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THERMAL PROPERTIES AND STRUCTURAL FEATURES OF ALKALI METAL (K, Rb, Cs) AND AMMONIUM MIXED BIFLUORIDES

V. E. Fedorov and T. D. Fedotova

Institute of Inorganic Chemistry, Siberian
Department of the Academy of Sciences of the U.S.S.R., Novosibirsk

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DTA and TG methods were used to study the melting, polymorphic transformation and thermal decomposition processes of alkali metal and ammonium mixed bifluorides formed by mutual replacement of the cations in the crystal lattice. We studied the structural features and the characteristics in the changes of thermal properties of individual compounds, solid solutions with unlimited solubility and solid solutions with limited solubility.

Under normal conditions potassium, rubidium and caesium bifluorides are isostructural, crystallizing in the tetragonal system (symmetry group $D_{4h}^{18}-I4/mcm$). When subjected to heating, they undergo polymorphic transformation into the cubic phase: KHF_2 and $RbHF_2$ assume the structural type of NaCl (O_h^5-Fm3m), $CaHF_2$ that of CsCl, which – close to its melting temperature – passes presumably into the structure of the NaCl type [1, 2]. The structure of ammonium bifluoride is defined by the presence of N – H . . . F type hydrogen bonds, besides the bifluoride ions. This structure corresponds to the symmetry group D_{2h}^7 – Pman [3].

The thermal properties of these compounds are of interest both from the theoretical view and for practice. They have been studied in great detail: There are numerous data at disposal on their polymorphic transformation, melting behaviour and thermal stability [4–7].

In the present paper we shall discuss thermal properties of mixed bifluorides. These are novel phases, which we were the first to prepare in system of the type $MHF_2-M'HF_2-H_2O$ (M and M' being K, Rb and Cs, resp.) [8–10]. The X-ray patterns and the parameters of the elementary cells, as well as their dependence on composition were determined, and the structure of the compounds was studied in earlier work [8–12].

Experimental

The substances were synthetized from aqueous solutions, amounts being calculated from the data on the corresponding ternary systems [8, 9] and identified by chemical analysis and X-ray analysis. For thermal analysis we used the derivatograph manufactured by MOM, with sample weights around 100 mg and heating rates of 2 . . . 5°/min. To determine phase transition temperatures, the samples were placed in air-tightly sealed platinum crucibles, to avoid eventual thermal decomposition and change in composition due to the evolution of volatile substances. When studying thermal decomposition processes, the samples were heated in open platinum crucibles in air.

Results and discussion

Our experiments [8] indicated that the isostructural bifluorides of alkali metals form a continuous series of solid solutions at 25°: for $(K\text{-}Rb)HF_2$ and $(Rb\text{-}Cs)HF_2$ the substitution is accompanied by a linear change in the parameters of the elementary tetragonal cell. In their thermal behaviour, the solid solutions $(K\text{-}Rb)HF_2$ are similar to those of the initial components. The first endothermic peak on the thermoanalytical curves of these phases is obviously related to the polymorphic transition from the tetragonal modification into the cubic modification. Hence the presence of solid solutions may be assumed also between the high-temperature phases of isostructural potassium and rubidium bifluorides. The second endothermic peak corresponds to the melting of the solid solutions, and finally, the subsequents raise of temperature results in splitting off hydrogen fluoride.

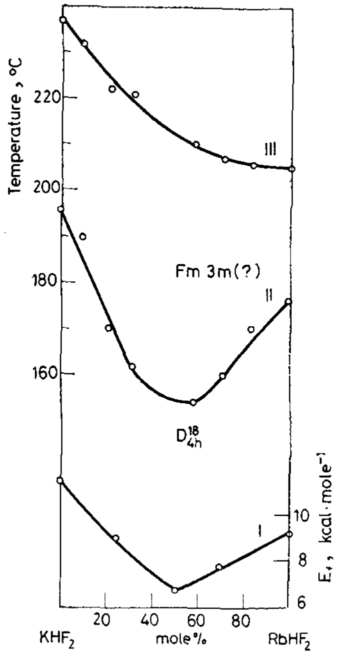

Fig. 1. Activation energy of flipping (I), temperature of polymorphic transformation (II) and melting temperature (III) *vs.* composition of $(K\text{-}Rb)HF_2$ solid solutions

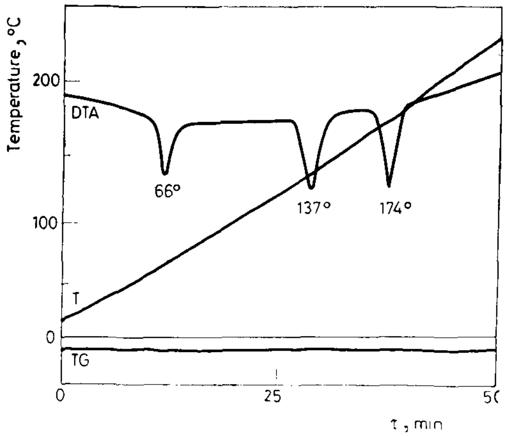

Fig. 2. Thermoanalytical curves of (Rb-Cs)HF_2 solid solution containing 80 mol-% $CsHF_2$

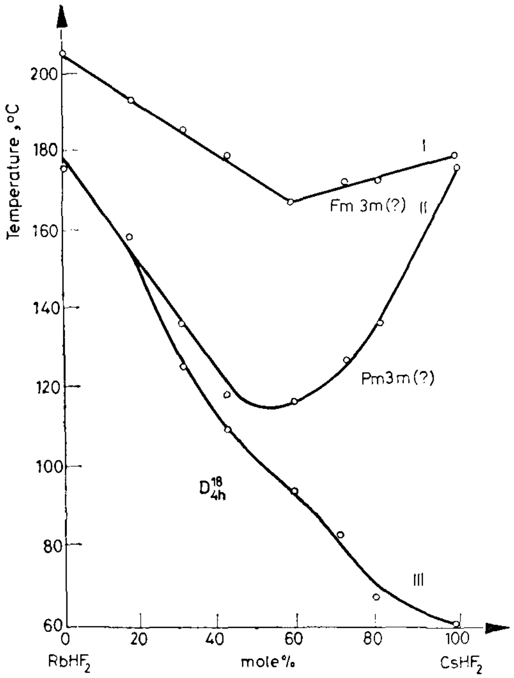

Fig. 3. Temperature of polymorphic transformations (I and II) and melting *vs.* composition of (Rb-Cs)HF_2 solid solutions

A well-defined relationship between the temperature of the first two endothermic peaks and the composition of the solid solution (K-Rb)HF_2 exists (Fig. 1). The relationship for the polymorphic transition temperature is a minimum curve, while the melting temperature increases monotonously. Also, these monovariant processes proceed within a narrow temperature interval. Figure 1 demonstrates the temperatures of the maximum development of the processes (for melting, the curve is identical with the liquidus line).

NMR data of the tetragonal modifications of potassium, rubidium and caesium bifluorides [13] indicate the presence of so-called flipping (re-orientation of HF_2^- ions by 180°), preceding phase transitions. At increasing temperatures, orientation disarrangement of the bifluoride ions is observed, and in the cubic lattice the HF_2^- ion will gain true spherical symmetry. From this view, the polymorphic transformation of alkali metal bifluorides is closely related to the dynamics of the HF_2^- ions. By using NMR relaxation spectrometry to study the dynamics of HF_2^- ions in (K-Rb)HF_2 solid solutions [14] we found that the relationship between concentration and activation energy of flipping is of the same type as that between concentration and temperature of polymorphic transformation (Fig. 1). This may be accepted as evidence for the mechanism described above. The position of the minimum in the plots presumably corresponds to the maximum disorientation state in the anionic sublattice, so that the elementary cell can be stretched in the direction of axis C to attain the symmetry group Fm3m.

Much more complex phase equilibria were found when heating (Rb-Cs)HF_2 solid solutions, presumably because three polymorphic modifications of caesium bifluoride exist. In solid solutions with large $CsHF_2$ shares, the DTA curve manifests, in addition to the peak corresponding to melting, and the subsequent rise due

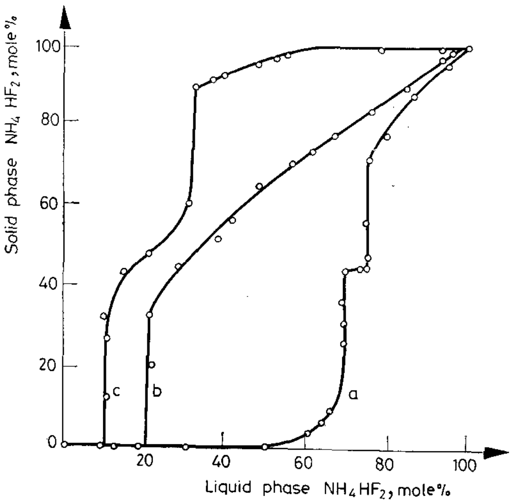

Fig. 4. Distribution diagrams of the systems NH_4HF_2 — MHF_2 — H_2O (25 °C)

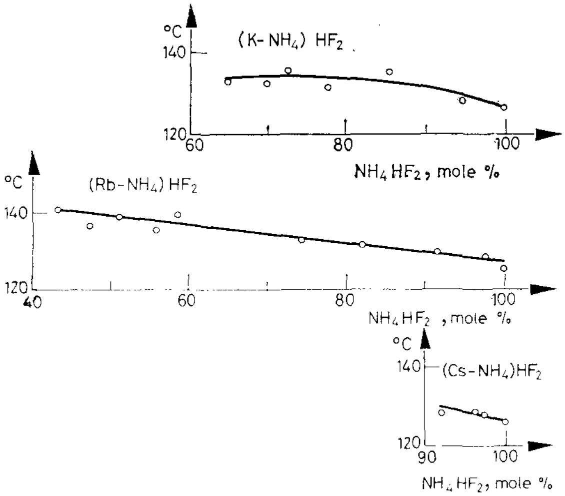

Fig. 5. Melting temperature of $(NH_4\text{-}M)HF_2$ solid solutions on the basis of NH_4HF_2 *vs.* composition

to decomposition, the existence of two endothermic processes, corresponding to reversible polymorphic transformations (Fig. 2). From data in the literature [2, 15] one may assume that these peaks indicate the transition of the solid solutions from the tetragonal into the cubic modification of the CsCl type ($O_h^1 - Pm3m$), and subsequently into the cubic type of NaCl. For solid solutions whose composition is close to $RbHF_2$, only a single polymorphic transition is recorded, obviously the one from the tetragonal modification into the cubic modification of the NaCl-type (Fig. 2), since under normal conditions the CsCl-type structure is not characteristic for rubidium bifluoride, this structure is achieved only at pressures exceeding 1.6 kbar [15].

The concentration dependence of the temperature of the first polymorphic transformation is monotonous, whereas minimum curves represent the relationship between concentration and transition temperature into the cubic modification of the NaCl type, as well as between concentration and melting point for the solid solutions $(Rb\text{-}Cs)HF_2$. Data on the structure on high-temperature solid solutions are not at disposal. None the less, our results, considering the structures of the initial bifluorides, allow to conclude that solid solutions $(Rb\text{-}Cs)HF_2$ can exist in three modifications: one tetragonal and two cubic structures, of the CsCl and NaCl type, resp. Also, with a growing share of rubidium in the solid solution, the temperature interval in which the CsCl-type phase can exist decreases, while for solid solutions with the NaCl-type structure, this interval first sharply increases, and reaches maximum values at relative proportions of the components around 1 : 1, similarly as in the case of the solid solutions $(K\text{-}Rb)HF_2$.

The systems $NH_4HF_2 - MHF_2 - H_2O$ (*M* being *K*, Rb, Cs, resp.), containing non-isostructural bifluorides, are characterized by the great diversity of their phase composition: together with the crystallizations areas of individual compounds and areas of solid solutions with limited solubility, two-phase areas are also present (Fig. 4).

The thermal behaviour of solid solutions on the basis of substituted NH_4HF_2 having a rhombic elementary cell appeared similar in all systems studied. When heated, they melt at temperatures only slightly higher than the melting point of the pure ammonium bifluoride [16, 17]. This was the case in systems with significant replacement of NH_4^+ by M^+, and also with $(Rb\text{-}NH_4)HF_2$ (Fig. 5), although the parameters of the elementary cell will be substantially changed [9]. The temperature interval between the liquidus and solidus lines does not exceed 10 . . . 15° (Fig. 5).

Obviously the melting process of solid solutions on the basis of NH_4HF_2 proceeds with their decomposition, and further heating results, in the first stage, in the evolution of ammonium bifluoride from the melt, and in the second stage, in the splitting off of hydrogen fluoride from the alkali bifluoride. When heating these solid solutions in open crucibles, substantial loss in weight will be observed already at 80°, and maximum rate of reaction will be reached at 210°. The first stage of decomposition will be terminated at 260 . . . 270°, in correspondance to thermal stability data of NH_4HF_2 [16]. The temperatures characterizing the two stages of decomposition are dependent only to a very slight degree on the relative contents of the components in the solid solution (Fig. 6).

The individual compound $0.8\ NH_4HF_2 \cdot KHF_2$, crystallizing in the system $NH_4HF_2-KHF_2-H_2O$ in the tetragonal system and having a two-step structure [9, 11, 12] has thermal properties very close to those of solid solutions on the basis of NH_4HF_2. It melts at 136° and is decomposed in two stages (Fig. 7).

Solid solutions on the basis of the tetragonal phase KHF_2, existing in a narrow composition range only (up to 10 mol-% NH_4HF_2), manifest a phase transition, when heated, presumably into the cubic modification, similarly to potassium bifluoride. The temperature of this polymorphic transformation is 196 . . . 197°, and is practically independent of the NH_4HF_2 content. This is in conformity with the finding that the parameters of the elementary cell, within the limits of homogeneity, remain practically unchanged when K^+ is replaced by NH_4^+ [9]. However, the melting temperature of these solid solutions will slightly decrease with increasing proportions of NH_4HF_2: from 238.7° for pure KHF_2 [18] to 225° for the solid solution corresponding to the solubility limit.

When heating tetragonal $(K\text{-}NH_4)HF_2$ solid solutions in open crucibles (Fig. 8), loss in weight appears around 80°, and the temperature of the maximum rate of the first stage of the decomposition process (evolution of NH_4HF_2) is close to the temperature of polymorphic transformation. Therefore the first endothermic peak on the thermoanalytical curves of the solid solutions $(K\text{-}NH_4)HF_2$ has a complex nature and corresponds to two processes taking place practically simultaneously: polymorphic transformation and evolution of NH_4HF_2. Subsequently an endothermic effect will be recorded on the heating curve corresponds to the melting of the pure potassium bifluoride, which in the following course of heating will be decomposed by splitting off hydrogen fluoride.

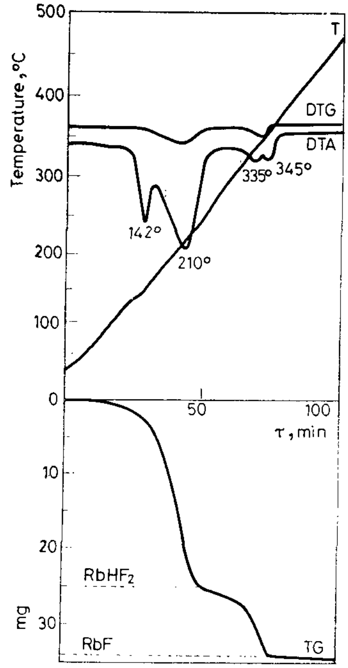

Fig. 6. Thermoanalytical curves of the $(NH_4\text{-}Rb)HF_2$ solid solution on the basis of NH_4HF_2, containing 50.9 mol-% NH_4HF_2

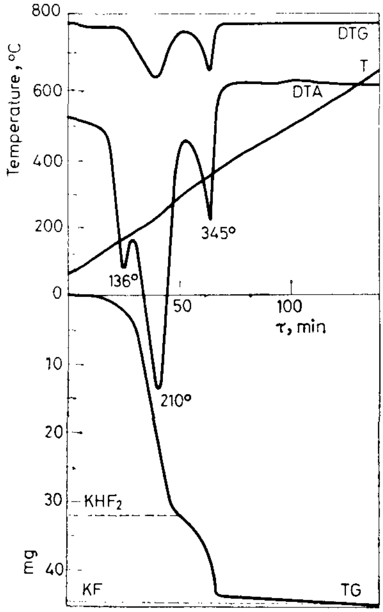

Fig. 7. Thermoanalytical curves of the compound 0.80 $NH_4HF_2 \cdot KHF_2$

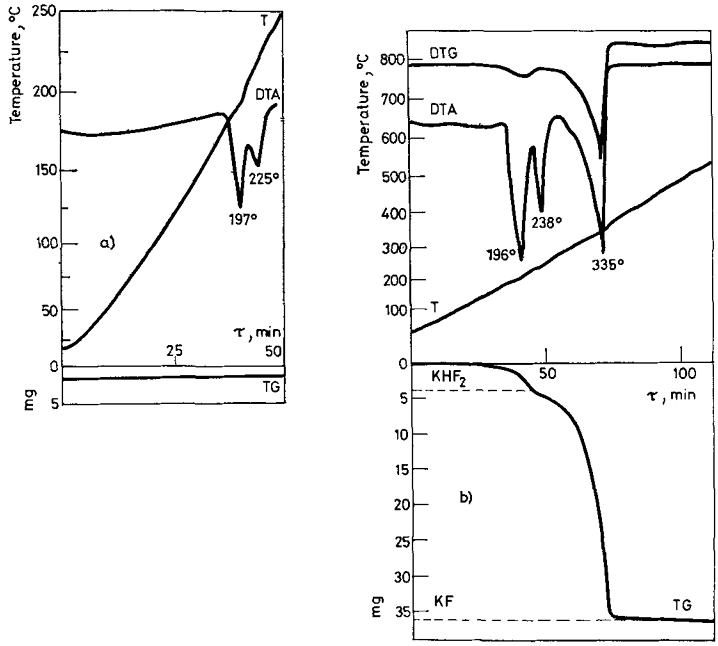

Fig. 8. Thermoanalytical curves of the solid solution $(K\text{-}NH_4)HF_2$ based on KHF_2, containing 9.5 mol-% NH_4HF_2

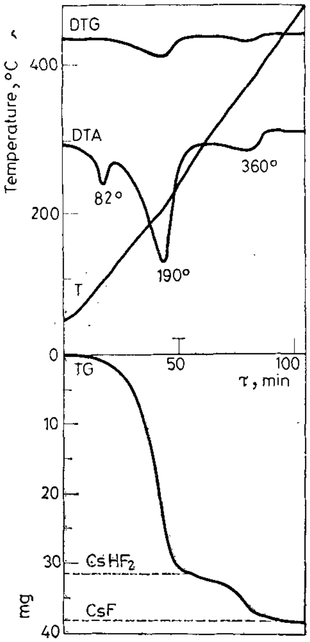

Fig. 9. Thermoanalytical curves of the solid solution $(Cs\text{-}NH_4)HF_2$ containing 55.7 mol-% NH_4HF_2

It should be noted that the samples of the two-phase area of the $NH_4HF_2-KHF_2-H_2O$ system (mixtures of the solid solution based on NH_4HF_2 corresponding to the solubility limit with the compound 0.80 $NH_4HF_2 \cdot KHF_2$) melt around 140°, independently of their composition, their liquidus and solidus lines being close to one another. The two-phase area of the system with potassium bifluoride, representing the mixtures of the solid solution on the basis of KHF_2 corresponding to the solubility limit with the compound 0.80 $NH_4HF_2 \cdot KHF_2$ is characterized by a solidus line around 140°, while the liquidus line decreases from 225° to 140° with increasing NH_4HF_2 content.

The solid solutions $(NH_4\text{-}Cs)HF_2$ formed in the intermediate concentration range of the system $NH_4HF_2-CsHF_2-H_2O$ with a tetragonal lattice differing from $CsHF_2$ [9] melt at lower temperatures as compared to the starting components (80 . . . 90°). (Fig. 4c). Their thermal decomposition also proceeds in two stages.

Conclusions

The results of the reported studies indicate that the phases formed when cations are being replaced in the crystal lattice of alkali metal and ammonium bifluorides are characterized by a great diverseness in thermal properties, depending both on their composition and on their structural features.

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RÉSUMÉ — On s'est servi des méthodes d'ATD et TG pour étudier les processus de fusion, de transformation polymorphe et de décomposition thermique des difluorures mixtes des métaux alcalins et d'ammonium, formés par substitution mutuelle des cations dans le réseau cristallin. On a étudié les caractéristiques structurales et les variations des propriétés thermiques des composés individuels et des solutions à solubilité limitée ou non.

ZUSAMMENFASSUNG — DTA- und TG-Methoden wurden zur Untersuchung des Schmelzens, der polymorphen Umwandlungs- und der thermischen Zersetzungsvorgänge der durch gegenseitige Substitution im Kristallgitter entstandenen gemischten Bifluoride von Alkalimetall und Ammonium eingesetzt. Die strukturellen Beschaffenheiten und Charakteristika der Änderungen der thermischen Eigenschaften der einzelnen Verbindungen und unbegrenzt bzw. begrenzt löslichen festen Lösungen, wurden studiert.

Резюме — Методами дифференциально-термического и термогравиметрического анализа исследованы процессы плавления, полиморфного превращения и термического разложения смешанных бифторидов щелочных металлов и аммония, образующихся в результате взаимозамещения катионов в кристаллической решетке. Обсуждаются структурные особенности и закономерности в изменении термических свойств и индивидуальных соединений, непрерывных и ограниченных твердых растворов.