delta S_{Pm3m\text{ - }P4/mnc} = \delta S_{Pm3m\text{ - }4/m} + \delta S_{4/m\text{ - }P4/mnc}$ and $\delta V_{Pm3m\text{ - }P4/mnc} = \delta V_{Pm3m\text{ - }4/m} + \delta V_{4/m\text{ - }P4/mnc}$. Using Clapeyron – Clausius equation $dT/dp = \delta V/\delta S$ and experimental data on dT_i/dp and δS_i, the δV_i values were evaluated as well as the baric coefficient $dT_{Pm3m\text{ - }4/m}/dp = -600$ K/GPa. Thus, at ambient pressure the $Pm\text{-}3m \leftrightarrow 4/m$ phase transition could take place at about 430 K, i.e. above the decomposition temperature of $(NH_4)_3TiF_7$.

The temperature interval of the $P4/mnc$ phase stability narrows with pressure increase (Fig. 3a). As a result, the second triple-point at $T_{trp2} = 298$ K and $p_{trp2} = 0.41$ GPa exists on the T-p phase diagram and a direct transformation $Pm3m \leftrightarrow Pa\text{-}3$ takes place above p_{trp2} characterized by negative baric coefficient -40 K/GPa. Using the above presented relation for entropy changes around the triple-point 2, the entropy jump $\delta S_{Pm3m\text{ - }Pa\text{-}3} \approx 17.3$ J/mole·K was evaluated, which is in a good agreement with experimental value of entropy jump in $(NH_4)_3SnF_7$ found at ambient pressure at the same phase transition $\delta S_{Pm3m\text{ - }Pa\text{-}3} = 20 \pm 3$ J/mole·K.
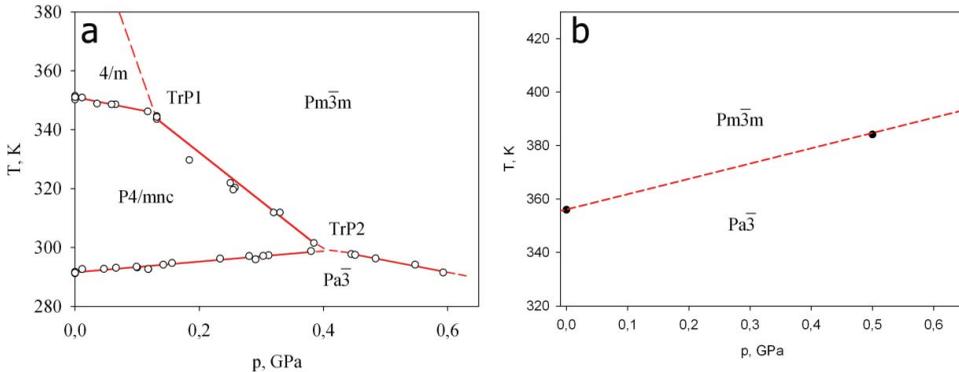
Figure 3. Temperature-pressure phase diagrams for $(NH_4)_3TiF_7$ (a) and $(NH_4)_3SnF_7$ (b).

Because of the closeness of the *Pm3m* ↔ *Pa*-3 phase transition and decomposition temperatures [2], the *T*-*p* phase diagram of $(NH_4)_3SnF_7$ was not studied experimentally. However, the positive volume change at T_0 with temperature increase shows that hydrostatic pressure elevates T_0 in this fluoride contrary to heptafluorotitanate in which $dT_{Pm3m - Pa-3}/dp < 0$. Using experimentally determined values of $\delta V_{Pm3m - Pa-3}$ and $\delta S_{Pm3m - Pa-3}$, baric coefficient $dT_{Pm3m - Pa-3}/dp = 91$ K/GPa for $(NH_4)_3SnF_7$ was calculated in the framework of Clapeyron – Clausius equation. On the one hand, the positive sign of $dT_{Pm3m - Pa-3}/dp$ showing the narrowing of the *Pm3m* phase stability range with pressure agrees with the T_0 temperature increase in $(NH_4)_3TiF_7$ having less unit cell volume compared to heptafluorostannate. On the other hand, T_0 decreases with pressure in titanium fluoride. One can suppose that the boundary between *Pm3m* ↔ *Pa*-3 phases in *T*-*p* phase diagram of $(NH_4)_3SnF_7$ can be nonlinear and at some pressure the $dT_{Pm3m - Pa-3}/dp$ value becomes negative. Similar situation was observed for instance for the series of fluorides $A_2A'MeF_6$ with the elpasolite structure undergoing phase transition between cubic *Fm*-3*m* and monoclinic $P2_1/n$ phases [8]. The corresponding phase boundary was nonlinear and the increase of the unit cell volume due to the substitution of the central atom was accompanied by the change of the initial $(dT/dp)_{p = 0}$ value from + 21 K/GPa to – 38 K/GPa from one crystal to another.

It should be remarked that recently the X-ray single crystal study has revealed the *Pm*-3*m* ↔ *Pa*-3 phase transition in oxide-fluoride double salt $(NH_4)_3WO_2F_5 = (NH_4)_2WO_2F_4 \cdot NH_4F$ [9]. The closeness of the transformation temperature to the room temperature permits to study thermodynamic properties, including *T*-*p* phase diagram, in wide ranges of temperature and pressure. Such investigations are now in progress.

Conclusions

Summarizing the results obtained one can make following conclusions.

1. Successive and single-phase transitions in fluoride double salts $(NH_4)_3TiF_7$ and $(NH_4)_3SnF_7$ are accompanied by rather large entropy changes characteristic for strong order-disorder transformations. The contribution of pre-transitional heat effects to entropy change is significant.

2. The results of the *T*-*p* phase diagrams study point to existence of *Pm*-3*m* phase under pressure in $(NH_4)_3TiF_7$ as well as a probability of nonlinear *Pm*-3*m* ↔ *Pa*-3 boundary in $(NH_4)_3SnF_7$.

3. Strong cell volume change at phase transition points is the reason of reversible cracking of both fluorides under study observed in previous polarizing-optic observations [2, 7].

Acknowledgment

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