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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis of Zirconium (Hafnium) Fluoride Compounds and Their X-ray Luminescence Properties

M. M. Godneva[a], **D. L. Motov**[a], **N. N. Boroznovskaya**[b], **and V. M. Klimkin**[c]

[a] *Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Research Center, Russian Academy of Sciences, ul. Fersmana 14, Apatity, Murmansk oblast, 184209 Russia*

[b] *Tomsk State University, pr. Lenina 36, Tomsk, 634050 Russia*

[c] *Institute of Atmosphere Optics, Siberian Division, Russian Academy of Sciences, Akademicheskii pr. 1, Tomsk, 634055 Russia*

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Abstract—-Twenty-five zirconium (hafnium) fluoride compounds have been synthesized at room temperature in the systems MO_2–H_2SO_4–M'_n A(HF)–H_2O (M = Zr (Hf); M' = Na, K, Rb, Cs, NH_4; A = F, SO_4) and their X-ray luminescence spectra (luminescence wavelengths and relative intensities) have been measured. The X-ray luminescence of the compounds has been considered as a function of the composition (cations, anions, water content) and different structural factors (CNs, polyhedra, H-bonds). Ammonium compounds do not luminesce, and sodium fluorozirconates and heptafluorozirconates are weakly luminescing. Hexafluorozirconates $M_2Zr(Hf)F_6$ (M= K, Rb, Cs) and $M_5Zr_4F_{21} \cdot 3H_2O$ (M = Rb, Cs), as well as oxofluorozirconate $Rb_2Zr_3OF_{12}$, are strongly luminescing compounds.

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The luminescence properties of compounds are among their most important characteristics, which reflect their composition and structure [1]. X-ray luminescence of compounds is widely used for the creation of phosphors [2–4]. In particular, halides, such as BaFCl, NaI, KI, and CsCl [2, 3], are used for X-ray visualization. Many salts containing *d*-metal oxo anions, such as tungstates, vanadates, tantalates, etc., exhibit strong X-ray-excited luminescence [4]. In some silicates and oxides containing titanium subgroup elements, X-ray luminescence of intrinsic defects has been documented [1]. In the present work, we synthesized zirconium (hafnium) fluoride compounds and studied their X-ray luminescence spectra with the aim of revealing the relationship between their X-ray luminescence properties and composition and structure.

EXPERIMENTAL

Compounds were synthesized at room temperature by introducing alkali-metal or ammonium fluoride into zirconium or hafnium sulfate solutions, the composition of mixtures being previously determined for each compound [5]. The following reagents were used for synthesis: $Zr(SO_4)_2 \cdot 4H_2O$ (chemically pure), $Hf(SO_4)_2 \cdot 4H_2O$ prepared by prolong treatment of HfO_2 with sulfuric acid followed by salting-out with sulfuric acid, H_2SO_4 (chemically pure), $KF \cdot 2H_2O$ (pure for analysis), NH_4F (pure for analysis), RbF (chemically pure), and CsF (chemically pure). The reaction mixtures were allowed to stand, and the resulting solid phases were filtered off, washed with water and alcohol, and identified by the chemical analysis and X-ray powder diffraction methods.

The X-ray luminescence spectra were recorded on a homemade setup containing a spectrometer with a DMR-4 double-prism monochromator. Luminescence was excited by γ quanta from a BSV-2 dc X-ray tube (a URS-55 apparatus) with a molybdenum anticathode operating at 25 kV and 10 mA. The luminescence intensity and spectral composition were measured in the visible and UV ranges. The spectral range 200–700 nm was covered by using FEU-79 and FEU-39 photomultipliers. Spectral scanning and calibration of wavelength scale were performed automatically. The luminescence intensities were measured with the use of internal references, natural and synthetic minerals. In addition, the X-ray luminescence spectrum of the standard phosphor ZnS was used as a reference. The luminescence yield was measured in arbitrary units (1 arb. unit is approximately equal to 1 nit).

RESULTS AND DISCUSSION

The following zirconium (hafnium) fluoride compounds were isolated: $Na_5Zr_2F_{13}$[1], β-Na_2ZrF_6[1], $Na_7Zr_6F_{31}$[1], K_3ZrF_7[1], K_2ZrF_6[1], δ-$KZrF_5$[1], γ-$KZrF_5$, $KZrF_5 \cdot H_2O$[1], $(NH_4)_3ZrF_7$[1], α-NH_4ZrF_5[1], Rb_3ZrF_7[1], Rb_2ZrF_6[1],

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[1] The composition was determined based on X-ray powder diffraction data.

Table 1. Chemical composition of compounds*

Compound	Found, wt %			Calculated, wt %		
	M^I	Zr^{IV}	F^-	M^I	Zr^{IV}	F^-
γ-$KZrF_5$	17.9	41.0	41.3	17.35	40.49	42.16
$RbZrF_5 \cdot H_2O$	25.0	31.8	32.4	29.50	31.48	32.79
β-$CsZrF_5 \cdot H_2O$	37.9	27.6	27.5	39.42	27.05	28.17
$Cs_2Zr_3F_{14} \cdot 1.5H_2O$	31.5	32.6	30.8	31.92	32.87	30.95
$Rb_2Zr_3OF_{12}$	22.2	39.0	31.7	24.82	39.74	33.11
β-$ZrF_4 \cdot 3H_2O$	–	41.9	29.0	–	41.22	34.34

* The Fe and SO_4^{2-} contents were no more than 0.04 and 2 wt %, respectively.

$RbZrF_5 \cdot H_2O$, $Rb_5Zr_4F_{21} \cdot 3H_2O$[1], Cs_2ZrF_6[1], $Cs_5Zr_4F_{21} \cdot 3H_2O$[1], α-$CsZrF_5 \cdot H_2O$[1], β-$CsZrF_5 \cdot H_2O$, $Cs_2Zr_3F_{14} \cdot 1.5H_2O$; oxofluorozirconates $K_2Zr_3OF_{12}$[1], $Rb_2Zr_3OF_{12}$, and β-$CsZrOF_3 \cdot H_2O$; fluorohafnate K_2HfF_6[1] (Table 1).

The compounds under consideration are characterized by luminescence in the range 310–440 nm (Tables 2 and 3). The X-ray luminescence spectra show complicated bands, which is evidence either of different electronic transitions for a given luminescence center or of the presence of several luminescence centers caused by different environments of zirconium and fluorine. Previously [6], we assigned similar centers in fluoro- and fluorosulfatozirconates to the excited states F* and O*, which agrees with the data on other halide compounds [1].

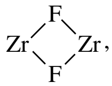
The variety of compounds synthesized makes it possible to establish some correlations between their luminescence properties, on the one hand, and their composition, structure, or crystal-chemical features, on the other hand.

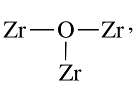
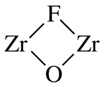
The fluorides NaF and CaF_2 are characterized by F* luminescence at λ = 290 nm [1]. The coordination of MF to ZrF_4 leads to a bathochromic shift of the luminescence maximum (310–390 nm) in the X-ray luminescence spectrum. The substitution of a heavier alkali metal for a lighter one leads to the shift of the maximum in the same direction (Fig. 1). Compounds with ZrF_8 and HfF_8 polyhedra (CN = 8) were found to luminesce at 310–320 nm. Compounds with ZrF_7 polyhedra (CN = 7) either have no luminescence or have weak luminescence at 390 nm. Compounds with ZrF_6 polyhedra (CN = 6) luminesce at 350 nm.

The oxygen-containing compounds under consideration exhibit X-ray luminescence in a wide spectral range, 290–600 nm (Table 3, Figs. 2 and 3). All compounds containing ZrF_7O and ZrF_7 coordination polyhedra with bridging bonds give rise to luminescence maxima in a wide range of wavelengths, mainly with a

Table 2. Structural and X-ray luminescence characteristics of zirconium (hafnium) fluoride compounds

Compound	Polyhedron*	CN_{Zr}	Types of bridging bonds	Average M–F distances, Å**	Luminescence maximum	
					λ, nm	intensity, arb. units
K_3ZrF_7 [7]	ZrF_7 (7)	7	–	–	None	
$Na_5Zr_2F_{13}$ [8]	ZrF_7 (6)	7	A	2.35	–	0.006
β-Na_2ZrF_6 [9]	ZrF_7 (5)	7	B	2.49	390	0.017
K_2ZrF_6 [10]	ZrF_8 (4)	8	B	2.90	320	0.510
Rb_2ZrF_6 [11]	ZrF_6 (6)	6	–	3.04	350	0.600
Cs_2ZrF_6 [11]	ZrF_6 (6)	6	–	3.18	350	0.460
$KZrF_5$ [12]	ZrF_8 (2)	8	A, B	–	–	–
γ-$KZrF_5$	Data are absent				330	0.275
δ-$KZrF_5$	Data are absent				360	0.065
K_2HfF_6 [13]	HfF_8 (4)	8	B	2.85	310	0.330

Notes: Here and in Table 3, the following designations are used for the types of bridging bonds: A, Zr–F–Zr; B, ,

C, 
$$Zr-\underset{\underset{Zr}{|}}{O}-Zr$$
, D,  .

* The number of terminal fluorine atoms is parenthesized.

** M is an alkali metal.

Table 3. Structural and X-ray luminescence characteristics of zirconium (hafnium) compounds with different ligands

Compound	Polyhedron	CN_{Zr}	Types of bridging bonds	Luminescence maximum	
				λ, nm	intensity, arb. units
$Rb_5Zr_4F_{21} \cdot 3H_2O$ [14, 15]	ZrF_7 (5), ZrF_7O (3), ZrF_6O (4)	7, 8	B	430	0.030
$Cs_5Zr_4F_{21} \cdot 3H_2O$* [15]	ZrF_7 (5), ZrF_7O (3), ZrF_6O (4)	7, 8	B	420	0.007
$KZrF_5 \cdot H_2O$ [16]	ZrF_7O (3)	8	A, B	310	0.028
$RbZrF_5 \cdot H_2O$	Data are absent			380	0.090
α-$CsZrF_5 \cdot H_2O$ [17]	ZrF_7O (3)	8	B	410	0.046
β-$CsZrF_5 \cdot H_2O$*	Data are absent			–	0.003
$Cs_2Zr_3F_{14} \cdot 1.5H_2O$	Data are absent			440	0.015
$K_2Zr_3OF_{12}$* [18, 19]	ZrF_7O (1)	8	A, B, C, D	–	0.013
$Rb_2Zr_3OF_{12}$ [18, 19]	ZrF_7O (1)	8	A, B, C, D	330	0.650
α-$ZrF_4 \cdot 3H_2O$ [20, 21]	$Zr_2F_8O_6$ (6)	8	B	280	0.040
β-$ZrF_4 \cdot 3H_2O$* [21, 22]	ZrF_6O_2 (2)	8	B	400	0.007

* Very weak broad luminescence bands without pronounced peaks.

shift to a long-wavelength region. The simultaneous presence of oxygen and fluorine atoms in the lattice increases the luminescence range; however, the luminescence intensity of hydrated fluoride compounds not subjected to heat treatment is considerably lower than that of anhydrous compounds, evidently due to the fact that water is coordinated to zirconium and fluorine is involved in a system of hydrogen bonds preventing the formation of F* luminescence centers.

The fact that it exhibits strong X-ray luminescence makes anhydrous $Rb_2Zr_3OF_{12}$ an exception among oxygen-containing compounds. This is likely due to the fact that the compound has four different bridges, which leads to easier excitation of F* and O*. In addition, the longer Rb–F bond can also favor luminescence excitation. This oxofluorozirconate is isostructural with the analogous thallium compound, with channels in the structure. The existence of such channels implies the possibility of isomorphous substitution, which allows one to improve the luminescence properties of the compound by doping.

For compounds with the same composition of the anion or polyhedron, the effect of the cation on the luminescence properties is observed: the ammonium

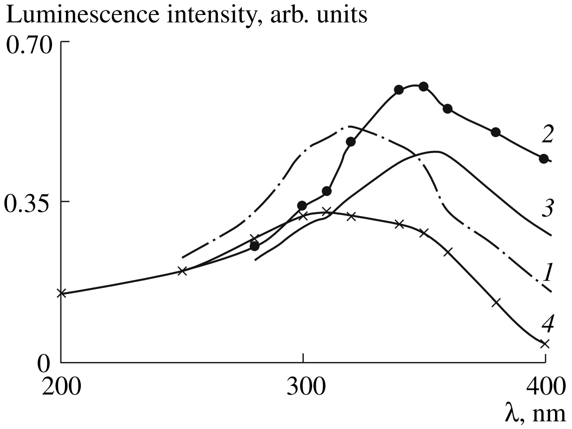


Fig. 1. UV range of the X-ray luminescence spectra of fluorometallates: (*1*) K_2ZrF_6, (*2*) Rb_2ZrF_6, (*3*) Cs_2ZrF_6, and (*4*) K_2HfF_6.

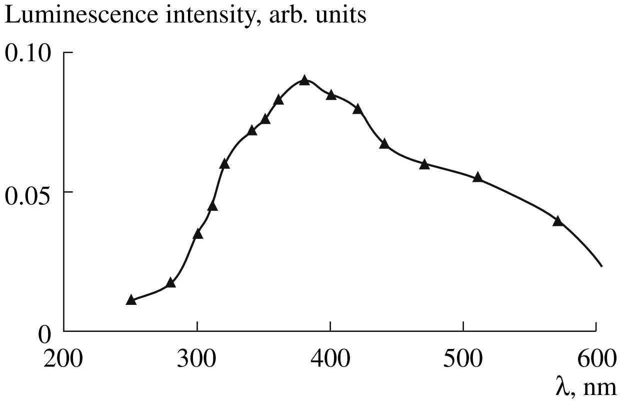


Fig. 2. X-ray luminescence spectrum of $Rb_5Zr_4F_{21} \cdot 3H_2O$.

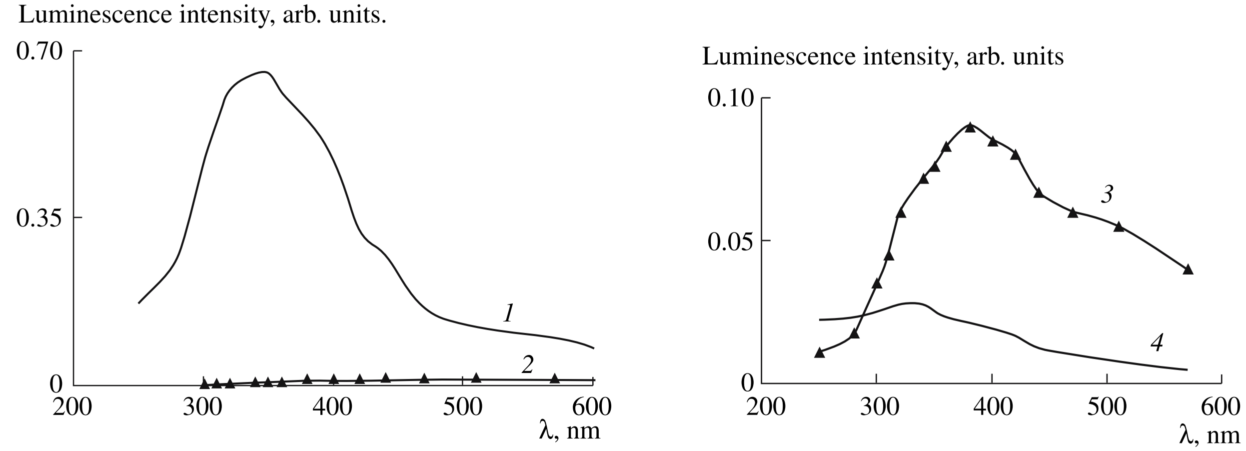


Fig. 3. Luminescence as a function of the composition of the cationic sublattice in fluorides with the same anions: (*1*) $Rb_2Zr_3OF_{12}$, (*2*) $K_2Zr_3OF_{12}$, (*3*) $RbZrF_5 \cdot H_2O$, and (*4*) $KZrF_5 \cdot H_2O$.

derivatives (NH_4^+ ($(NH_4)_3ZrF_7$, α-NH_4ZrF_5)) do not luminesce, the sodium compounds ($Na_5Zr_2F_{13}$, Na_2ZrF_6, $Na_7Zr_6F_{31}$) exhibit weak luminescence, whereas the potassium, rubidium, and cesium derivatives have better luminescence properties. The following trends are observed for the luminescence intensity:

M_2ZrF_6: Na < K(Rb) > Cs

$MZrF_5$: H_2O K < Rb > Cs

$M_2Zr_3OF_{12}$: K < Rb,

The last two compounds are isostructural; thus, they obey the rule of higher luminescence intensity for heavier cations.

We found that the polymorphs of compounds differ in both the luminescence range and intensity (Fig. 4). Significant differences in X-ray luminescence between α- and β-$ZrF_4 \cdot 3H_2O$ can be due to their structural features, exemplified by $HfF_4 \cdot 3H_2O$ [21], isostructural with β-$ZrF_4 \cdot 3H_2O$: α modification is composed of discrete dimers $Zr_2F_8O_6$, each of which contributes to the X-ray luminescence, whereas β-$ZrF_4 \cdot 3H_2O$ is composed of infinite chains linked with one another by H-bonds of water molecules, which are not incorporated in ZrF_6O_2 units and quench the X-ray luminescence of a sample. It is likely that similar differences in X-ray luminescence between hydrates α- and β-$CsZrF_5 \cdot H_2O$ are due to the role of water molecules. For the

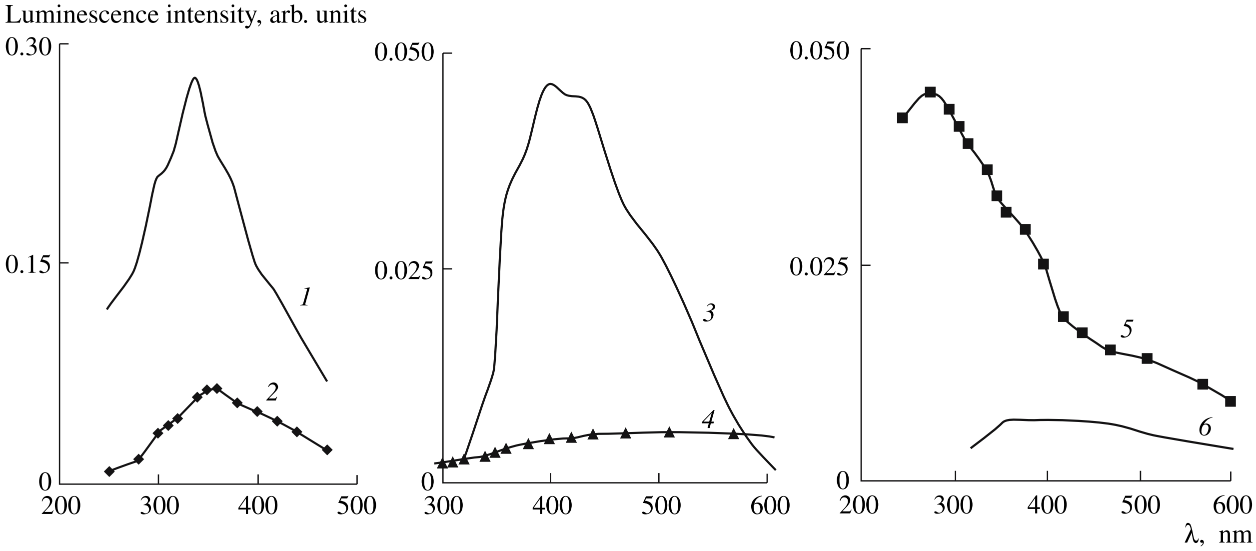


Fig. 4. X-ray luminescence spectra of polymorphs of zirconium fluoride compounds: (*1*) γ-$KZrF_5$, (*2*) δ-$KZrF_5$, (*3*) α-$CsZrF_5 \cdot H_2O$, (*4*) β-$CsZrF_5 \cdot H_2O$, (*5*) α-$ZrF_4 \cdot 3H_2O$, and (*6*) β- $ZrF_4 \cdot 3H_2O$.

Table 4. X-ray luminescence characteristics of anhydrous zirconium (hafnium) compounds*

Initial compound	Luminescence maximum	
	λ, nm	intensity, arb. units
$Rb_5Zr_4F_{21} \cdot 3H_2O$	340	0.230
$Cs_5Zr_4F_{21} \cdot 3H_2O$	360	0.265
$KZrF_5 \cdot H_2O$	340	0.425
$RbZrF_5 \cdot H_2O$	350	0.175
α-$CsZrF_5 \cdot H_2O$	370–400	0.008
β-$CsZrF_5 \cdot H_2O$	360	0.030
$K_2Zr_3OF_{12}$	350–360	0.018
$Rb_2Zr_3OF_{12}$	340–350	1.100
β-$CsZrOF_3 \cdot H_2O$**	365	0.138
α-$ZrF_4 \cdot 3H_2O$	200–250	0.022
β-$ZrF_4 \cdot 3H_2O$*	370	0.115

Notes: * After dehydration of the initial compound at 280°C.
** The compound was heated to 600°C.

anhydrous modifications δ- and γ-$KZrF_5$, the difference in X-ray luminescence is presumably caused by other factors, for example, by the CN or the mode of connection of polyhedra.

Analogous hafnium and zirconium compounds exhibit virtually the same luminescence intensity, the luminescence band for hafnium being shifted toward shorter wavelengths.

Analysis of the X-ray luminescence of zirconium (hafnium) fluoride compounds allows us to conclude that it considerably depends on the fluorine–alkali metal bond length: the longer the bond, the higher the probability of F* centers forming. For the same anion, this distance decreases with the radius of the cation. It is evident that, for smaller cations, this bond is stronger and the formation of luminescence centers is more impeded. Among Na, K, Rb, and Cs fluorozirconates with the same complex anion, the strongest luminescence is expected for the Rb and Cs compounds. As for the O* excited states, the strongest X-ray luminescence due to these centers should be observed for oxofluorozirconates. For the hydrated fluoride compounds in which water is coordinated to zirconium and fluorine is involved in hydrogen bonding, luminescence intensities comparable with those of anhydrous fluorides are unattainable without breaking of these bonds.

The removal of water from hydrated compounds (Table 4) leads to a hyprochromic shift of their luminescence maxima and to a considerable increase in luminescence intensity. The enhancement of the luminescence intensity of hygroscopic oxofluorozirconate $Rb_2Zr_3OF_{12}$ after heating is likely caused by water removal as well [16].

Our findings show that, for the same anion, the luminescence intensity increases in the series Na $\longrightarrow$ K $\longrightarrow$ Cs $\longrightarrow$ Rb. For the same cation, the luminescence intensity builds up with an increase in the number of MF molecules coordinated to ZrF_4: it passes through a maximum in hexafluorozirconates and vanishes in heptafluorozirconates. The presence of coordinated and crystal water decreases the luminescence intensity and shifts its maximum toward longer wavelengths.

No dependence of luminescence on the CN is observed. For the same polyhedron (ZrF_7), the luminescence intensity increases with a decrease in the number of terminal fluorine atoms or with an increase in the number of bridging bonds. Hydrogen bonds suppress the luminescence intensity. The absence of hydrogen bonds and the presence of bridging fluorine atoms and only one terminal fluorine atom in the zirconium polyhedron in $Rb_2Zr_3OF_{12}$ are responsible for its strong luminescence.

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