Internal Mobility, Phase Transitions, and Ionic Conductivity in (NH₄)₆KZr₄F₂₃ and (NH₄)₆KHf₄F₂₃


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Abstract—The ion mobility, phase transitions (PTs), and conductivity in (NH₄)₆KZr₄F₂₃ (I) and (NH₄)₆KHf₄F₂₃ (II) have been studied by ¹H and ¹⁹F NMR, DSC, and impedance spectroscopy. Types of ion motion in the fluorides and ammonium sublattices have been determined in the temperature range 150–480 K, and their activation energies have been evaluated. Compounds I and II undergo phase transitions in the temperature ranges 400–440 and 419–440 K, respectively, to form high-temperature modifications. The high ionic conductivity in (NH₄)₆KZr₄F₂₃ and (NH₄)₆KHf₄F₂₃ (>10⁻³ S/cm at 473 K) makes it possible to classify these compounds with superionic conductors.

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Previously, the crystal structure of (NH₄)₆LiZr₄F₂₃ has been reported, and the character of ion motion in this compound in the temperature range 170–440 K has been considered [1]. The (NH₄)₆LiZr₄F₂₃ structure is composed of isolated infinite [ZrF₆]ₙ⁻, chains extended parallel to each other along the x axis. The NH₄⁺ and Li⁺ cations are located between the chains. The zirconium polyhedra with CN = 7 and 8 share F(1)'⋅⋅⋅F(1)' edges. In the chains, tetranuclear [–ZrF₆–ZrF₆–ZrF₆–ZrF₆–]– fragments can be discerned. Inside these fragments, the zirconium polyhedra are edge-sharing, and the tetramers are combined with each other through the bridging F(6) atoms. According to ¹⁹F NMR and ¹H NMR data, the phase transition near 415 K leads to the modification in which the diffusion of fluoride and ammonium ions begins at lower temperatures than in the initial phase, and the specific conductivity σ of the high-temperature phase is higher at 300 K than that of the initial phase [2]. The same character of ion motion and phase transitions is valid for the (NH₄)₆NaZr(Hf)₄F₂₃ compounds [2]. The specific conductivities of (NH₄)₆NaZr(Hf)₄F₂₃ and (NH₄)₆LiZr₄F₂₃ (σ ≈ 4 × 10⁻³ S/cm at T = 420 K [2]) made it possible to classify these fluoro complexes with superionics.

Recently, analogous compounds (NH₄)₆KZr₄F₂₃ and (NH₄)₆KHf₄F₂₃ have been synthesized [3, 4]; they are isostructural to (NH₄)₆NaZr₄F₂₃, which implies the same character of dynamic processes in these compounds as in (NH₄)₆NaZr₄F₂₃.

The aim of this work is to study thermal properties, ion mobility, and conductivity in new ammonium fluorozirconate (−hafnate) and compare them with the earlier data obtained for (NH₄)₆LiZr₄F₂₃ [1] and (NH₄)₆NaZr₄F₂₃ [2].

EXPERIMENTAL

The (NH₄)₆KZr₄F₂₃ and (NH₄)₆KHf₄F₂₃ compounds were synthesized by adding ammonium and potassium fluorides to zirconium (hafnium) oxide preliminarily dissolved in 40% hydrofluoric acid; the reagents were combined in the molar ratio NH₄F : KF : Zr(Hf)O₂ = 6 : 1 : 4. The resulting solutions were heated in a water bath until transparent solutions were formed; then, these solutions were evaporated until a crystalline precipitate formed [3, 4]. The purity of the compounds was proved by chemical analysis, X-ray diffraction, DSC measurements, IR spectroscopy, and NMR.

X-ray powder diffraction (Bruker D8 ADVANCE, CuKα radiation) confirmed the single-phase character of the samples. The unit cell parameters of the compounds were determined by indexing the X-ray powder diffraction patterns by an iterative method using unit cell parameters of isostructural compounds found for a single crystal.

The ¹⁹F and ¹H NMR spectra were recorded on a Bruker AV-300 multinuclear digital spectrometer at Larmor frequencies of 282.404 and 300.13 MHz, respectively, in the temperature range 150–480 K. The mean-square width (or second moments S₂) of the NMR spectra (in G²) were calculated with an original program using formalism presented in [5]. The line width ΔH (in kHz), chemical shifts (δ), and integrated
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The electrophysical characteristics of polycrystalline samples pressed into pellets 13 mm in diameter were determined by the impedance spectroscopy method. To measure the conductivity, the pellets were coated with electro-conductive DOTITE silver paint D-550 providing the electrode/solid electrolyte contact. Measurements were carried out on a high-precision setup consisting of an Impedance/Gain-Phase Analyzer SI 1260 and Solartron Dielectric Interface 1296 with the use of an ac signal with an amplitude of 0.5 V in the frequency range from 1 Hz to 1 MHz; the spectra were recorded with 10 measurement points per decade. The specific conductivity \( \sigma \) was calculated through fitting the resulting impedance spectra using ZView software for equivalent circuit modeling with taking into account the sample geometry: \( \sigma = l/R S \) (where \( l \) is the pellet thickness, \( S \) is the electrode surface area, \( R \) is the pellet resistance calculated on modeling the experimental data). The samples were heated and cooled in a helium flow in the temperature range 297–473 K in the heating–cooling cycle with a step of 5 K and kept at fixed temperatures when an impedance spectrum was recorded.

Results and Discussion

It has been shown that the \((\text{NH}_4)_6\text{KZrF}_{23}\) fluoro complexes are isostructural to \((\text{NH}_4)_6\text{NaZrF}_{23}\) [3, 4]. The crystal system and unit cell parameters of the compounds were determined by the reciprocal lattice method: \((\text{NH}_4)_6\text{KZrF}_{23}\) is orthorhombic, \(a = 30.178 \text{ Å}, b = 25.150 \text{ Å}, c = 6.642 \text{ Å}, Z = 8\); \((\text{NH}_4)_6\text{KHfF}_{23}\) is orthorhombic, \(a = 30.844 \text{ Å}, b = 23.496 \text{ Å}, c = 6.803 \text{ Å}, Z = 8\). The IR spectra of these compounds are similar to the IR spectra of \((\text{NH}_4)_6\text{Li(Na)ZrF}_{23}\) [8]; in addition to the X-ray diffraction data, this fact allows us to assume that the \((\text{NH}_4)_6\text{KZr(Hf)}_4\text{F}_{23}\) compounds have a chain structure analogous to the structure of \((\text{NH}_4)_6\text{LiZrF}_{23}\) [1, 2] and, hence, can be treated as potential candidates for compounds with high ionic conductivity.

Since the \((\text{NH}_4)_6\text{LiZrF}_{23}\) and \((\text{NH}_4)_6\text{NaZrF}_{23}\) compounds have phase transitions [1, 2], such transitions are also expected for the \((\text{NH}_4)_6\text{KZr(Hf)}_4\text{F}_{23}\) compounds. The presence of phase transitions in these compounds was confirmed by DSC data. Figure 1 shows the DSC curves for the \((\text{NH}_4)_6\text{KZrF}_{23}\) compound in the temperature range 303–473 K. In the course of the first heating, the DSC curve shows three thermal events with maxima at 358, 382, and 419 K. When the sample is cooled, the heat anomaly corresponding to the DSM signal maximum at 419 K is reproduced, which is evidence of the formation of the reversible high-temperature \(\alpha\) modification. On second heating of the sample (Fig. 1), the DSC curve (2) shows a new heat anomaly with a maximum at 431 K, which can be attributed to the phase transition to the high-temperature \(\beta\) modification. In the course of the second cooling, a hysteresis of the transition temperature corresponding to the DSM signal maximum at 431 K (DSC curve 2') is observed: \(\delta T = (8 \pm 1) \text{ K}\). In the course of the second thermocycling, the temperatures of heat anomalies remain unaltered. The reproducibility of the thermal events during thermocycling allows us to state that \((\text{NH}_4)_6\text{KZrF}_{23}\) undergoes enantiotropic transitions. Large hysteresis values are evidence in favor of first-order phase transitions. X-ray diffraction analysis of the samples obtained in the course of thermocycling of compound I to 358 and 380 K demonstrates that the X-ray diffraction patterns of the products differ insignificantly from the X-ray diffraction pattern of the initial compound; these differences

![Fig. 1. DSC curves for \((\text{NH}_4)_6\text{KZrF}_{23}\); (1') first heating, (2) second heating, (1') cooling of the sample after the first heating, and (2') cooling of the sample after the second heating.](image-url)