

Thermal Stability and X-ray-Luminescent Properties of Fluorozirconates and Fluorosulfatozirconates

M. M. Godneva^a, N. N. Boroznovskaya^b, D. L. Motov^a,
V. M. Klimkin^{c†}, and N. L. Mikhailova^a

^a Tananaev Institute of the Chemistry and Technology of Rare Elements and Minerals, Kola Research Center, Russian Academy of Sciences, ul. Fersmana 14, Apatity, Murmansk oblast, 184200 Russia

^b Tomsk State University, pr. Lenina 36, Tomsk, 634050 Russia

^c Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia

Received December 24, 2007

Abstract—The thermolysis of fluorozirconates (M_2ZrF_6 , $M_5Zr_4F_{21} \cdot 3H_2O$, $MZrF_5 \cdot H_2O$, $Rb_2Zr_3OF_{12}$, and $Cs_2Zr_3F_{14} \cdot 1.5H_2O$) and fluorosulfatozirconates ($M_2ZrF_4SO_4$, $Rb_3Zr_2F_9SO_4 \cdot 2H_2O$, and $Cs_8Zr_4F_2(SO_4)_{11} \cdot 16H_2O$) with $M = K, Rb,$ or Cs in undried air was studied by thermal analysis in tandem with X-ray powder diffraction. The X-ray luminescence (XRL) intensity was determined for these compounds and their thermolysis products. A mixture of $Rb_2Zr_3OF_{12}$ and Rb_2ZrF_6 luminescent phases was detected in the thermolysis products of $Rb_5Zr_4F_{21} \cdot 3H_2O$ and $RbZrF_5 \cdot H_2O$ for the first time. After heat treatment, a considerable quantum yield was observed for $ZnZrF_6 \cdot 5H_2O$, $ZnZrF_6 \cdot 6H_2O$, and $ZnZrF_{10} \cdot 7H_2O$. The XRL luminescence was affected by the composition of the phase and the density of excited states (F^* and O^*).

DOI: 10.1134/S0036023609040123

X-ray luminescence (XRL) is an informative tool for studying crystal structures, in particular, for revealing structural defects. Earlier [1, 2] we studied broadband XRL spectra for a number of fluorozirconates and fluorosulfatozirconates synthesized in this work. A set of compounds with intensive luminescence (primarily, in the UV) was recognized, and they were recommended for use as luminophors (X-ray converters). The luminescence centres responsible for XRL intensity were assigned to intrinsic defects (F^* and O^* excited states). Heat treatment can either enhance or weaken XRL intensity [2].

Thermal analysis in tandem with X-ray powder diffraction was used to study the thermolysis of fluorozirconates (FZs) and fluorosulfatozirconates (FSZs) [3]. For some compounds (M_2ZrF_6 , γ - $KZrF_5$, $Rb_2Zr_3OF_{12}$, Cs_2ZrF_6 , $Cs_5Zr_4F_{21} \cdot 3H_2O$, $Cs_2Zr_3F_{14} \cdot 1.5H_2O$; $Rb_3Zr_2F_9SO_4 \cdot 2H_2O$, $Cs_8Zr_4F_2(SO_4)_{11} \cdot 16H_2O$), thermolysis schemes were presented; for others ($Rb_5Zr_4F_{21} \cdot 3H_2O$, $MZrF_5 \cdot H_2O$, and $M_2ZrF_4SO_4$), provisional assignment of thermal features was carried out, in some cases requiring refinement [3–5]. For $M_5Zr_4F_{21} \cdot 3H_2O$ and $MZrF_5 \cdot H_2O$, endotherms observed below 500°C in undried air were assigned to polymorphic transitions and melting (by analogy with hexafluorozirconates) or to $MZrF_5$ and M_2ZrF_6 formation [4]. Phase diagrams for MF– ZrF_4 systems are known. When they were studied in hermetically sealed vessels or in helium, oxide com-

pounds were not formed [6, 7]; in undried air, where pyrohydrolysis occurs, oxides can appear.

This work studies the thermal stability of FZs and FSZs in undried air and the influence of heat treatment on their X-ray luminescent properties.

EXPERIMENTAL

Synthesis was carried out at room temperature by adding alkali fluorides to sulfuric acid solutions of zirconium; to prepare zinc compounds, $Zn(NO_3)_2 \cdot 6H_2O$ and HF were used. The compositions of precursor mixtures for each compound were determined elsewhere [3].

Heating curves were recorded in undried air on an NTR-70M device with Pt–Pt/Rh thermocouples. Sample sizes were 0.11–0.27 g; heating rates were 8–10 K/min. After a number of DTA effects appeared, heat treatment was stopped; the sample was cooled to room temperature, and the X-ray diffraction pattern of the product was recorded on a DRF-2 or DRON-2 diffractometer. X-ray luminescence was excited by X-ray quanta irradiated by a BSV-2 d c tube (voltage: 25 kV; current: 10 mA; Mo anticathode). The radiation intensity and spectral composition were recorded in the visible and UV ranges with reference to the XRL spectrum of a ZnS standard luminophor.

[†] Deceased.

Table 1. Thermolysis products of anhydrous fluorozirconates and their XRL

Compound	T, °C	Phase composition of thermolysis products	Maximal luminescence range λ , nm	Maximal luminescence intensity, arb. un.
K ₂ ZrF ₆	20	–	300–310	0.550
	280	–	300–320	0.200
	590	K ₃ ZrF ₇ + ZrO ₂	No luminescence	
γ -KZrF ₅	20	–	320–340	0.275
	280*	–	320–340	0.400
	400	α -K ₂ ZrF ₆ + K ₂ Zr ₃ OF ₁₂	–	–
Rb ₂ ZrF ₆	20	–	350–370	0.250–0.450
	100	Rb ₂ ZrF ₆	340–350	0.425
	300	Rb ₂ ZrF ₆	340–350	0.420
	510	Rb ₂ ZrF ₆ **	350–380	0.200
Rb ₂ Zr ₃ OF ₁₂	20	–	355–380	0.650
	280*	–	350–410	0.140
	480	Rb ₂ Zr ₃ OF ₁₂ *** + Zr(F,O) _{2.7} + RbF	355–380	0.200
	620	Rb ₂ Zr ₃ OF ₁₂ *** + Zr(F,O) _{2.7} + RbF + ZrO ₂ (incongruent melting)		
Cs ₂ ZrF ₆	20	–	350–375	0.430
	280*		350–360	0.375

Note: Here and in Tables 2 and 3, nonisothermal ignition at 8–10 K/min or

* at 70 K/min.

** Reversible polymorphic transition at 474–481°C.

*** Incompletely thermolyzed.

RESULTS AND DISCUSSION

Most anhydrous fluorides have maximal radiation in the UV (290–380 nm). Some of them (K₂ZrF₆, Rb₂ZrF₆, and Cs₂ZrF₆) have XRL intensity in the UV commensurate with standard luminophors, such as BaSO₄ · Pb. Anhydrous hexafluorozirconates do not decompose while heated to 450°C, but in cases of polymorphic transitions, the XRL intensity decays (Table 1). In cases of reversible transitions, exposure restores the XRL intensity.

In the test oxide compounds, XRL was found over a wide spectral range (290–600 nm). The presence of oxygen together with fluorine in the crystal lattice wid-

ens the spectral range [2]. In general, the XRL intensity of heat-untreated hydrous fluoro compounds is far lower than for anhydrous compounds. For M₅Zr₄F₂₁ · 3H₂O, MZrF₅ · H₂O, and Rb₃Zr₂F₉SO₄ · 2H₂O, which contain zirconium-coordinated water and fluorine involved in the hydrogen-bond system [3], XRL intensity commensurate to anhydrous compounds cannot be achieved unless these bonds are broken. Dehydration during heat treatment up to 300°C breaks fluorine–hydrogen bonds and, accordingly, increases the density of F* excited states. Oxygen enters O* excited states located along dislocations and interfaces or fills in F

Table 2. Thermolysis products of hydrous fluorozirconates and their XRL

Compound	T , °C	Phase composition of thermolysis products	Maximal luminescence range λ , nm	Maximal luminescence intensity, arb. un.
$\text{Rb}_5\text{Zr}_4\text{F}_{21} \cdot 3\text{H}_2\text{O}$	20	–	320–440	0.005
	220	$\text{RbZrF}_5 + \text{RbF}$	340–390	0.025
	280*	–	330–340	0.240
	300	$\text{RbZrF}_5 + \text{Rb}_2\text{ZrF}_6 + \text{ZrF}_4$	–	–
	430	$\text{Rb}_2\text{Zr}_3\text{OF}_{12} + \text{Rb}_2\text{ZrF}_6$	330–350	0.520
$\text{RbZrF}_5 \cdot \text{H}_2\text{O}$	20	–	360–390	0.220
	120	$\beta\text{-RbZrF}_5$	360–390	0.065
	280	–	–	0.130
	280*	–	370	0.175
	430	$\text{Rb}_2\text{ZrF}_6 + \text{Rb}_2\text{Zr}_3\text{OF}_{12}$	360–390	0.550
$\text{Cs}_5\text{Zr}_4\text{F}_{21} \cdot 3\text{H}_2\text{O}$	20	–	280–480	0.015–0.025
	260	$\text{Cs}_2\text{ZrF}_6 + \text{CsZrF}_5$	–	Weak luminescence
	280*	–	340–360	0.280
	390	$(\alpha + \beta)\text{CsZrF}_5 + \text{CsF}$	350–380	0.300
	505	$\alpha\text{-Cs}_2\text{ZrF}_6 + \text{ZrF}_4 + \text{CsF}$ (partially fused product)	–	–
$\alpha\text{-CsZrF}_5 \cdot \text{H}_2\text{O}$	20	–	400–420	0.045
	120	$\alpha\text{-CsZrF}_5$	–	–
	250	$\beta\text{-CsZrF}_5$	–	–
	280*	–	380–390	0.030
$\text{Cs}_2\text{Zr}_3\text{F}_{14} \cdot 1.5\text{H}_2\text{O}$	20	–	420–490	0.022
	260	$\text{Cs}_2\text{Zr}_3\text{F}_{14}$	350–450	0.022
	295	$(\beta\text{-CsZrF}_5 \rightleftharpoons \alpha\text{-CsZrF}_5) + \text{ZrF}_4$	320–340, 410–450, 510–520	0.030, 0.035, 0.040
	580	$\text{Cs}_2\text{ZrF}_6 + \text{ZrF}_4 + \text{ZrO}_2$ (partially fused product)	500–520	0.135

vacancies ($V_F + O_F$)¹ and enhances XRL within 390–450 nm.

Certain heat-treatment conditions can generate luminescent phases. For example, $\text{Rb}_5\text{Zr}_4\text{F}_{21} \cdot 3\text{H}_2\text{O}$ before heating has practically no luminescence, but its decomposition involves the formation of strongly luminescing phases (Rb_2ZrF_6 and $\text{Rb}_2\text{Zr}_3\text{OF}_{12}$). Similar compounds are formed for $\gamma\text{-KZrF}_5$ and $\text{RbZrF}_5 \cdot \text{H}_2\text{O}$ with an attendant increase in luminescence intensity (Tables 1, 2; Fig. 1). Under our thermal analysis condi-

¹ V_F denotes a fluorine vacancy, and O_F denotes oxygen in place of fluorine.

tions, fluorozirconates decompose to reach equilibrium. The exception is $\text{Rb}_2\text{Zr}_3\text{OF}_{12}$, which is more stable and does not decompose completely; it is detected in the heat-treatment product.

Our earlier studies showed that $\text{Rb}_2\text{Zr}_3\text{OF}_{12}$ has the strongest XRL, but its preparation from solution in the $\text{Zr}(\text{SO}_4)_2\text{-RbF-H}_2\text{O}$ system is difficult because of the slow crystallization of the precipitate (it takes more than 2 months) [1, 3]. Here, we discovered that $\text{Rb}_2\text{Zr}_3\text{OF}_{12}$ is formed during the heat treatment at 430°C of $\text{RbZrF}_5 \cdot \text{H}_2\text{O}$ and $\text{Rb}_5\text{Zr}_4\text{F}_{21} \cdot 3\text{H}_2\text{O}$; these hydrates are easy to prepare. We also found that the XRL intensity of $\text{Rb}_2\text{Zr}_3\text{OF}_{12}$ can considerably decay

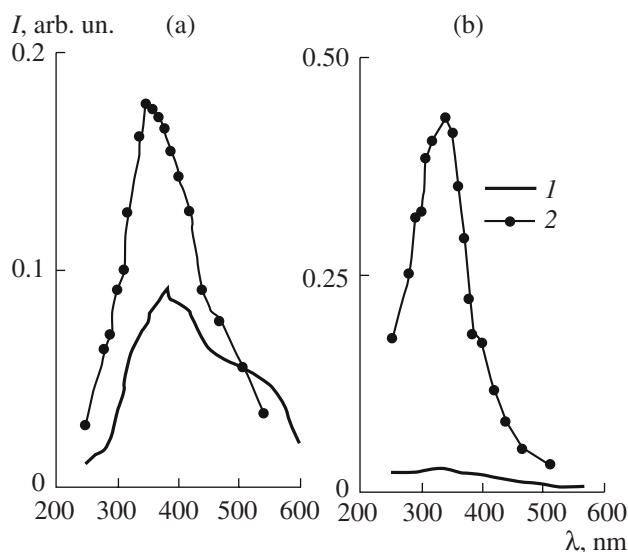


Fig. 1. Influence of heat treatment on the XRL intensity in (a) $\text{RbZrF}_5 \cdot \text{H}_2\text{O}$ and (b) $\gamma\text{-KZrF}_5$: (1) the untreated compound and (2) the same after heat treatment.

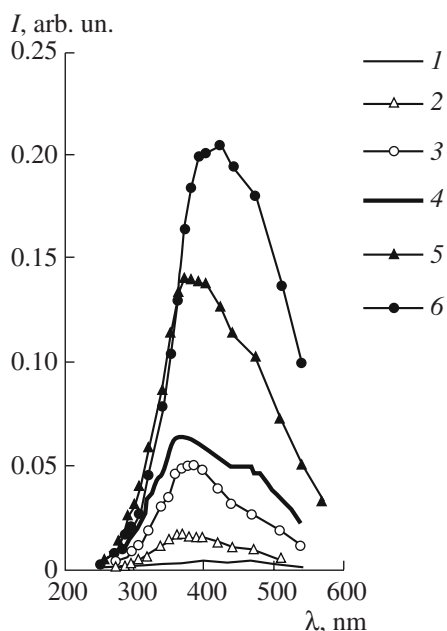


Fig. 2. Influence of heat treatment on the XRL intensity in (1, 4) $\text{ZnZrF}_6 \cdot 5\text{H}_2\text{O}$, (2, 5) $\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}$, and (3, 6) $\text{ZnZr}_2\text{F}_{10} \cdot 7\text{H}_2\text{O}$. (1–3) the untreated compound; (4–6) the same after heat treatment.

with time. This decay might arise from progressive structure ordering and defect healing².

Cesium compounds are thermolyzed without producing oxofluorozirconates. Intermediates— $\text{Cs}_5\text{Zr}_4\text{F}_{21} \cdot$

² Apart from this compound, XRL decay with time was observed for some FSZs ($\text{Rb}_3\text{Zr}_2\text{F}_9\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_8\text{Zr}_4\text{F}_2(\text{SO}_4)_{11} \cdot 16\text{H}_2\text{O}$) and can arise, apart from defect healing, from partial degradation.

$3\text{H}_2\text{O}$ and $\text{Cs}_2\text{Zr}_3\text{F}_{14} \cdot 1.5\text{H}_2\text{O}$ —contain the Cs_2ZrF_6 luminescent phase, which considerably enhances luminescence intensity.

In studying the CsF-ZrF_4 system in helium, Robbins et al. [7] found that $\beta\text{-CsZrF}_5$ is stable below 330°C and $\alpha\text{-CsZrF}_5$ is stable above this temperature; the onset melting temperature of CsZrF_5 is 425°C [8]. Here, we found that anhydrous pentafluorozirconates during $\text{CsZrF}_5 \cdot \text{H}_2\text{O}$ thermolysis in air are formed at lower temperature than in helium. In addition, the α phase was detected at 120°C and the β phase at 250°C ; that is, the phase formation order is inverted (Table 2). The XRL intensity in α - and β - CsZrF_5 is low.

Of the zinc FZs, pentafluorozirconate $\text{ZnZr}_2\text{F}_{10} \cdot 7\text{H}_2\text{O}$ has the highest quantum yield after heating because of pyrohydrolysis with the production of $\text{ZnZr}_2\text{O}_{3.25}\text{F}_{3.5}$ [3], which is characterized by considerable $V_F + O_F$ site density and a spoiled fluorine–hydrogen bond system (Fig. 2).

Thus, heat treatment with rupture of F–H bonds in the structure of hydrous fluorozirconates increases the XRL intensity via increasing the F^* site density (300–360 nm) and the $V_F + O_F$ site density (400–440 nm). This is enhanced by pyrolysis with fluorozirconate and oxofluorozirconate production.

Broad-band XRL spectra, which cover the UV and visible ranges, with maximal luminescence within 390–440 nm, are characteristic of most FSZs. In calcined samples, the strongest luminescence intensity is usually observed at shorter wavelengths (Table 3); their XRL spectra are the superposition of several radiation bands from different XRL centres. Fluorosulfatozirconates, as fluorozirconates, considerably increase their XRL intensity after heating in cases where thermolysis produces luminescent phases. The heat treatment of $\text{Rb}_3\text{Zr}_2\text{F}_9\text{SO}_4 \cdot 2\text{H}_2\text{O}$ is an illustrative example: first (at 220°C), the XRL luminescence decays dramatically; then (above 300°C), the luminescence intensity recovers the initial level because of the presence of luminescent phases in the products. Further heating gives a solidified cake, and the XRL intensity decreases in association.

To summarize, thermal analysis in tandem with X-ray powder diffraction was used to study the thermolysis of a number of fluorozirconates and fluorosulfatozirconates. A mixture of Rb_2ZrF_6 and $\text{Rb}_2\text{Zr}_3\text{OF}_{12}$ luminescent phases was detected for the first time in the thermolysis products of $\text{RbZrF}_5 \cdot \text{H}_2\text{O}$ and $\text{Rb}_5\text{Zr}_4\text{F}_{21} \cdot 3\text{H}_2\text{O}$. During $\text{CsZrF}_5 \cdot \text{H}_2\text{O}$ thermolysis in air, the $\alpha\text{-CsZrF}_5$ phase is formed at far lower temperature than during $\text{CsZrF}_5 \cdot \text{H}_2\text{O}$ thermolysis in a helium atmosphere. High quantum yield after heat treatment was observed for zinc compounds: $\text{ZnZrF}_6 \cdot 5\text{H}_2\text{O}$, $\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}$, and $\text{ZnZr}_2\text{F}_{10} \cdot 7\text{H}_2\text{O}$. The XRL intensity is affected by the composition of the phase and the density of excited states (F^* and O^*).

Table 3. Thermolysis products of fluorosulfatozirconates and their XRL

Compound	T, °C	Phase composition of thermolysis products	Maximal luminescence range λ , nm	Maximal luminescence intensity, arb. un.
Rb ₂ Zr ₄ SO ₄	20	–	420–440	0.012
	280	Rb ₂ ZrF ₄ SO ₄	380–390	–
	400	Rb ₂ ZrF ₄ SO ₄	–	–
Rb ₃ Zr ₂ F ₉ SO ₄ · 2H ₂ O	20	–	380–390	0.170
	220–280	Rb ₂ ZrF ₄ SO ₄ + Rb ₂ ZrF ₅	350–360	–
	300	–	350–380	–
	340	Rb ₂ ZrF ₄ SO ₄ + RbZrF ₅ + Rb ₂ Zr ₃ OF ₁₂	–	–
	420	Rb ₂ Zr ₃ OF ₁₂ + Rb ₂ ZrF ₄ SO ₄ (solidified cake)	–	–
Cs ₂ Zr ₄ F ₄ SO ₄	20	–	370–390	0.320
	100	Cs ₂ ZrF ₄ SO ₄	380–390	–
	200	Cs ₂ ZrF ₄ SO ₄	365–390	0.165
	240	Cs ₂ ZrF ₄ SO ₄	365–390	–
	315	Cs ₂ ZrF ₄ SO ₄	360–390	0.040
	430	Cs ₂ ZrF ₄ SO ₄ (cake)	420–470	0.025
Cs ₈ Zr ₄ F ₂ (SO ₄) ₁₁ · 16H ₂ O	20	–	300–450	0.010–0.020
	295	Cs ₈ Zr ₄ F ₂ (SO ₄) ₁₁ (practically amorphous product)	420–440	0.370

REFERENCES

1. M. M. Godneva, D. L. Motov, N. N. Boroznovskaya, and V. M. Klimkin, *Zh. Neorg. Khim.* **52** (5), 725 (2007) [*Russ. J. Inorg. Chem.* **52** (5), 661 (2007)].
2. N. N. Boroznovskaya, M. M. Godneva, D. L. Motov, and V. M. Klimkin, *Neorg. Mater.* **43** (4), 490 (2007).
3. M. M. Godneva and D. L. Motov, *The Chemistry of the Titanium Subgroup: Sulfates, Fluorides, and Fluorosulfates from Aqueous Solutions* (Nauka, Moscow, 2006) [in Russian].
4. R. L. Davidovich, V. B. Logvinova, and L. V. Teplukhina, *Koord. Khim.* **18** (1), 48 (1992).
5. I. V. Tananaev, L. S. Guzeeva, and K. I. Petrov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser.: Khim., vyp. 1, No. 2*, 10 (1968).
6. Yu. M. Korenev, V. V. Govorov, A. A. Kosorukov, et al., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser.: Khim., vyp. 1, No. 2*, 10 (1968).
7. G. D. Robbins, R. E. Thoma, and H. Insley, *J. Inorg. Nucl. Chem.* **27**, 559 (1965).
8. *The Powder Diffraction File* (International Centre for Diffraction Data), Card 11-0082.