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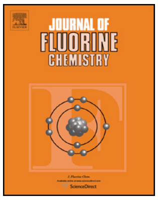

Thermal, structural, optical, dielectric and barocaloric properties at ferroelastic phase transition in trigonal $(NH_4)_2SnF_6$: A new look at the old compound

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ABSTRACT

Structural phase transition P-3m1 ↔ P-1 of the first order and nonferroelectric nature was found in $(NH_4)_2SnF_6$ at about 110 K in the process of thermal, optical, dielectric and X-ray studies.

Order-disorder transformation is accompanied by large changes of entropy ($\Delta S_0 = 16.4$ J/mol K) and volume ($\Delta V_0/V \approx 1\%$). The structural model associated with three orientations of NH_4 tetrahedra in P-3m1 phase and their complete ordering in P-1 phase was suggested with the entropy change ($\Delta S_0 = 18.3$ J/mol K) close to the experimental value. A good agreement between baric coefficients measured in a direct way ($dT_0/dp = -157$ K/GPa) and evaluated using entropy and volume changes at phase transition (-170 K/GPa) was found. Barocaloric effects in $(NH_4)_2SnF_6$ are comparable with those of known solid state refrigerants and are characterised by a low-pressure need for realising their maximum values.

1. Introduction

Recent pioneering observations of phase transitions in fluoride double salts $(NH_4)_3TiF_7$ and $(NH_4)_3SnF_7$ have shown that these structural transformations were accompanied by the decomposition process at high temperatures, followed by the emergence of the $(NH_4)_2TiF_6$ and $(NH_4)_2SnF_6$ phases, which were used as the initial substances for the synthesis of both heptafluorocompounds [1,2]. The symmetry of both hexafluorocompounds was trigonal with the P-3m1 space group, $Z = 1$. In $(NH_4)_3TiF_7$, the decomposition process started at temperature rather far from phase transition points and did not prevent the study of physical properties, in particular, thermal properties [3]. X-ray powder studies of ammonium heptafluorostannate showed that the temperatures of both the direct phase transition between two cubic phases and the decomposition process were rather close to each other [2]. This circumstance could complicate the investigation of the physical properties behaviour at structural transformation especially integral thermodynamic characteristics such as enthalpy and entropy. Thus, before the studying thermal properties of $(NH_4)_3SnF_7$ in details we needed to know the same properties of $(NH_4)_2SnF_6$.

It was surprising that, despite the fact that ammonium hexafluorostannate has been known for many years [4], we have found scant information concerning this compound. The room temperature structure (sp. gr. P-3m1, $Z = 1$) containing isolated $[SnF_6]^{2-}$ octahedra and $[NH]^{4+}$ tetrahedra was first determined by X-ray powder diffraction [5] and then refined by the single crystal experiment [6]. It was also found that $(NH_4)_2SnF_6$, like other A_2SnF_6 compounds (A: K, Rb, Cs, Tl), can be obtained either in trigonal or cubic (sp. gr. Fm-3m, $Z = 4$) modification depending on the conditions of crystallisation [7]. In DTA-measurements only one reversible peak meaning the P-3m1 → Fm-3m transition was found in the range 450–520 °C for different alkaline hexafluorostannates.

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Table 1
Main parameters of processing and refinement of the $(NH_4)_2SnF_6$ sample.

Compound	$(NH_4)_2SnF_6$
Sp.Gr.	P-3m1
a, Å	6.0711(2)
c, Å	4.8542(2)
V, Å^3	154.95(1)
Z	1
2θ-interval, °	5–120
No. of reflections	104
No. of refined parameters	29
R_{wp},%	8.15
R_p,%	5.98
R_{exp},%	5.33
χ^2	1.53
R_B,%	1.22

The same polymorphism was observed in the related compound $(NH_4)_2SiF_6$ [8,9].

Calorimetric experiments have revealed that the trigonal P-3m1 modification underwent order-disorder phase transition at about 38.6 K, whereas cubic modification remained stable at least down to 25 K, which was the lowest temperature of measurements [10]. Because the standard entropy found for P-3m1 phase ($S^\circ = 280.4 \pm 0.6$ J/mol K) was less than that for Fm-3 m phase ($S^\circ = 285.6 \pm 0.6$ J/mol K), trigonal modification can be considered as metastable. One can suppose that this is the reason of the conversion from trigonal phase to cubic observed at room temperature over time [10]. There is no information about the symmetry of phase realized below 38.6 K for trigonal $(NH_4)_2SiF_6$. Also, the mechanism of structural distortions has not been established. Order–disorder reorientations were attributed to either the $SiF_6{}^{2-}$ anion [10] or the ammonium cation [11].

The study of optical and structural properties of $(NH_4)_3TiF_7$ and $(NH_4)_3SnF_7$ has shown that the increase of the central atom size Ti → Sn led to strong increase of the temperature of the phase transition from the low temperature cubic phase P-3a [1,2]. Taking into account the stronger difference between the Si and Sn ionic sizes one can suppose that a reversible structural phase transition observed in $(NH_4)_2SiF_6$ [10] could exist in trigonal $(NH_4)_2SnF_6$ at much higher temperatures compared to ammonium hexafluorosilicate.

In this paper, we present the results of structural, polarizing-optic and differential scanning calorimetric searching for phase transition in trigonal $(NH_4)_2SnF_6$ as well as detailed data on heat capacity, thermal dilatation and dielectric properties in a wide temperature range. Hydrostatic pressure effect as well as barocaloric efficiency were also investigated.

2. Sample preparation and characterization

Ammonium hexafluorostannate, $(NH_4)_2SnF_6$, was synthesised using metallic tin platelets (β-Sn) of the 99.9% purity as a starting material. Such a synthesis has been previously described [5], where the starting reagent was freshly precipitated meta-tin acid. We used chemically pure nitric acid (56 mass.% HNO_3) and hydrofluoric acid (40% HF) for tin oxidation and complexation in accordance with the reaction:

$$Sn + 6HF + 4HNO_3 = H_2SnF_6 + 4NO_2 + 4H_2O$$

Chemical etching tin platelets was carried out in the excess of HF with accurate dropwise addition of HNO_3 at room temperature because of high exothermal character of the above reaction. Ammonia aqueous solution (NH_3 aq, 25%) was then added to increase the solution pH from 0 to 2:

$$H_2SnF_6 + 2NH_3 = (NH_4)_2SnF_6$$

Thin hexagonal plates of $(NH_4)_2SnF_6$ were formed in the course of evaporation (the PXRD pattern were matching with the JCPDS file No. 026-0094)

The powder diffraction data of $(NH_4)_2SnF_6$ for Rietveld analysis were collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu-K radiation) and linear VANTEC detector. The step size of 2θ was 0.016°, and the counting time was 0.6 s per step. Rietveld refinement was performed using TOPAS 4.2 [12]. All peaks were indexed by the trigonal unit cell (P-3m1) with parameters close to those determined from single crystal experiments [6]. Therefore this crystal structure was chosen as the starting model for Rietveld refinement. Hydrogen atoms were omitted in the model considered. Refinement was stable and gave low R-factors (Table 1, Fig. 1).

Atomic coordinates presented in Table 2 are also in a good agreement with the single crystal data [6].

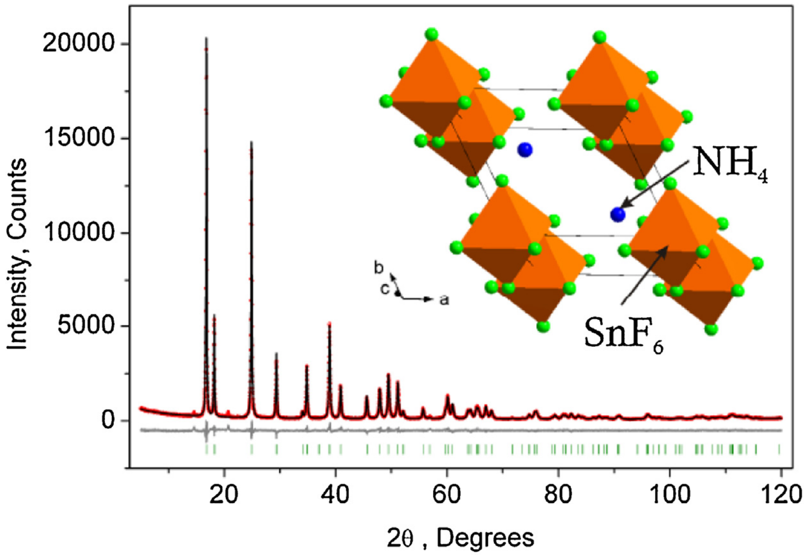

Fig. 1. Difference Rietveld plot of $(NH_4)_2SnF_6$. Inset shows the crystal structure.