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Study of vibrational spectra and thermal behavior of sodium fluorocirconate $Na_5Zr_2F_{13}$

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The structure and thermal stability of the compound $Na_5Zr_2F_{13}$ in the range of temperatures 20−800°C was studied by differential thermal and thermogravimetric analysis (DTA-TGA), X-ray diffraction analysis (XRDA) and vibrational spectroscopy.The phase transition to the high-temperature modification α-$Na_5Zr_2F_{13}$ with dynamically disordered structure was confirmed. Infrared (IR) spectroscopy and Raman scattering (RS) spectroscopy data of the compound β-$Na_5Zr_2F_{13}$ and its decomposition products upon heating were obtained, systematized and generalized. Based on the results of quantum-chemical calculations, the bands in the vibrational spectra of $Na_5Zr_2F_{13}$.

Keywords: complex zirconium fluorides, sodium fluorocirconates, thermogravimetry, vibrational spectroscopy.

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Introduction

Among the complex zirconium fluorides with alkali metal cations and ammonium, sodium fluoride zirconates have been less studied. In double system NaF-ZrF_4 the formation of sodium fluorocirconates (SFC) has been established: Na_3ZrF_7, $Na_5Zr_2F_{13}$, Na_2ZrF_6, $Na_3Zr_2F_{11}$, $Na_7Zr_6F_{31}$, $Na_3Zr_4F_{19}$, formed respectively at the molar ratios of the components 3 : 1, 2.5 : 1, 2 : 1, 1.5 : 1, 1.15 : 1, 0.75 : 1 [1]. From aqueous solutions of the system $ZrF_4-NaF-H_2O$, SFC solid phases were obtained: $NaZrF_5\cdot H_2O$, Na_2ZrF_6, $Na_5Zr_2F_{13}$, Na_3ZrF_7, which are also formed sequentially with increasing NaF content in the solution [2].

To the present day, the SFC of the composition Na_3ZrF_7 have been structurally characterized (coordination number (CN) Zr = 7) [3], $Na_5Zr_2F_{13}$ (CN Zr = 7) [4,5], γ-Na_2ZrF_6 (CN Zr = 7) (high-temperature phase) [6], $Na_7Zr_6F_{31}$ ($Na_6Zr_6F_{30}\cdot NaF$) (CN Zr = 8) [7]. X-ray diffraction studies of the compound $Na_7Zr_6F_{31}$ (F/Zr = 5. 16) have shown that three-dimensional structure corresponding to stoichiometry $6(NaZrF_5) = Na_6Zr_6F_{30}$ with additional ions Na^+ and F^- (one per cell) is formed in the structure, that is the compound may be considered as mixed Na-salt. Decreasing the F/Zr ratio from 7 to 5 in FZN leads to a successive transition from island to dimeric and framework structures. It should be noted that there are no compounds with Zr-polyhedra connected by their vertices and/or edges in a continuous chain of anions.

Fluorocirconates of the composition $M_5Zr_2F_{13}$ (F/Zr = 6.5) are formed with Na^+ and K^+ (high temperature phase) [8]. Their anionic sublattice is based on $[Zr_2F_{13}]^{5-}$ dimers. In structures of other compounds with excess fluorine ions (F/Zr(Hf) ¿ 6. 5), such as $Ag_3Hf_2F_{14}$ ($Ag_3Hf_2F_{13}\cdot F$) [9] and $ThZrF_8$ ($Th_2Zr_2F_{13}\cdot F_3$) [10], dimeric complex anions of similar composition were determined $[Hf_2F_{13}]^{5-}$ and$[Zr_2F_{13}]^{5-}$.

The compound $Na_5Zr_2F_{13}$ is formed from the melt of the NaF-ZrF_4 double system by a peritectic reaction ($T = 640$°C). As noted above, this salt is also an equilibrium phase with respect to aqueous solutions of the NaF-ZrF_4-H_2O [2] system. Also during the synthesis of mixed fluorophosphate-circonates from aqueous solutions of $ZrO(NO_3)_2-H_3PO_4-NaF(HF)-H_2O$ under certain conditions one of the co-crystallizing phases is $Na_5Zr_2F_{13}$ [11].

The currently available IR spectroscopic data for the compound $Na_5Zr_2F_{13}$,, as well as the description of the thermogram do not give a complete picture of its structure and thermal behavior [12].

In the present paper with the aim of clarification, addition, systematization and generalization of the data on the structure, thermal stability $Na_5Zr_2F_{13}$ its complex study by the methods of vibrational (IR, RS) spectroscopy and thermal analysis was carried out.

Experimental part

The compound $Na_5Zr_2F_{13}$ is formed by adding an aqueous Na_2CO_3 (5.2 g, 0.05 M) in 30 ml H_2O to solution ZrO_2 (6.2 g; 0.05 M) in 30 ml 40% HF. The precipitate formed immediately on mixing the components is filtered off, washed with acetone on the filter and dried at room temperature. The X-ray diagram of the resulting product is identical to that of the phase β-$Na_5Zr_2F_{13}$ (chart 00-049-0107 (Q)) (Fig. 1, curve *1*). Although the initial Na^+/Zr^{4+} component ratio during synthesis is 2 : 1, however under these conditions the $Na_5Zr_2F_{13}$ phase crystallizes, whose solubility is lower than that of Na_2ZrF_6 [13]. The resulting

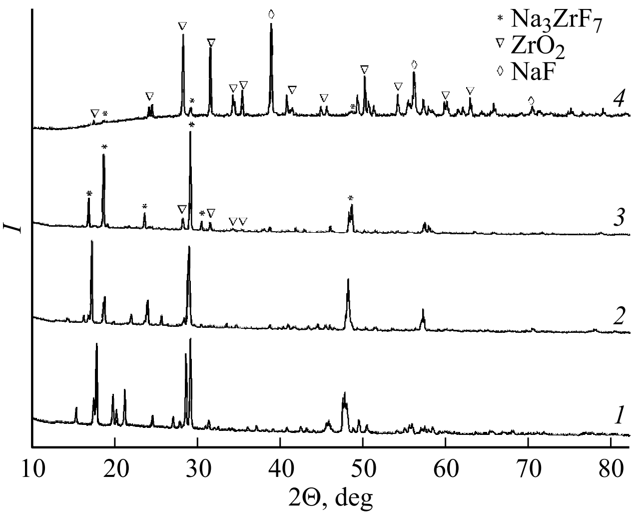

Figure 1. X-ray radiographs of the compoundβ-$Na_5Zr_2F_{13}$ (*1*) and its products heated to temperatures of 530 (*2*), 650 (*3*) and 800°C (*4*).

Na-salt is stable and does not change during recrystallization from water.

Thermal study of the samples was carried out on a Q-1000 MOM derivatograph in air at a heating rate of 5 deg/min. The weight of the samples was 200 mg. A calcined Al_2O_3 was used as a reference. X-ray diffraction data for the synthesized compounds were obtained on a diffractometer „STOE STADI P" ((Cu$K_{\alpha 1}$-radiation, $\lambda = 1.5406$ Å, Ge monochromator). Powder data bank PDF-2 was used to obtain the information on the composition of the products.

Infrared (IR) spectra were obtained at 4000 −400 cm $^{-1}$ at room temperature using an IR-Affinity instrument on a KRS-5 window for samples prepared as a suspension in Vaseline oil. Raman scattering (RS) spectra of the compounds studied were recorded using a WiTec alpha500 Raman microscope (laser wavelength 532 nm). The spectra are discussed in the area 700−150 cm $^{-1}$ corresponding to the fluorocirconate anions.

To assign the bands in $Na_5Zr_2F_{13}$ spectra, quantum-chemical calculations were performed using the GAMESS [14] software package. The calculations are performed within the framework of the local density functional theory combined with the B3lyp exchange-correlation potential. For Zr(IV) and Na atoms LANL2DZ basis set with core potential and functions basis set 6311g(dp) for F atoms were used. The choice of model clusters was made taking into account the known structural data. The calculation of the equilibrium geometry and the normal oscillation frequencies is carried out in the harmonic approximation. The results were obtained with the equipment of the Shared Resource Center „Far Eastern Computing Resource" of Institute of Automation and Control Processes, Far Eastern Branch of RAS (https://cc.dvo.ru).

Results and discussion

X-ray diffraction analysis

The crystal structure $Na_5Zr_2F_{13}$ was originally determined by photometric determination with a high unreliability factor (12.6%) [4], which was later [5] refined by diffractometric method on single-crystal. The compound β-$Na_5Zr_2F_{13}$ crystallizes in monoclinic syngony (space group $C2/m$, $a = 11.5600$ Å, $b = 5.4759$ Å, $c = 8.3989$ Å, $\alpha = 97.361°$, $Z = 2$).

The β-$Na_5Zr_2F_{13}$ crystal lattice is formed by isolated $[Zr_2F_{13}]^{5-}$ complex anions and Na^+ cations. The $[Zr_2F_{13}]^{5-}$ dimers are constructed from ZrF_7 polyhedra connected by a common bridging (F_m) vertex. The average Zr-F distance in the $[Zr_2F_{13}]^{5-}$ anion is 2.042 Åand the Zr-F_m bond length is 2.104 Å. When Zr polyhedrons are joined by a common vertex, the distance Zr. . .Zr depends on the angle ZrFZr — the closer this angle is to 180°, the greater the distance between Zr. In dimeric anion $Na_5Zr_2F_{13}$ the distance Zr. . .Zr is 4.208 Å. The $[Zr_2F_{13}]^{5-}$ complex anions are surrounded by Na^+ cations with different IFs. When the NaF polyhedrons connect, they form channels containing the dimeric anions $[Zr_2F_{13}]^{5-}$. The crystal lattice is stabilized by the strong Na-F ionic bonds. Hf analogue [15] iso-structured $Na_5Zr_2F_{13}$. The average distance Hf-F in the dimeric anion $[Hf_2F_{13}]^{5-}$ is 2.054 Å.

Vibrational spectroscopy and thermal analysis

Methods of vibrational (IR, RS) spectroscopy provide additional information on the structure of the compound under study, detect the presence of phase transitions (PT) and identify the decomposition products [16,17]. It is known that in IR spectra below 600 cm $^{-1}$, the bands of characteristic vibrations of complex fluorocirconate anions [18] are located. Experimental IR, RS-spectra of the parent compound β-$Na_5Zr_2F_{13}$ and its heating products are shown in Fig. 2.

As quantum chemical calculations show, the isolated high charge ion $[Zr_2F_{13}]^{5-}$ is unstable — energetically its disintegration into separate ions $[ZrF_7]^{3-}$ and $[ZrF_6]^{2-}$ is most advantageous. Consideration of the cationic environment leads to stabilization of the anion. The equilibrium geometry of the $[Na_{12}Zr_2F_{13}]^{7+}$cluster was searched to relate the bands in the experimental spectra (Fig. 3, *a*). Optimization of the dimer $[Zr_2F_{13}]^{5-}$ geometry was performed with Na^+ cations frozen in crystallographic positions Na^+ (distances Na. . .Na are 3.60, 3.72, 5.48 Å) [5]. In equilibrium geometry the frequencies of normal vibrations of the anion $[Zr_2F_{13}]^{5-}$ are calculated and the bands in the experimental IR, RS-spectra $Na_5Zr_2F_{13}$ are related (Table).

When surrounded uniformly by cations, the local symmetry of the anion $[Zr_2F_{13}]^{5-}$ is close to D_{2h}. The bridging fluorine atom (F_m) is in the center of symmetry,

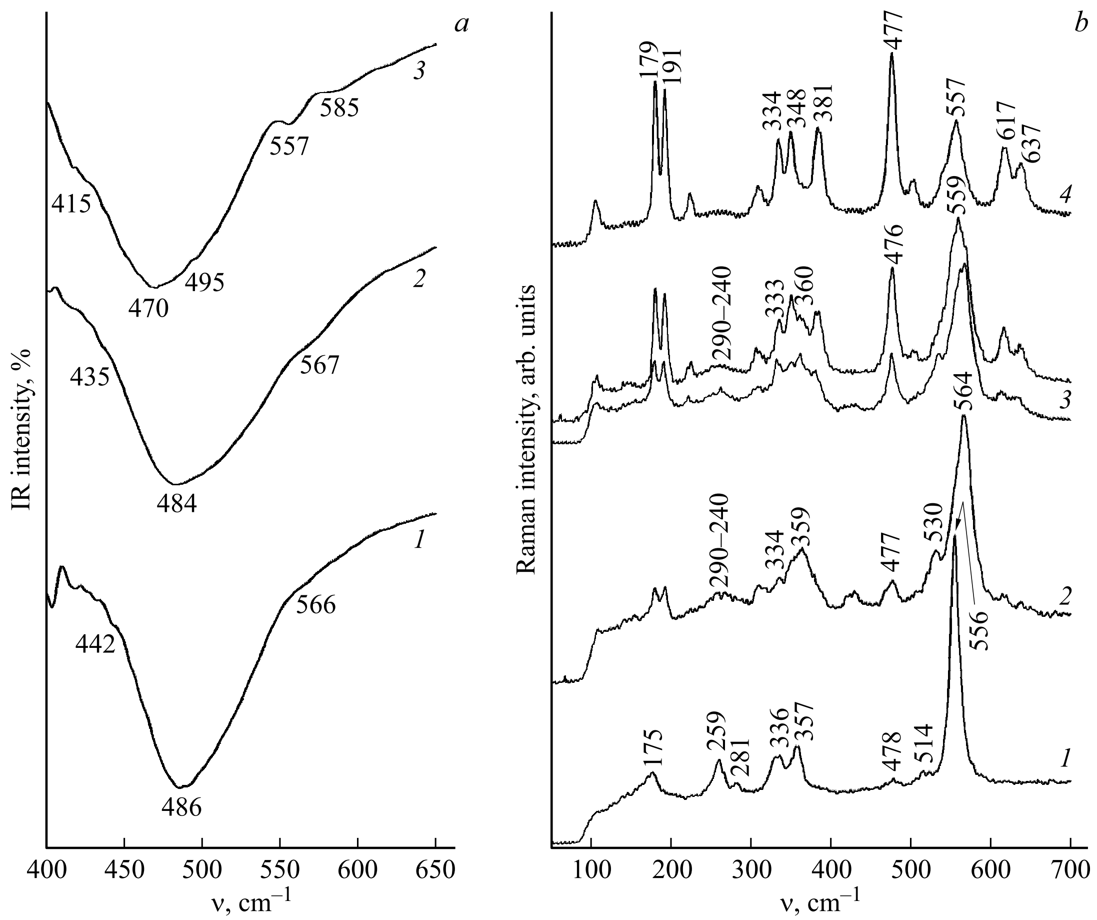

Figure 2. IR (*a*) and RS-spectra (*b*) β-$Na_5Zr_2F_{13}$ (*1*) and products of its heating to temperatures 530 (*2*), 650 (*3*), 800°C (*4*).

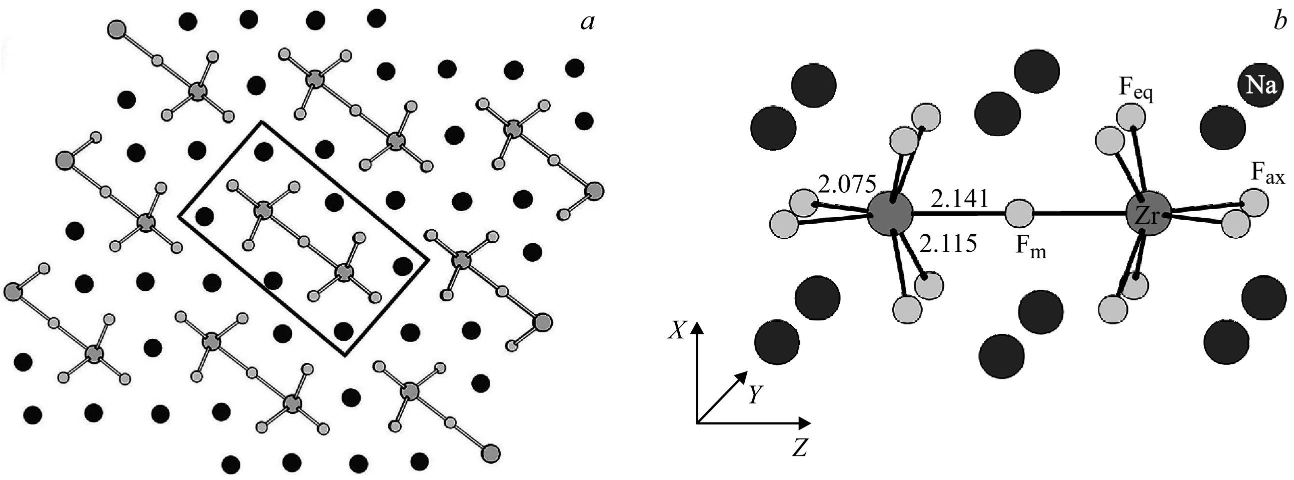

Figure 3. Fragment of the β-$Na_5Zr_2F_{13}$ compound structure in plane (010) (*a*) and the equilibrium cluster geometry $[Na_{12}Zr_2F_{13}]^{7+}$ (*b*).

linking two identical ZrF_6 polyhedra (trigonal symmetry prisms C_{2v}) (Fig. 3, *b*). Thus, the vibrational spectrum of the dimer $[Zr_2F_{13}]^{5-}$ (D_{2h}) should show fifteen $(5A1 + 3A2 + 3B1 + 4B2)$ bands each from the ZrF groups $_6$ (C_{2v}). In calculated dimer $[Zr_2F_{13}]^{5-}$ (D_{2h}) each vibration corresponds to two modes — their symmetrical and asymmetrical combinations, and additionally three Zr-F$_m$-Zr bridge bond vibrations (valence and two strain symmetries $B3u, B2u, B1u$) are active. According to the

$$\Gamma_{D2h} = 5(Ag + B3u) + 3(Au + B3g) + 3(B1g + B2u)$$
$$+ 4(B2g + B1u) + (B3u + B1u + B2u)$$

Experimental position of the bands (in cm^{-1}) in the spectra β-, α-$Na_5Zr_2F_{13}$, calculated frequencies (in cm $^{-1}$) of the anion $[Zr_2F_{13}]^{5-}$ and attribution

β-$Na_5Zr_2F_{13}$		α-$Na_5Zr_2F_{13}$ (520°C)		Calculation $[Zr_2F_{13}]^{5-}$			Assignment
IR	RS	IR	RS	ν	D_{2h}	I	
566 wk		567 wd wk		570	$B3u$	1.5/0.0	$\nu_s \mathrm{ZrF}(\mathrm{eq+ax+F}_m)$
	555 s		564 wd s	556	Ag	0.0/22.7	$\nu_s \mathrm{ZrF}(\mathrm{eq+ax})$
			530 av	531	$B1u$	22.0/0.0	$\nu_{as} \mathrm{ZrF}_k(\mathrm{eq+ax})$
	521o wk		520 v wk	512	$B2g$	0.0/1.1	
486 wd s	514 v wk	485 wd s	506 v wk	478	$B2u$	19.0/0.0	$\nu_{as} \mathrm{ZrF}_k(\mathrm{eq})$
				446	$B1g$	0.0/0.3	
				513	$B3u$	24.0/0.0	$\nu_{as} \mathrm{ZrF}(\mathrm{ax\text{-}F}_m)$
	478 wk		477 wk	479	Ag	0.0/3.5	$\nu_{as} \mathrm{ZrF}(\mathrm{ax})$
				434	$B3g$	0.0/0.4	$\nu_s \mathrm{ZrF}_k(\mathrm{eq})$
				421	Au	0.0/0.0	
442 sh		435 sh		424	$B3u$	1.9/0.0	$\nu_s \mathrm{ZrF}(\mathrm{ax+F}_m\mathrm{\text{-}eq})$
416 wk		415 wk		427	$B1u$	3.6/0.0	$\nu_{as} \mathrm{ZrF}_k(\mathrm{ax})$
				412	$B2g$	0.0/0.0	
				372	$B2u$	3.2/0.0	$\delta_\omega \mathrm{ZrF}_k(\mathrm{ax+eq})$
				368	$B1g$	0.0/1.8	
	357 av		359 av	359	Ag	0.0/2.3	$\gamma \mathrm{ZrF}_k(\mathrm{eq})+\delta_{sc} \mathrm{ZrF}_k(\mathrm{ax})$
				326	$B3u$	2.1/0.0	
				342	$B1u$	2.8/0.0	$\delta_\omega \mathrm{ZrF}_k(\mathrm{ax+eq})$
	331 av		334 wk	339	$B2g$	0.0/0.5	
			316 wk	317	$B3g$	0.0/0.9	$\delta_{tw} \mathrm{ZrF}_k(\mathrm{ax+eq})$
				316	Au	0.0/0.0	
				307	$B1u$	0.3/0.0	$\delta_\omega \mathrm{ZrF}(\mathrm{eq+F}_m)$
	281 wk		290–240 wd av	230	$B2g$	0.0/0.9	
	259 cp			295	Ag	0.0/0.8	$\gamma \mathrm{ZrF}_k(\mathrm{eq})+\delta_{sc} \mathrm{ZrF}_k(\mathrm{ax})$
				273	$B3u$	5.0/0.0	
				294	$B2u$	1.1/0.0	$\delta_\omega \mathrm{ZrF}(\mathrm{eq+F}_m)$
				215	$B1g$	0.0/0.4	
				211	$B3g$	0.0/0.0	$\delta_{tw} \mathrm{ZrF}_k(\mathrm{eq\text{-}ax})$
				199	Au	0.0/0.0	
				212	Ag	0.0/0.5	$\delta_{sc} \mathrm{ZrF}_k(\mathrm{eq})$
				195	$B3u$	0.0/0.0	
				191	$B2u$	0.0/0.0	$\rho \mathrm{ZrF}_k(\mathrm{eq+ax})$
				175	$B1g$	0.0/0.1	
	175 wd av		175 wk	186	Ag	0.0/0.7	$\nu(\mathrm{ZrF}_n\text{-}\mathrm{F}_m\text{-}\mathrm{ZrF}_n)$
				147	$B1u$	1.3/0.0	$\delta(\mathrm{ZrF}_n\text{-}\mathrm{F}_m\text{-}\mathrm{ZrF}_n)$
				136	$B2u$	0.1/0.0	

Note. Relative intensities: v — very, s — strong, av — average, wk — weak, sh — shoulder, wd — wide. Assignment: ν — valence vibrations, δ — strain vibrations, γ — umbrella vibrations, δ_{sc} — scissor vibrations, δ_ω — fan vibrations, δ_{tw} — twist vibrations, ρ — pendulum vibrations. ax, eq — axial and equatorial positions of fluorine atoms.

representation, all asymmetric modes are active in the IR and symmetric — in the Raman spectra.

Results of calculations show (table), that to characteristic vibrations with preferential contribution of bridge bond Zr-F_m-Zr can be attributed valence mode ~ 513 cm $^{-1}$ (ν_{as}, $B3u$) and two strain modes $\sim 307, 294$ cm $^{-1}$ ($\delta, B1u, B2u$), they are active in the infrared spectrum. In addition, the F atom $_m$ is involved in asymmetric valence vibrations ($570, 424\,\mathrm{cm}^{-1}$) and in bending vibrations ($290-230\,\mathrm{cm}^{-1}$), which appears in the RS-spectra.

In the experimental RS-spectrum β-$Na_5Zr_2F_{13}$ (Fig. 2, *b*, curve *1*) the band at 556 cm $^{-1}$ (with halfwidth FWHM $\sim 15\,\mathrm{cm}^{-1}$) can be attributed to a fully symmetric valence vibration (ν_sZrF, Ag). The lines at 357 and 336 cm $^{-1}$ correspond to strain vibrations (symmetries $B1g$, $B2g$), occurring along the dimer axis direction involving all end bonds, and the bands at 281 and 259 cm $^{-1}$ (symmetries $B1g$, $B2g$) — vibrations involving both end and bridge bonds (Fig. 3,*b*). The band at 175 cm $^{-1}$ was predominantly assigned to the lattice oscillation corresponding to the symmetrical motion of the polyhedra towards each other $\nu_s \mathrm{ZrF}_6 \rightarrow \mathrm{F}_m \leftarrow \mathrm{ZrF}_6$ (Ag), since, according to the calculated data, it is the most intense in the RS-spectrum (Table).

In the IR spectrum of the compound β-$Na_5Zr_2F_{13}$ one broadened band (FWHM $\sim 80\,\mathrm{cm}^{-1}$) with a maximum at 486 cm $^{-1}$ can be observed in the valence vibration area which can be attributed to asymmetrical stretching of the bonds ν_{as}ZrF$_k$. According to calculated data three modes contribute to the band ($B1u$, $B2u$, $B3u$), the splitting is due to removal of degeneracy c ν_{as}ZrF due to nonuniformity of surrounding the anion with cations in different directions (Fig. 3, b).

Heated to 530°C. When the compound β-$Na_5Zr_2F_{13}$ is heated in air (with relative humidity 20 – 30%) a small endothermic effect at 520°C is observed on the DTA curve, corresponding, according [1], to the polymorphous transformation of β-form into a high-temperature α-form (Fig. 4). According to XRDA data, the obtained product is predominantly α-$Na_5Zr_2F_{13}$ (map 00-019-1195) (Fig. 1, curve *2*). It should be noted that the authors [19,20] did not have a consensus in interpreting the same X-ray data: initially they attributed them to the compound β_1-Na_2ZrF_6in the presence of Na_3ZrF_7, and later — to phase α-$Na_5Zr_2F_{13}$.

When the compound β-$Na_5Zr_2F_{13}$ till 530°C, a mass loss (approx. 1%) is observed due to the onset of pyrohydrolysis of the sample with air moisture. The incorporation of oxygen into the lattice of a compound is possible in the form of isomorphic impurity with partial substitution of fluorine and/or the formation of particles of an independent oxide phase ZrO_2.

The overall appearance of the RS-spectrum of the product heated to 530°C is broadly similar to that of the parent compound (Fig. 2). This fact confirms the conservation of the dimeric composition of the anion $[Zr_2F_{13}]^{5-}$ in the structure of the resulting α-$Na_5Zr_2F_{13}$. However, it can be seen that there is a broadening of the ν_sZrF (FWHM $\sim 26\,cm^{-1}$) full-symmetric band and a shift of its maximum to $564\,cm^{-1}$. Taking into account the increasing mobility of cations Na^+ and ions F^-in structure $Na_5Zr_2F_{13}$ upon heating [21], the shape and position of ν_sZrF band can be explained by the weakening of cation-anion interactions leading to the general strengthening of Zr-F bonds in the anion. The appearance of an additional valence band at $530\,cm^{-1}$ and the blurring of the strain band at $290-240\,cm^{-1}$ are due to increased mobility in the anion sublattice, primarily of the bridging fluorine atom in the dimer. In this case one may conventionally consider that two different ZrF_7 and ZrF_6 groups take part in dimer formation and spectral changes — the presence of two maxima ν_sZrF (564, $530\,cm^{-1}$) and band broadening δZrF ($290-240\,cm^{-1}$) — are natural.

There is no noticeable shift of the maximum ν_{as}ZrF ($484\,cm^{-1}$) in the spectra of the sample (530°C) relative to its position in the original spectrum. There is an increase in half-width ν_{as}ZrF (FWHM $\sim 120\,cm^{-1}$) and an appearance of asymmetry in the high frequency area (Fig. 2, a, curve *2*), which agrees with calculation data — increase in contribution of Zr-F$_m$-Zr bridge bond valent vibrations (calculated value $513\,cm^{-1}$). Also the band at $567\,cm^{-1}$ becomes wider and more intense, which can be attributed to the asymmetric combination ν_sZrF (calculated value $570\,cm^{-1}$), due to decreased local dimer symmetry with increased mobility F$_m$. It can be assumed that all the described spectral changes are due to an increased degree of disorder in the anion sublattice as a result of the Na cation inequivalence in the $^+$ structure of the α-modification.

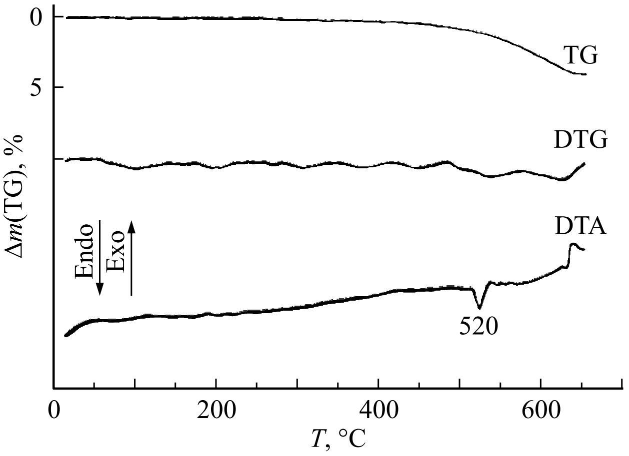

Figure 4. Thermal analytical curves of the compounds $Na_5Zr_2F_{13}$.

Thus, the general form of the IR, RS-spectra corresponds to the formation of high-temperature phase α-$Na_5Zr_2F_{13}$, in the structure of which the dimeric anion $[Zr_2F_{13}]^{5-}$ with asymmetrical (disordered) position of the fluorine bridge atom is conserved.

The product is heated to **650°*C*.** When the sample is heated above 530°C, the DTA curve shows a broad, low-intensity endo-effect with a gradual mass loss, which at 650°C is 3.8% (Fig. 4). The changes listed are due to the deeper pyrohydrolysis process of the compound formed by the moisture in the air. According to XRDA data (Fig. 1, curve *3*) the tetragonal phase Na_3ZrF_7 (card 01-074-0808(C)) and monoclinic ZrO_2 (card 00-013-0307(D)) form as a result of pyrohydrolysis, which agrees with the authors [22] conclusion. Decomposition of$Na_5Zr_2F_{13}$ to form a mixture of phases, one of which is Na_3ZrF_7 (others have not been identified), is noted in [5].

Thus, the thermal decomposition $Na_5Zr_2F_{13}$ when heated to 650°C in air is described by the general reaction

$$2Na_5Zr_2F_{13} + 2H_2O \rightarrow 3Na_3ZrF_7 + ZrO_2 + NaF + 4HF\uparrow.$$

The estimated mass loss is 4.04%. In the X-ray sample ($T = 650$°C) the most intense NaF phase (cube) reflex with interplanar spacing $d = 2.32\,Å$ is superimposed on one of the reflexes of compound Na_3ZrF_7

A set of bands with maxima at 637, 617, 504, 476, 381, 348, 334, 306, 224, 191, $179\,cm^{-1}$ (Fig. 2, b, curve *3*), which are well identified and refer to the monocline modification of ZrO_2 [23], is observed in the RS-spectrum of the heating product up 650°C. Besides, the band at $559\,cm^{-1}$ has higher intensity in the RS-spectrum and additional bands (narrow $\sim 360\,cm^{-1}$ and fuzzy wide $\sim 290-240\,cm^{-1}$) are present in the background of the characteristic bands of ZrO_2, they can be attributed to the vibrations of $[ZrF_7]^{3-}$ anion. According to [24] data, the Na_3ZrF_7 monophase is characterized by RS-peaks at 556, 351 and $250\,cm^{-1}$.

The infrared spectrum of the sample heated to 650°C also corresponds to a two-phase mixture. In the background of the broadened band with a maximum at $470\,cm^{-1}$ a number of additional maximums are observed $\sim$ 585, 557, 495 and $415\,cm^{-1}$. Probably, the weak band at $557\,cm^{-1}$ and the intense band at $470\,cm^{-1}$ belong to vibrations of ν_sZrF and ν_{as}ZrF of ion$[ZrF_7]^{3-}$and the rest - to vibrations of ZrO_2 monoclinic modification.

When comparing the RS-spectra of samples heated to 530 and 650°C, it can be noted that already in the product of heating to 530°C an impurity of ZrO_2 is present (Fig. 2, *b*, curves *2, 3*).

The product is heated to 800°***C.*** At temperatures above 650°C the resulting intermediate compound Na_3ZrF_7 decomposes by reacting with water vapor in the reaction

$$Na_3ZrF_7 + 2H_2O \rightarrow ZrO_2 + 3NaF + 4HF\uparrow .$$

According to XRDA data, the product of heating the compound $Na_5Zr_2F_{13}$ to 800°C in the air in the muffle furnace is mainly a mixture of ZrO_2 and NaF with small amount of Na_3ZrF_7 (Fig. 1, curve *4*). The estimated mass loss is 15.1%. For the complete hydrolytic decomposition of $Na_5Zr_2F_{13}$ on ZrO_2 and NaF the calculated yield of volatile products is 16.18%. In the RS-spectra of the sample ($T = 800°C$) a decrease in the intensity of the characteristic bands INa_3ZrF_7 and the well resolved bands of monoclinic modification ZrO_2 remain (Fig. 2, *b*, curve *4*).

Conclusion

Thus, according to DTA data the compound $Na_5Zr_2F_{13}$ in the temperature range 500–530°C undergoes FP, which, according to vibrational spectra, results in a metastable α-phase $Na_5Zr_2F_{13}$ with a dynamically disordered structure. When $Na_5Zr_2F_{13}$ is heated to 650°C in air, partial pyrohydrolysis proceeds with the formation of the intermediate more thermostable fluoride phase Na_3ZrF_7 and ZrO_2. Note, that a similar thermal behavior is characteristic for K_2ZrF_6 [22]. In humid air, potassium hexafluorocirconate decomposes at 700°C to form a mixture of K_3ZrF_7 and ZrO_2. This fact suggests that the high-temperature precursor phases with K K^+ and Na^+ cations have the same composition, and their thermolysis and pyrohydrolysis follow similar schemes.

Previously, it was found by NMR ^{19}F $Na_5Zr_2F_{13}$ that the appearance of motions in the fluorine sublattice (dimer reorientation and partial diffusion of fluorine) starts at temperatures 277–297°C [21]. In this connection one may assume that in the anion sublattice α-$Na_5Zr_2F_{13}$ dynamic equilibrium exists at high temperatures: $ZrF_6\ldots$(F-ZrF_6) $\leftrightarrow$(ZrF_6-F)$\ldots ZrF_6$ (Fig. 3, *b*). On this basis, the structure α-$Na_5Zr_2F_{13}$ can be regarded as a transition from a dimeric to a monomeric structure. In the transition state in the anion complex $[Zr_2F_{13}]^{5-}$, the structural nonequivalence of the F atoms is smoothed due to dynamic processes.

As a result of the thermal dissociation of the α-phase, whose degree of dissociation increases with increasing temperature, the gradual dissociation with the decomposition of the apical bridge bond Zr-F_m-Zr and the formation of the fluorocirconates Na_3ZrF_7 and Na_2ZrF_6. In turn, the compound Na_2ZrF_6 at temperature 544°C [1] by peritectic reaction decomposes into a mixture Na_3ZrF_7 and melt (NaF, ZrF_4), and pyrohydrolysis of the latter gives a mixture ZrO_2 and NaF. The proposed mechanism is indirectly confirmed by the fact that the pyrohydrolysis rate increases markedly above 540°C when Na_2ZrF_6 decomposes in the sample volume.

The temperature-conjugate possible stages of the thermolysis and pyrohydrolysis process are described by the following reactions:

$$2Na_5Zr_2F_{13} \rightarrow 2Na_3ZrF_7 + Na_4Zr_2F_{12},$$

$$Na_4Zr_2F_{12} \rightarrow Na_3ZrF_7 + (NaF, ZrF_4),$$

$$(NaF, ZrF_4) + 2H_2O \rightarrow ZrO_2 + NaF + 4HF\uparrow,$$

or a general cumulative equation

$$2Na_5Zr_2F_{13} + 2H_2O \rightarrow 3Na_3ZrF_7 + ZrO_2 + NaF + 4HF\uparrow .$$

According to the general equation, only with an equimolar ratio of the starting components does the volatile yield correspond to the experimental mass loss obtained by heating $Na_5Zr_2F_{13}$ till 650°C.

Conclusions

It was found that according to DTA data at 520°C in the compound $Na_5Zr_2F_{13}$ the FP from β- to α -modification occurs.

It is shown that the gradual thermolysis of the high-temperature phase α-$Na_5Zr_2F_{13}$ in the temperature range 530–650°C is complicated by hydrolytic decomposition, and above 650°C is connected with pyrohydrolysis of the resulting intermediate compound Na_3ZrF_7. The occurrence of these reactions in a non-desiccated atmosphere is described by the sequence of transformations

$$\alpha\text{-}Na_5Zr_2F_{13} \rightarrow Na_3ZrF_7 + ZrO_2 + NaF \rightarrow ZrO_2 + NaF.$$

In the present paper vibrational spectra of the two modifications are obtained for the first time: β-, α-$Na_5Zr_2F_{13}$. With the help of quantum-chemical calculations, the bands in the experimental spectra were assigned. Changes in the vibrational spectra of the decomposition products $Na_5Zr_2F_{13}$ are traced and discussed.

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Conflict of interest

The authors declare that they have no conflict of interest.

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