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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Formation in the $ZrO(NO_3)_2$–H_3PO_4–CsF(HF)–H_2O System

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Abstract—The phase formation in the system $ZrO(NO_3)_2$–H_3PO_4–CsF(HF)–H_2O was studied at the molar ratio CsF/Zr = 1 along the sections $PO_4^{3-}/Zr = 0.5$ and 1.5 at a ZrO_2 concentration in the initial solution of 2–14 wt %. The following compounds were isolated: $Cs_5Zr_4F_{21} \cdot 3H_2O$, $CsZr_2(PO_4)_3 \cdot 2HF \cdot 2H_2O$, $CsZrF_2PO_4 \cdot H_2O$, $CsZr_2F_6PO_4 \cdot 4H_2O$ (for the first time), $CsHZrF_3PO_4$ (for the first time), $Cs_{0.70}ZrF(PO_4)_{1.23} \cdot nH_2O$, and $CsHZr_2F_2(PO_4)_{2.66} \cdot nH_2O$. The compositions of $CsZrF_2PO_4 \cdot H_2O$, $Cs_{0.70}ZrF(PO_4)_{1.23} \cdot nH_2O$, and $CsHZr_2F_2(PO_4)_{2.66} \cdot nH_2O$ are conditional. All the compounds were characterized by crystal-optical, X-ray powder diffraction, thermal analyses, and IR spectroscopy. The formula $CsHZrF_3PO_4$ was established by energy-dispersive analysis with a LEO-1450 scanning electron microscope and an MS-46 CAMECA X-ray microanalyzer.

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We previously studied the system $ZrO(NO_3)_2$–H_3PO_4–CsF–H_2O at the molar ratios $PO_4^{3-}/Zr = 0.5$ and 1.5 [1, 2]. We isolated the crystalline phases $CsZr_2(PO_4)_3 \cdot 2HF \cdot 2H_2O$ and $CsZrF_2PO_4 \cdot H_2O$, two modifications of $CsZrF_2PO_4 \cdot 0.5H_2O$, and the amorphous phases $Cs_2Zr_3O_2F_4(PO_4)_2 \cdot 3H_2O$ and $CsZr_3O_{1.25}F_4(PO_4)_2(NO_3)_{0.5} \cdot 4.5H_2O$. The compound $Cs_3Zr_3O_{1.5}F_6(PO_4)_2 \cdot 3H_2O$ was also obtained, which forms in the crystalline or glassy state, depending on conditions. The formation of new compounds, $Cs_2Zr_3O_{1.5}F_5(PO_4)_2 \cdot 2H_2O$, $Cs_2Zr_3F_2(PO_4)_4 \cdot 4.5H_2O$, and $Zr_3O_4(PO_4)_{1.33} \cdot 6H_2O$, was established, which crystallize only in a mixture with known phases. It can be assumed that, in the system in the presence of HF, cesium fluorophosphatezirconates of unknown compositions with valuable properties may form.

The system $ZrO(NO_3)_2$–H_3PO_4–CsF(HF)–H_2O was studied within the molar ratio range F : Zr = 1–5 at the molar ratios CsF : Zr = 1 and $PO_4^{3-}/Zr = 0.5$ and 1.5. HF and CsF were added while continuously stirring to $ZrO(NO_3)_2 \cdot 2H_2O$ solutions at room temperature. After the mixtures became homogeneous, 85% H_3PO_4 was added dropwise to them. The ZrO_2 content in solution was calculated with the consideration of H_3PO_4 before adding MF. After storing the obtained mixtures for 7–45 days, precipitates were filtered off, washed successively with water and alcohol, and dried in air.

Identification and elemental analysis of the phases were performed as previously [1].

Table 1 presents data on the compositions of the initial mixtures and isolated precipitates, and Fig. 1 shows a schematic of phase formation fields.

At the molar ratio $PO_4^{3-}/Zr = 0.5$ (Fig. 1a) in the initial solution and high F^- ion content (F : Zr = 5), the known fluorozirconate $Cs_5Zr_4F_{21} \cdot 3H_2O$ forms. Decreasing molar ratio F : Zr in low-zirconium solutions leads to precipitation of multiphase precipitates containing phases II and III (Table 1) and also impurities we failed to identify, in particular, inclusions with refractive index < 1.470, which can be Cs_2ZrF_6 or $Cs_5Zr_4F_{21} \cdot 3H_2O$, with phase III dominating. At $PO_4^{3-}/Zr = 1.5$, phases II, V, and VI were obtained (Fig. 1).

The X-ray powder diffraction pattern of phase II differs from that of the phase $CsZr_2(PO_4)_3 \cdot 2HF \cdot 2H_2O$ isolated before [2] only in band intensity (Table 2). After long storage, phase II loses a part of HF; therefore, its HF content varies. The shape of the IR spectrum (a broad band in the range 900–1210 cm^{-1}) suggests that the compound is ill-decrystallized (Fig. 2). There is evidence [4] that, in the presence of H_2PO_4- and HPO_4 groups, the IR spectra of phosphates exhibit absorption δ(POH) at 1210–1400 cm^{-1}. However, the presence of a band at 1210 cm^{-1} is not a proof of the existence of an HPO_4 group [3]. Such a band is also present in the spectra of a number of trisubstituted phosphate, e.g., $Na_2Hf(PO_4)_2$ or $CaZr_4(PO_4)_6$ [4]. Because there are no other bands assigned to POH, then we can believe that phase II also contains a PO_4 group and hydrogen is bound to fluorine.

Table 1. Data on the formation of solid phases in the sections of the system $ZrO(NO_3)_2$–H_3PO_4–CsF(HF)–H_2O

ZrO_2 content of initial solution, wt %	F : Zr molar ratio in additive	Precipitate composition						
		chemical composition, wt %						phase composition
		Cs^+	Zr(IV)	F^-	PO_4^{3-}	NO_3^-	H_2O	
molar ratio $PO_4^{3-}/Zr = 0.5$								
2	3	19.9	22.2	6.4	43.9	0	7.43	II, VIII
4.5	3	29.6	27.1	11.1	23.77	0	8.4	III, VIII
5	4	30.0	25.2	10.5	26.1	0	8.2	III, VIII
5	5	–	–	–	–	–	–	I
14	3	24.5	30.6	17.6	16.1	0	11.2	IV
14*	3	25.8	28.6	16.6	16.2	0	12.8	IV
molar ratio $PO_4^{3-}/Zr = 1.5$								
2	3	18.7	26.6	3.5	42.0	3.8	5.5	II, VIII
2	4	–	–	4.7	–	–	–	II, VIII
5	2	18.7	29.3	5.5	40.5	0	6.0	VII, VIII
5	3	26.4	24.5	9.8	29.8	5.9	3.5	V, VI

* Initial $ZrOCl_2 \cdot 8H_2O$.

Phase notation: (I) $Cs_5Zr_4F_{21} \cdot 3H_2O$, (II) $CsZr_2(PO_4)_3 \cdot 2HF \cdot 2H_2O$, (III) $CsZrF_2PO_4 \cdot H_2O$, (IV) $CsZr_2F_6PO_4 \cdot 4H_2O$, (V) $CsHZrF_3PO_4$, (VI) $Cs_{0.70}ZrF(PO_4)_{1.23} \cdot nH_2O$, (VII) $CsHZr_2F_2(PO_4)_{2.66} \cdot nH_2O$, and (VIII) crystalline impurities of undetermined composition.

The differential thermal analysis curve for the phase that was isolated from HF-free solutions and stored for 10 months (the fluorine content of the precipitate is 5.4%) shows only two endothermic events, whereas the curve for the phase that was obtained in this work and stored for 2 years (the fluorine content of the precipitate is 3.1%) presents several effects (Fig. 3). The low-temperature endothermic effect was assigned

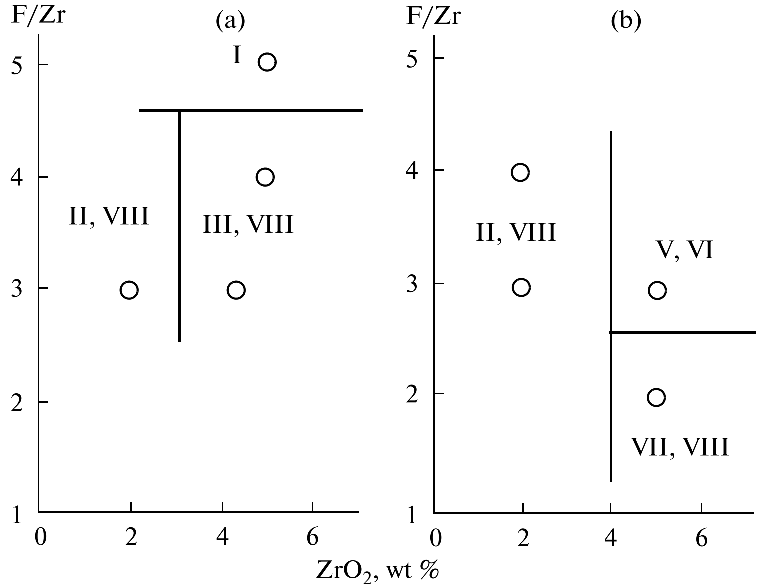

Fig. 1. Phase formation fields. The sections at Cs : Zr = 1 and PO_4^{3-}/Zr = (a) 0.5 and (b) 1.5. The circles are experimental points. The Roman numerals in the fields are the phase numbers.

Table 2. X-ray powder diffraction data of cesium fluorophosphatezirconates

Phase										
III		IV		V				VI	
d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}
7.10	11	7.4	98	7.27	22	1.833	5	8.9	84
6.0	17	6.2	18	6.45	8	1.808	19	7.2**	24
4.56	7	5.75	62	4.49	32	1.787	16	6.4	19
3.67	13	5.25	12	3.69	27	1.768	27	5.75	24
3.54	19	4.50*	15	3.60	61	1.691	16	5.60	29
3.40	100	3.68	38	3.55	100	1.683	16	5.25	44
3.31	10	3.50	81	3.37	67	1.609	19	4.48	20
3.26	9	3.40	100	3.16	26	1.592	8	4.13	16
3.13	11	3.16*	70	3.02	13	1.5417	25	3.97	67
3.03	14	2.86	44	2.98	38			3.66**	56
2.70	6	2.68	28	2.87	26			3.62	75
2.60	23	2.52	41	2.63	17			3.55**	97
2.23	11	2.43	12	2.59	13			3.37**	32
2.07	9	2.36	21	2.53	40			3.21	45
2.04	11	2.33	23	2.46	5			3.15**	20
1.944	26	2.26	26	2.37	27			3.03**	27
1.910	9	2.03	16	2.36	27			2.97**	100
1.824	16	1.950	29	2.28	13			2.87	32
1.604	15	1.930	60	2.19	21			2.78	15
		1.855	16	2.14	21			2.60**	23
		1.840	30	2.12	5			2.53**	48
		1.660	14	2.02	6			2.38	13
		1.616	31	2.009	31			2.18	20
		1.545	10	1.990	14			2.15	20
		1.515	17	1.973	14			2.01**	28
		1.475	20	1.938	27			1.993	37
				1.912	12			1.945	25
				1.888	12			1.940**	19
				1.857	11			1.775	32

Note: The data on phase V are recorded at a heating rate of 0.25 deg/min with Si as an internal standard (performed by V.Ya. Kuznetsov). * $CsNO_3$ line. ** $CsHZrF_3PO_4$ line.

to water removal, and the endothermic effect at 417–463°C was attributed to a solid-phase transformation [5]. The latter is accompanied by a small (0.8 wt %) weight loss. The exothermic event at 657–690°C is characteristic of an amorphous-to-crystalline phase transition, and the product of calcinations of both phases to 970°C is the crystalline fluorozirconate $CsZr_2(PO_4)_3$. Although the first curve shows no exothermic effect, the final calcinations product is also crystalline.

Phase III crystallizes with about 15 vol % impurities; therefore, its composition is conditional.

Phase IV was isolated from zirconium-rich solutions (Table 1), both when using $ZrO(NO_3)_2 \cdot 2H_2O$ and when using $ZrOCl_2 \cdot nH_2O$. In Fig. 1, the formation field of this phase is not indicated because it is outside of the zone covered by this figure.

For $CsZr_2F_6PO_4 \cdot 4H_2O$ anal. calcd., wt %: Cs^+, 22.28; Zr(IV), 30.59; F^-, 19.11; PO_4^{3-}, 15.92; H_2O, 12.08.

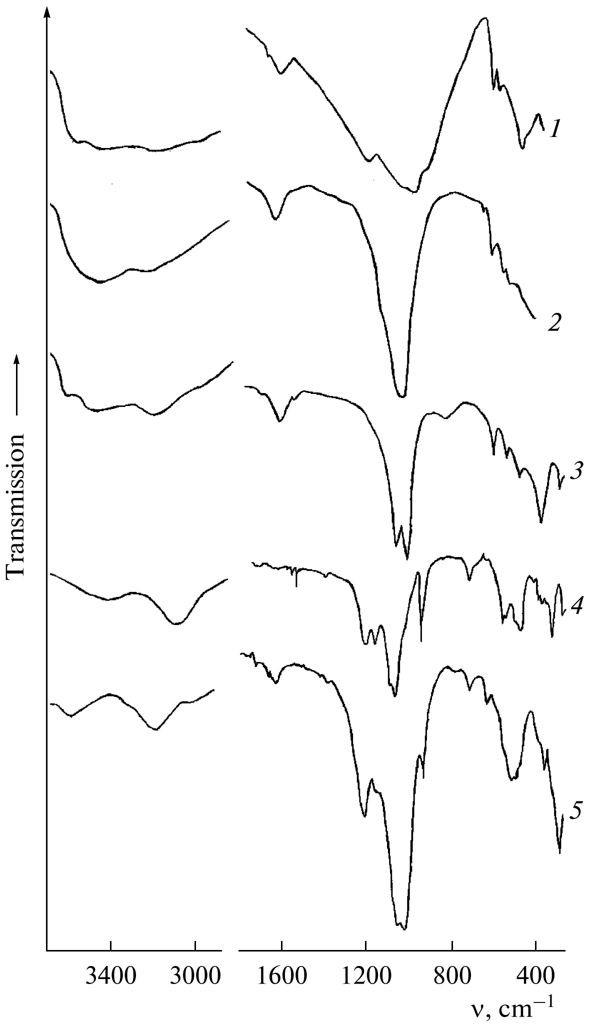

Fig. 2. IR spectra of fluorophosphatezirconates:(*1*) $CsZr_2(PO_4)_3 \cdot 2HF \cdot 2H_2O$, (*2*) $CsZrF_2PO_4 \cdot H_2O$, (*3*) $CsZr_2F_6PO_4 \cdot 4H_2O$, (*4*) $CsHZrF_3PO_4$, and (*5*) a mixture of $CsHZrF_3PO_4$ and phase VI.

For phase IV found, wt %: Cs^+, 22.9; Zr(IV), 28.3; F^-, 17.6; PO_4^{3-}, 15.4; H_2O, 12.0.

The IR spectrum of phase IV in the range 1000–1100 cm^{-1} exhibits a single, rather narrow, band with two maxima (Table 3; Fig. 2, curve *3*), which is assigned to PO_4 group and similar to the band attributed to SO_4 group in the spectrum of the double salt $KZr_2F_9(H_2O)_2K_2SO_4$ [6]. In phase III, the PO_4 group has symmetry close to T_d, i.e., is not coordinated to the zirconium.

The products of calcination of phases II, III, and IV at 970°C under the thermal analysis conditions consist of mixtures of ZrO_2 with $Cs_3Zr_{1.5}(PO_4)_3$, or Cs_2ZrF_6 with $CsZr_2(PO_4)_3$, or $Cs_3Zr_{1.5}(PO_4)_3$ with $CsZr_2(PO_4)_3$ (Table 4).

Phase V in the acidic region contains large uniform granular crystals in the form of monoliths, twins, and triplets, some of which, in their turn, comprise fan-shaped scales (Fig. 4). Individual crystals of this phase are lamellar and form characteristic polycrystalline aggregates (Table 5).

The IR spectrum of the crystals has no bands due to water bending vibrations, which is indicative of the absence of water. The spectrum presents bands assigned to γ (POH), ν (PO(H)), δ (POH), and ν (OH), which are characteristic of HPO_4 group, but shows no bands at 840–910 cm^{-1}, which are inherent only in the spectrum of $H_2PO_4^-$ group and are absent from the spectrum of HPO_4 group [3] (Table 2). This suggests that this compound contains a disubstituted phosphate group. Because the substance has a thin-plate structure and is highly brittle, we failed to obtain a polished sample for further studying the chemical composition with an electron-probe X-ray microanalyzer. For this reason, the chemical composition of the crystals was found by energy-dispersive analysis with a

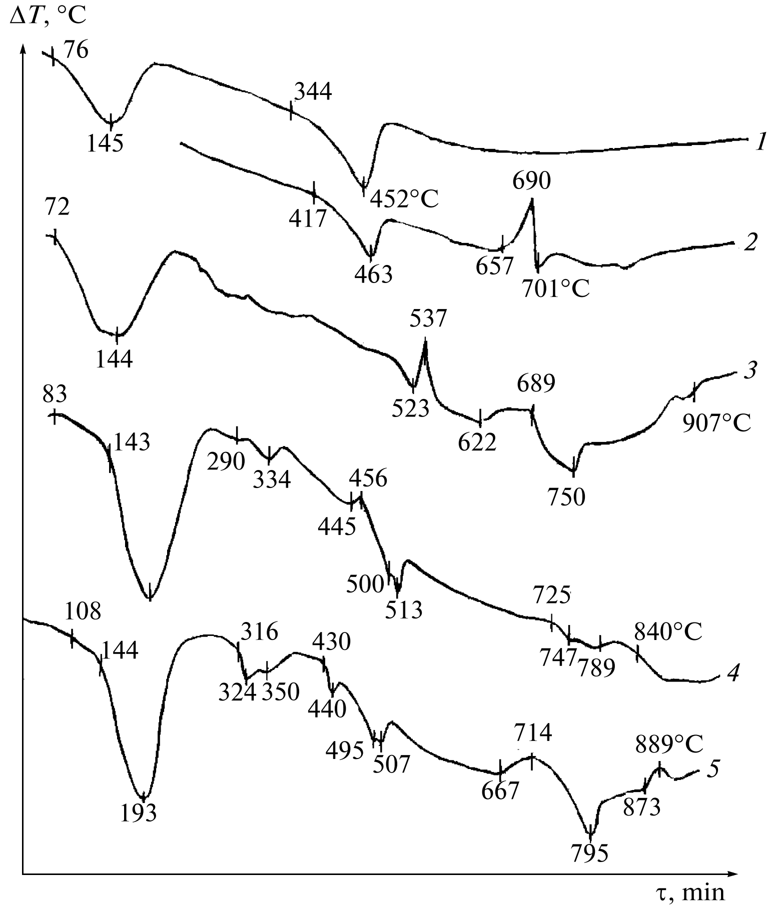

Fig. 3. Differential thermal analysis curves of (*1*, *2*) $CsZr_2(PO_4)_3 \cdot 2HF \cdot 2H_2O$, (*3*) $CsZrF_2PO_4 \cdot H_2O$, and (*4*, *5*) $CsZr_2F_6PO_4 \cdot 4H_2O$. The phases were obtained in the (1) absence or (*2*) presence of HF. The initial reactant is (*1*–*4*) $ZrO(NO_3)_2 \cdot nH_2O$ or (*5*) $ZrOCl_2 \cdot nH_2O$. The sample weights (*1*) 0.18, (*2*) 0.17, (*3*, *4*) 0.16, and (*5*) 0.14 g.The heating rate is 9 deg/min.

LEO-1450 scanning electron microscope and an MS-46 CAMECA X-ray microanalyzer.

For $CsHZrF_3PO_4$ anal. calcd., wt %: Cs^+, 35.24; Zr(IV), 24.19; F^-, 15.11; PO_4^{3-} 25.18.

For phase V found, wt %: Cs^+, 35.3; Zr(IV), 23.9; F^-, 13.4; PO_4^{3-}, 24.2.

Fine-crystalline phase VI is plates with near-isometric habit. For this phase found, wt %: Cs^+, 26.5; Zr(IV), 26.0; F^-, 5.4; PO_4^{3-}, 33.4. In comparison with the chemical composition of phase V, the fine-crystalline phase contains noticeably less cesium and fluorine and more PO_4^{3-} and, according to the IR spectrum, includes water. The composition of phase VI is conditional and corresponds to the formula $Cs_{0.70}ZrF(PO_4)_{1.23} \cdot nH_2O$.

Phase VII is isotropic, probably amorphous, formations constituting 85 vol %. As judged from a high (1.610) refractive index and the IR spectrum, this phase is a water-containing cesium fluorophosphatezirconate. The average precipitate composition $CsHZr_2F_2(PO_4)_{2.66} \cdot nH_2O$.

Thus, in the HF-containing and previously studied HF-free systems $ZrO(NO_3)_2$–H_3PO_4–CsF–H_2O,we isolated cesium fluorophosphatezirconates with the molar ratios Cs : Zr = 0.5 ($CsZr_2(PO_4)_3 \cdot 2HF \cdot 2H_2O$, $CsZr_2F_6PO_4 \cdot 4H_2O$) and 1.0 ($CsZrF_2PO_4 \cdot nH_2O$, $Cs_3Zr_3O_{1.5}F_6(PO_4)_2 \cdot 3H_2O$, and $CsHZrF_3PO_4$). Moreover, in the HF-free system, compounds with Cs : Zr = 0.33 and 0.66. However, unlike fluorine-free cesium phosphatezirconates, among which there is a compound with the molar ratio Cs : Zr = 2.0, no cesium fluorophosphatezirconate with this ratio was isolated, although solutions at the molar ratios CsF : Zr = 2–5 contain enough cesium. On the other hand, in pure fluoride systems without PO_4^{3-}, compounds with the molar ratios F : Zr > 3 form, and the addition of H_3PO_4 to the system prevents the formation of cesium fluorophosphatezirconates with the molar ratios F : Zr > 3. In the studied systems, the interplay between the

Table 3. Wavenumbers (cm^{-1}) at the maxima of absorption bands in the IR spectra of cesium fluorophosphatezirconates

II	III	IV	IV*	V	VI , V	VIII, VII	Assignment [3, 4]
–	–	–	–	320 n	300 n	–	
–	–	–	–	360 w st	340 st	–	
–	–	–	–	370 w	370	–	
–	–	390	380	390 v w	395 v w	395	ν(Zr–F–Zr)
–	–	415 w	–	410 w	405	–	ν(Zr–F)
460 st	–	–	480	480	470 st	460	
500	–	–	–	500 st	500	500	
–	–	515	–	–	520	–	
–	530	530 n w	545	540	550 st	–	$\delta_{as}(PO_4)$, ν(Zr–F)
–	–	575	–	560	590 st	–	
600	610 w	–	600	–	–	610 n	$\nu_4(PO_4)$
640 n	660 w	630	–	–	630	680 v w	$\delta(PO_4)$
–	–	–	–	720	720	–	γ(POH)
–	–	870	820 b	–	–	–	
940 st	–	–	–	940 n	940 n	–	$\nu_s(PO_3)$
1000	–		1005 n	–	1020 s	1010 s	
1060 st w	1040 s	1040 s	–	1060 s	1050	1060 st	$\nu_{as}(PO_3)$
–	–	1085 s	1060	1080 st	1080 w st	–	
–	–	–	–	1150	1150	–	
1210	–	–	–	1200	1210	1210	
1630	1630	1630	1620	–	1630	1620	δ(H–O–H)
–	–	–	–	3080 b	3080		
3200 b d	3250 st d	3210	3200	–	–		ν(O–H)
3400 b d	3450 b d	3520	3500	3400 w d	3470	3450	
3560	–	3640	3610	–	3580	3570	

* The sample was obtained using $ZrOCl_2 \cdot nH_2O$.

Note: b, broad; d, diffuse; n, narrow; s, strong; st, step; v s, very strong; v w, very weak; w, weak.

Table 4. X-ray powder diffraction data of the products of calcination of phase IV to 970°C

Sample 1				Sample 2				Sample 3	
d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}
5.03$*^{4}$	24	1.907$*^{2}$	17	9.5$*^{3}$	16	1.824$*^{4}$	52	**11.6**	9
4.25$*^{2}$	15	1.860$*^{1}*^{4}$	35	**6.70**	16	**1.790**	25	9.40$*^{3}$	10
4.16$*^{2}$	70	1.834	51	5.05$*^{4}$	21	**1.750**	41	4.71$*^{3}$	18
4.00	23	1.819$*^{4}$	27	4.74$*^{3}$	24	1.700$*^{4}$	32	4.27$*^{2}$	41
3.81$*^{2}$	10	1.794$*^{4}$	17	**4.45**	26	1.665$*^{4}$	81	4.20$*^{3}$	61
3.73$*^{1}*^{4}$	52	1.710$*^{4}$	14	4.21$*^{3}$	69	1.650$*^{4}$	31	3.88$*^{2}$	15
3.65$*^{4}$	36	1.666$*^{4}$	27	**3.82**	12	1.614$*^{4}$	32	3.82$*^{4}$	13
3.51	11	1.619$*^{2}*^{4}$	22	3.70$*^{4}$	33	1.600	20	3.70$*^{1}*^{4}$	28
3.40	7	1.610$*^{1}*^{2}$	19	**3.66**	24	1.590	21	3.64$*^{4}$	11
3.18$*^{1}*^{4}$	78	1.593$*^{2}$	16	**3.50**	15	1.574	27	3.36$*^{3}$	100
3.10	43	1.590$*^{4}$	15	3.34	88	1.549$*^{4}$	37	3.21$*^{1}$	16
2.99$*^{2}$	44	1.555$*^{4}$	20	3.17$*^{3}*^{4}$	100	1.514	16	3.15$*^{3}*^{4}$	92
2.86$*^{2}*^{4}$	100	1.511$*^{2}$	8	**3.10**	39	1.500$*^{4}$	19	2.99$*^{2}$	33
2.72$*^{1}$	8	1.506$*^{2}$	9	**3.00**	21	1.477	30	2.85$*^{2}*^{4}$	53
2.61$*^{4}$	58	1.500$*^{4}$	14	2.85$*^{4}$	83	1.453	15	2.70$*^{3}$	62
2.55$*^{4}$	32	1.484$*^{1}*^{4}$	19	2.72$*^{3}$	73	1.420	38	2.60$*^{3}*^{4}$	26
2.50$*^{1}*^{2}*^{4}$	16	1.475$*^{1}$	8	2.62$*^{3}*^{4}$	43	1.360	38	2.52$*^{1}*^{4}$	16
2.44$*^{1}$	29	1.450$*^{2}$	10	2.54$*^{3}*^{4}$	42	1.327	17	2.49$*^{2}$	14
2.32$*^{4}$	13	1.422$*^{4}$	23	2.50$*^{4}$	11	1.296	19	2.42$*^{1}$	7
2.29$*^{1}*^{4}$	12	1.350$*^{2}$	11	**2.36**	26	1.270	14	**2.35**	17
2.22$*^{4}$	19	1.310$*^{1}$	11	**2.35**	23			2.26$*^{3}$	20
2.20$*^{4}$	17			2.295$*^{3}$	35			**2.21**	11
2.15$*^{2}*^{4}$	14			2.22	32			**2.16**	9
2.06$*^{2}$	9			2.195$*^{4}$	25			2.10$*^{3}$	63
2.02$*^{4}$	13			2.105$*^{3}$	80			2.06$*^{3}$	41
2.00$*^{4}$	11			2.06$*^{3}$	59			**2.01**	19
1.970$*^{1}$	11			2.03$*^{4}$	21			**1.986**	10
1.940$*^{1}$	30			2.00$*^{3}$	40			**1.937**	5
1.915	23			1.856$*^{4}$	53			1.906$*^{2}$	16

Note: Samples 1 and 3 were obtained using $ZrO(NO_3)_2 \cdot nH_2O$; sample 2, using $ZrOCl_2 \cdot nH_2O$. Lines: ($*^1$) Cs_3ZrF_6 [7], ($*^2$) $CsZr_2(PO_4)_3$ [8, card 34-0176], ($*^3$) $Cs_3Zr_{1.5}(PO_4)_3$ [8, card 52-1181], and ($*^4$) ZrO_2 [8, card 36-420]. The semibold numbers are the lines of phases of undetermined composition.

Table 5. Crystal-optical characteristics of compounds

Phase	Crystal shape	N_g	N_p
II	Uniform granular spherolites	1.560	1.530
III	Procrystalline mass	1.562	
IV	Optically isotropic, without definite habit	1.531–1.538	
IV*	Same	1.542 ± 0.003	
V	Polycrystals	1.606	1.534
VI	Tabular	<1.539	
VII	Without definite habit	1.610	
VIII	–	1.578 1.590	1.512 1.540

* The initial reactant is $ZrOCl_2 \cdot nH_2O$.

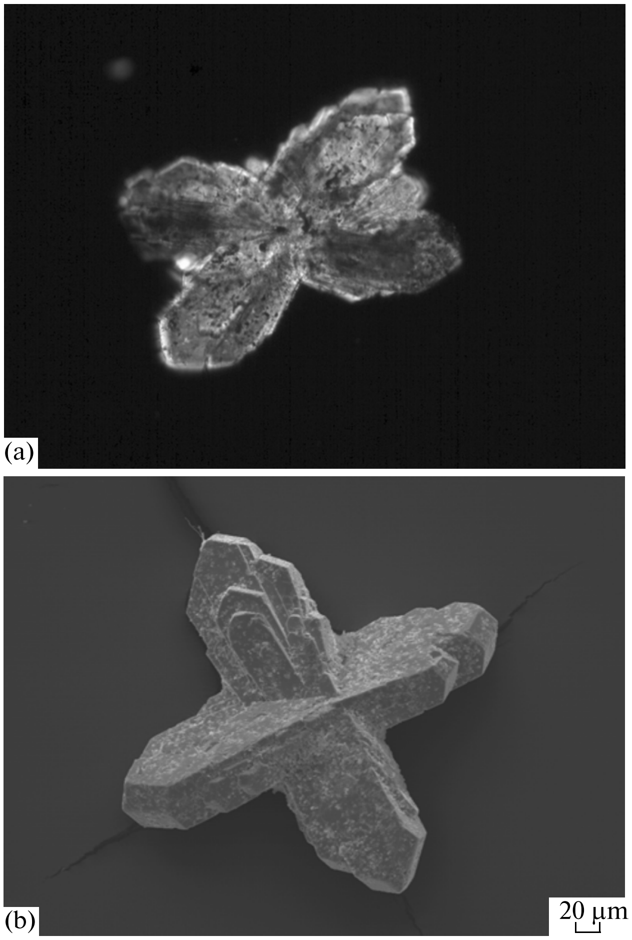

Fig. 4. Twin crystals of the fluorophosphatezirconate $CsHZrF_3PO_4$: (a) polarized light image (×200) and (b) scanning electron microscope image.

fluoride and phosphate components clearly manifests itself.

REFERENCES

1. M. M. Godneva, D. L. Motov, and M. P. Rys'kina, Russ. J. Inorg. Chem. **56,** 1363 (2011).
2. M. M. Godneva, D. L. Motov, V. Ya.Kuznetsov, and T. E. Shchur, Russ. J. Inorg. Chem. **57,** 554 (2012).
3. V. V. Pechkovskii, R. Ya. Mel'nikova, E. D. Dzyuba, et al., *Atlas of Infrared Spectra of Phosphates: Orthophosphates* (Nauka, Moscow, 1981) [in Russian].
4. V. V. Pechkovskii, N. N. Chudinova, R. Ya.Mel'nikova, et al., *Atlas of Infrared Spectra of Phosphates: Double Mono- and Diphosphates* (Nauka, Moscow, 1990) [in Russian].
5. R. G. Lepilina and N. M. Smirnova, *Thermograms of Inorganic Phosphate Compounds: Reference Book* (Nauka, Leningrad, 1984) [in Russian].
6. M. M. Godneva, S. D. Nikitina, D. L. Motov, V. Ya. Kuznetsov, and O. A. Zalkind, Russ. J. Inorg. Chem. **46,** 705 (2001).
7. R. L. Davidovich, T. A. Kaidalova, T. F. Levchishina, and V. I. Sergienko, *Atlas of Infrared Absorption Spectra and X-ray Diffraction Data on Complex Fluorides of Group IV and V Metals*, (Nauka, Moscow, 1972) [in Russian].
8. The Powder Diffraction File (International Centre for Diffraction Data).