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Phase Formation along the PO_4^{3-}/Zr = 1.5 Section of the $ZrO(NO_3)_2$–H_3PO_4–CsF–H_2O System

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Abstract—The phase formation in the system $ZrO(NO_3)_2$–H_3PO_4–CsF–H_2O was studied along the section at the molar ratios $PO_4^{3-}/Zr = 1.5$ and CsF/Zr = 2–5 at a ZrO_2 concentration in the initial solution of 2–5 wt %. New fluorophosphate zirconates, $CsH_2Zr_2F_2(PO_4)_3 \cdot 1.5H_2O$ and two modifications of $CsZrF_2PO_4 \cdot 0.5H_2O$, were isolated, and the known phosphate zirconate $CsZr_2(PO_4)_3$ was obtained for the first time by calcining acidic fluorophosphate zirconate.

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We previously studied the phase formation in sulfuric acid solutions of titanium subgroup element compounds in the presence of alkali metal fluorides [1]. Under "mild" synthesis conditions, we isolated about a hundred of alkali metal fluorometallates and fluorosulfate metallates, most of which were obtained for the first time. Investigation of a number of the compounds showed that some of them are characterized by intense X-ray luminescence. X-ray luminophores promising for practical applications are hexafluorozirconates $M_2Zr(Hf)F_6$ (M = K, Rb, Cs) and also $Rb_3Zr_2F_9SO_4 \cdot 2H_2O$ [2, 3]. Two important results were obtained: on the one hand, the synthesized materials exhibit relatively intense X-ray luminescence over a wide wavelength range, and on the other, it was found that the efficiency of the X-ray luminescence efficiency can be enhanced and its spectrum and temporal characteristics can be optimized by transforming some crystal lattice defects to others, being X-ray luminescence centers.

Phosphate zirconates $CsZr_2(PO_4)_3$ [4, card 34-0196], α-$Cs_2Zr(PO_4)_2$ [4, card 28-0356], and $Cs_3Zr_{1.5}(PO_4)_3$ [4, card 52-1181] are known. At low concentration of the phosphorus component, we isolated crystalline cesium fluorophosphate zirconate $CsZrF_2PO_4 \cdot H_2O$ and also amorphous oxofluorophosphate $Cs_2Zr_3O_2F_4(PO_4)_2 \cdot 3H_2O$ and amorphous oxofluorophosphate nitrate $CsZr_3O_{1.25}F_4(PO_4)_2(NO_3)_{0.5} \cdot 4.5H_2O$. The compound $Cs_3Zr_3O_{1.5}F_6(PO_4)_2 \cdot 3H_2O$ was obtained, which forms in the crystalline or glassy state, depending on the conditions. The formation of the 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 mixtures with the known phases [5].

The system $ZrO(NO_3)_2$–H_3PO_4–CsF–H_2O was studied along the section at the molar ratio F/Zr = 2–5 at 2–5 wt % ZrO_2. The initial substances were $ZrO(NO_3)_2 \cdot 2H_2O$ and 85% H_3PO_4 (both of analytical grade), and CsF (chemically pure). CsF was added while continuously stirring to $ZrO(NO_3)_2 \cdot 2H_2O$ solutions. After the mixtures became homogeneous, H_3PO_4 was added to them. After keeping the obtained mixtures for 7–45 days, precipitates were filtered off, washed successively with water and alcohol, and dried in air. The ZrO_2 content in solution was calculated with the consideration of H_3PO_4 before adding CsF. Phases in the precipitates were identified by X-ray powder diffraction, crystal-optical, thermal, elemental, and IR spectroscopic analyses. The X-ray powder diffraction patterns were recorded with a DRF-2 instrument (graphite monochromator, CuK_α radiation). The crystal-optical measurements were performed using immersion liquids. The thermograms were recorded in air using a Pt–Pt/Rh thermocouple. The reference substance was calcined aluminum oxide. The weight loss was determined with a VT-1000 torsion balance at a heating rate of ~9 deg/min. The IR spectra in the frequency range 400–3800 cm^{-1} were recorded with a Specord-80 spectrometer. Samples for recording were prepared by compacting pellets with KBr or CsI. The chemical analysis was carried out according to standard procedures. The contents of phosphorus, zirconium, and cesium were determined by X-ray spectroscopy by the fundamental parameter method with a Spectroscan MAKC-GV spectrometer; fluorine after double distillation, by potentiometry; NO_3 group, by the Kjeldahl method; and water, by thermogravimetry or from weight loss after keeping samples at 250°C in undried air.

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† Deceased.

Table 1. Formation of solid phases

Initial solution: ZrO_2 content, wt %	Addition: F/Zr molar ratio	Precipitate composition						
		chemical composition, wt %						phase composition
		Cs^+	Zr(IV)	F^-	PO_4^{3-}	NO_3^-	H_2O	
1.9	2	21.7	24.7	5.4	43.7	0	3.8	III
1.9	4	38.7	20.0	8.6	22.9	0	–	II
2	4.7	36.0	24.1	9.6	26.7	4.1	3.6	II
4.8	2	20.5	28.8	5.8	39.3	–	5.6	III, V
4.8	3	37.5	19.7	14.8	24.4	1.4	3.6	IV, V
5	3.8	40.4	23.8	10.3	16.9	5.4	3.2	IV, VI
4.8	5	32.4	21.8	19.5	24.0	–	2.2	I, II

Note: Phase notation: I–Cs_2ZrF_6, II–α-$CsZrF_2PO_4 \cdot 0.5H_2O$, III–$CsH_2Zr_2F_2(PO_4)_3 \cdot 1.5H_2O$, IV–β-$CsZrF_2PO_4 \cdot 0.5H_2O$, V–phase *y*, VI–$CsNO_3$.

The targeted synthesis of cesium fluorophosphate compounds was performed according to published data [5, 6, 10].

Table 1 presents selected data on the compositions of the initial mixtures and isolated precipitates, and Fig. 1 shows a schematic of phase formation fields. Three single-phase regions are outlined. With increasing molar ratio F/Zr, the phases that contain more fluorine atoms, in particular, Cs_2ZrF_6, form and begin to dominate in the system.

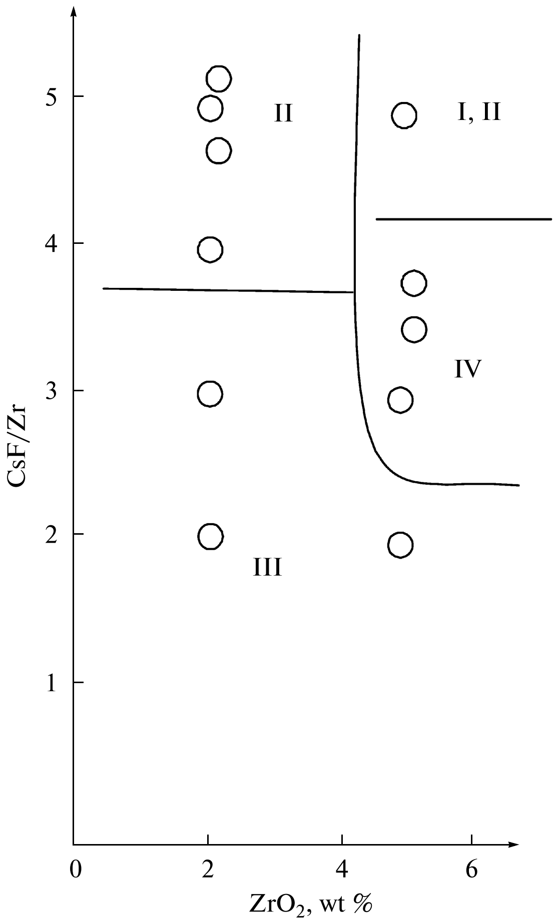

Fig. 1. Phase formation fields. The circles are experimental points. The Roman numerals in the fields correspond to the phase numbers.

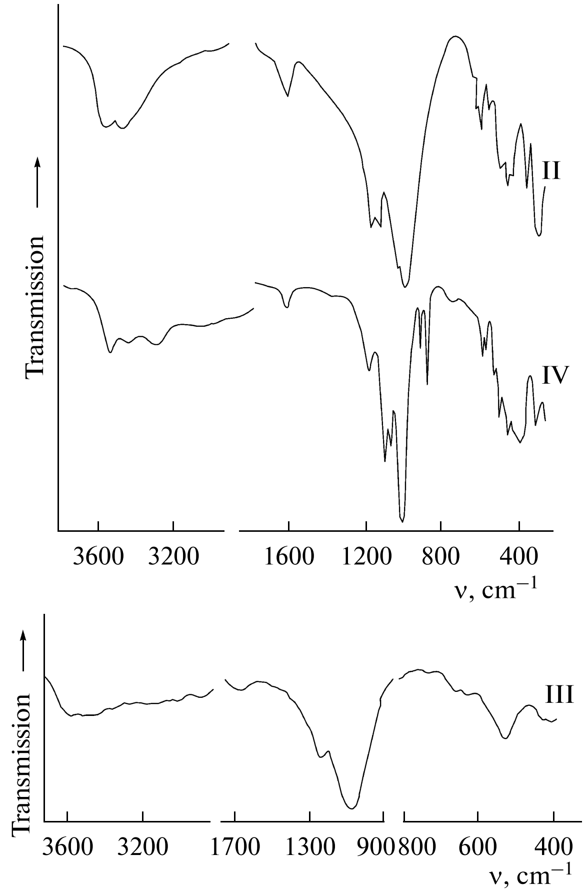

Fig. 2. IR spectra of fluorophosphates zirconates The Roman numerals at the curves are the phase numbers. Spectra II and IV were recorded with a Specord-80 spectrometer; spectrum III, a UR-20 spectrometer.

Table 2. X-ray powder diffraction data of cesium fluorophosphate zirconates

II		III				IV			
d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}
9.0	15	9.0	29	1.670	10	12.4	17	1.822	18
5.25	16	6.90	16	1.606	16	9.0	11	1.813	20
4.70	29	6.30	15	1.566	16	7.1	12	1.700	11
4.40	46	5.80	38			6.75	14	1.615	14
3.84	63	5.30	10			6.30	8	1.556	9
3.40	57	4.42	15			5.50	9		
3.31	100	4.10	62			5.00	7		
3.16	39	4.00	68			4.69	9		
2.96	13	3.80	13			4.31	26		
2.87	14	3.67	15			4.05	25		
2.82	17	3.56	17			3.91	11		
2.65	10	3.33	40			3.57	100		
2.61	9	3.20	100			3.30	14		
2.53	18	3.14	57			3.21	18		
2.45	14	2.97	17			3.16**	57		
2.42	13	2.95	23			2.99	57		
2.34	11	2.91	35			2.90	12		
2.23	33	2.78	28			2.82	14		
2.18	30	2.64	10			2.63	17		
2.12	19	2.50	15			2.56**	12		
1.985	20	2.32	18			2.44	15		
1.925	19	2.25	16			2.32	19		
1.915	19	2.16	10			2.27	10		
1.895	18	2.08	12			2.14	15		
1.870	17	2.05	12			2.10	12		
1.780	29	2.00	23			2.05	25		
1.640	16	1.970	22			1.996**	16		
1.568	18	1.949	23			1.960	18		
1.489	13	1.804	17			1.904	18		
1.465	16	1.730	15			1.855	17		

* Cs_2ZrF_6, ** $CsNO_3$.

Table 2 provides the X-ray powder diffraction data on crystalline cesium fluorophosphate zirconates, which have no analogues in the ICDD database.

The IR spectra of cesium fluorophosphate zirconate (Fig. 2) contain absorption bands due to the bending (1500–1730 cm^{-1}) and stretching (3300–3650 cm^{-1}) vibrations of water. The strong absorption bands within the range 900–1300 cm^{-1} are assigned to the vibrations of the PO_4 group. The zirconium–fluorine bands manifest themselves at low frequencies (<550 cm^{-1}) [7]. In analyzing the IR spectra, we were proceeded from the fact that the symmetry of the tetrahedral PO_4 group reduces in the following cases: as this group coordinates to Zr, for terminal groups as compared to bridging ones, in the transition from *trans*- to *cis*-isomers, and in the interaction of PO_4 groups with hydrogen to give hydrophosphate groups.

In diluted (2 wt % ZrO_2) solutions at the molar ratio F/Zr > 3, phase II forms, which contains less water than at lower concentration of PO_4^{3-} groups ($PO_4^{3-}/Zr\ = 0.5$) [5].

For $CsZrF_2PO_4 \cdot 0.5\ H_2O$ anal. calcd. (wt %): Cs^+, 36.3; Zr(IV), 24.92; F^- 10.38; PO_4^{3-} 25.94; H_2O 2.46. Found, wt %: Cs^+, 36.0; Zr(IV), 24.1; F^- 9.6; PO_4^{3-} 26.7; H_2O 2.0.

According to the IR spectrum, the phase contains a trisubstituted phosphate group (Table 3). The splitting of the bands ν_3 and ν_4 can be caused by the coordination of PO_4 groups to zirconium and also by the formation of *cis* and *trans* isomers [8]. Two absorption bands due to water stretching vibrations and a step in the bending vibration band are because of the presence of two types of water molecules with different hydrogen bond strengths. The absence of water rotational vibrations ρ in phase II indicates that the water in this phase is crystallization water [7]. After dewatering, the product is virtually thermally stable until 720°C, at which temperature it is likely to incongruently melt (Fig. 3).

The composition of phase II is similar to the composition $CsZrF_2PO_4 \cdot H_2O$ obtained previously at the molar ratio $PO_4^{3-}/Zr\ = 0.5$ [5]. The two compounds are characterized by similar, but not identical, X-ray powder diffraction patterns and different crystal shapes, with the refractive index being higher for hemihydrate (Table 4). Their IR spectra are also different. After heating to ~1000°C, $Cs_2Zr(PO_4)_2$ and monoclinic ZrO_2 were found in the heating product, which confirmed the composition of the initial phase.

Phase III is represented by uniform granular crystals

For $CsH_2Zr_2F_2(PO_4)_3 \cdot 1.5\ H_2O$ anal. calcd. (wt %): Cs^+, 19.91; Zr(IV), 27.33; F^- 5.69; PO_4^{3-} 42.69; H_2O 4.05. Found, wt %: Cs^+, 20.9; Zr(IV), 26.9; F^- 5.4; PO_4^{3-} 42.9; H_2O 4.2.

The IR spectra of hydrophosphates are characterized by the presence of bands at the frequencies 700–900, 860–915, 1210–1400, and 2600–3250 cm^{-1}, which are assigned to the vibrations γ(POH), ν(PO(H)), δ(POH), and ν(OH), respectively [9]. The spectrum of phase III exhibits absorption at 1230 and 2850 cm^{-1} but does not show the vibrations γ(POH) and ν(PO(H)). In this compound, hydrogen is likely to be bonded to fluorine, rather than to the PO_4 group. Within the range of vibrations of PO_4 groups, the spectrum is similar to those of the compounds $M_3H_3Zr_3F_3(PO_4)_5$ (M = K or Rb) [6, 10], to which the formulas of phosphatohydrophosphates $M_3Zr_3F_3(HPO_4)_3(PO_4)_2$ were assigned.

Table 3. Wavenumbers (cm^{-1}) of absorption bands in IR spectra

II	III	IV	Assignment [7, 9]
300		300	
320		340	
380 n			ν(Zr–F–Zr)
–	400	420	ν(Zr–F)
470 st	450		
480 n		480	
510		520 n	
	535		$\delta_{as}(PO_4)$, ν(Zr–F)
580	580 st	550	
620 n		600	$\nu_4(PO_4)$
640	625 b	620	$\delta(PO_4)$
650 n	660		
	740 b w	770 b	$\rho(M\text{-}OH_2)$, γ(POH)
	820 w		ν(PO(H))
		900 n	$\rho(M\text{-}OH_2)$, ν(PO(H))
1000 vs		930 n	$\nu_1(PO_4)$
		1020	$\nu_3(PO_4)$
1050		1040 s	
	1080 s	1090	
1140		1120	
1180	1230	1200	
1630		1600 st	δ(H–O–H)
1650 st	1680	1630	
	2850 w b		ν(OH)
		3300	ν(O–H)
3480		3450	
3580	3500 b w	3550	

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

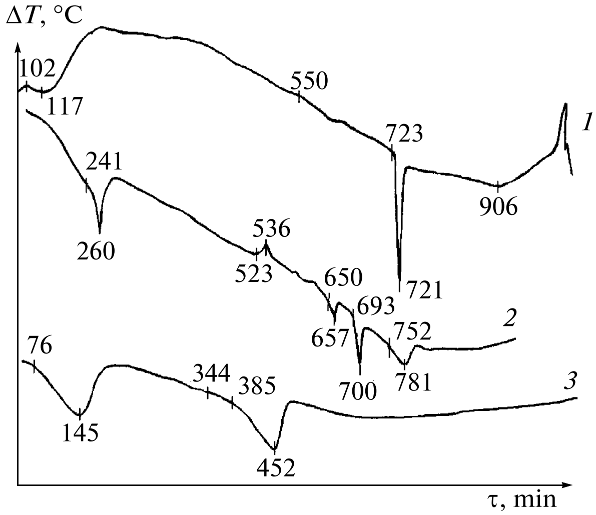

Fig. 3. Differential thermal analysis curves of cesium fluorophosphate zirconates (*1*) α-$CsZrF_2PO_4 \cdot 0.5H_2O$, (*2*) β-$CsZrF_2PO_4 \cdot 0.5H_2O$, and (*3*) $CsZr_2(PO_4)_3 \cdot 2HF \cdot 1.5H_2O$ at sample weights of (*1*) 0.20, (*2*) 0.13 and (*3*) 0.18 g at a heating rate of 9 K/min.

After water removal, no weight loss is observed until 320°C. Then, within the range 320–460°C, there is a 3.2% weight loss, which is approximately a half of the total HF loss. In this case, the composition of the product after the endothermic event is $CsHZr_2F(PO_4)_3$. The little excess over the theoretical value (6.02%) is caused by the insignificant formation of polyphosphates. The final calcination product is $CsZr_2(PO_4)_3$ (Table 5). No lines due to polyphosphates are seen in the X-ray powder diffraction pattern.

Phase IV crystallizes with impurities. From a mixture of this phase and $CsNO_3$, mechanically large $CsNO_3$ crystals were removed. The composition of the residue was found.

For $CsZrF_2PO_4 \cdot 0.5\ H_2O$ anal. calcd. (wt %): Cs^+, 36.3; Zr(IV), 24.92; F^- 10.38; PO_4^{3-} 25.94; H_2O 2.46. Found, wt %: Cs^+, 37.5; Zr(IV), 25.2; F^- 10.3; PO_4^{3-} 24.4; H_2O 3.2.

As judged from its composition and structure (Table 2), phase IV is a modification of phase II. The IR spectrum of phase IV contains the bands that can be simultaneously assigned both to the vibrations of the HPO_4 group and to the wagging and rocking vibrations of water, which are characteristic of water coordinated to zirconium. The number of absorption bands of PO_4 groups in the spectrum of phase IV is much larger than that in the spectrum of phase II; i.e., the former groups are less symmetric, which can be explained both by the hydrogen bond in the hydrophosphate group and by the *cis* isomerism in phase IV as compared to the *cis–trans* isomerism in phase II [7]. Three absorption bands due to water stretching vibrations and a step in the bending vibration band are because of the presence of two types of water molecules.

The low-temperature (241–260°C) endothermic event in the differential thermal analysis curve is caused by water removal; then, an amorphous product crystallizes (exothermal event at 523–536°C). After water removal up to 420°C, the weight loss is 1.6%. The main loss occurs above 600°C. The last endothermic event (752–781°C) is caused by decomposition to form a mixture of solid phases of the gross composition $CsZrO_{1.75}(PO_4)_{0.5}$, which contains ZrO_2 and, probably, $Cs_2ZrO_{1.5}PO_4$.

The total weight loss at ~1000°C is 15.2 wt %, which exceeds the theoretical weight loss due to fluorine by 4.5%. Isothermal calcination at the same temperature leads to a 25% weight loss, which is caused by the transformation of phosphate to polyphosphate. The final calcination product is fire-polished and changes to a sticky mass because of hygroscopicity while being ground to a powder. Few weak lines in the X-ray powder diffraction pattern are unidentifiable.

Phase V (denoted by *y*) is amorphous and is not isolated individually; its composition is not found.

The compounds mainly form small crystals 2–6 μm in size.

Approximate schemes of thermal decompositions are the following:

Table 4. Crystal-optical characteristics

Phase	Crystal shape	N_g	N_p
II	Radiated aggregates	1.580	1.540
III	Spherolites, uniform granular	1.560–1.580	1.530
IV	Needle	1.545*	
V	Undetermined	1.595*	

* Average value.

Table 5. X-ray powder diffraction data of calcination products

II		III				IV	
1000°C		480°C		970°C		760°C[3]	
d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}
9.4[1]	9	6.30	18	4.30	82	5.0[2]	13
4.72[1]	17	5.60	20	3.82	37	4.61	12
4.20[1]	49	5.00	18	3.58	10	4.47	17
3.70[2]	19	4.49	100	3.20	8	4.21	6
3.32[1]	100	3.98	50	2.99	100	3.67[2]	19
3.15[12]	79	3.81	31	2.90	16	3.43	100
3.03	7	3.60	21	2.75	10	3.29	82
2.84[2]	12	3.40	59	2.48	30	3.20	84
2.71[1]	39	3.16	46	2.40	7	3.16[2]	67
2.61[2]	8	3.09	84	2.34	3	3.05	17
2.53[12]	5	2.88	92	2.13	32	2.83[2]	30
2.36	24	2.59	30	2.08	12	2.75	58
2.28[1]	16	2.50	43	1.907	35	2.68	30
2.21[2]	6	2.22	37	1.860	14	2.61[2]	16
2.14	5	2.14	37	1.780	3	2.50	14
2.11[1]	50	2.12	35	1.720	8	2.48	12
2.05[1]	32	1.994	20	1.623	20	2.26	10
2.02	9	1.862	35	1.595	23	2.22	16
1.863	14	1.820	35	1.508	21	2.17	22
1.818[2]	8	1.775	21	1.430	5	2.08	10
1.750	19	1.727	31	1.352	9	2.04	19
1.694[2]	4	1.717	37	1.319	4	2.01	17
1.661[2]	5	1.698	41	1.278	6	1.980	10
1.570	23	1.680	36	1.233	9	1.925	14
1.545	7					1.880	16
1.472	7					1.843[2]	23
1.410	13					1.820[2]	19
1.402	8					1.723	12
1.367	20					1.680	18
1.293	12					1.662	18
1.254	7					1.635	18
1.132	11						

Note: The superscripts at the numbers refer to the following: (1) $Cs_3Zr_{1.5}(PO_4)_3$ (4, card 52-1181), (2) ZrO_2 (4, card 36-420), and (3) isothermal calcination.

$$2\alpha\text{-}CsZrF_2PO_4 \cdot 0.5H_2O \xrightarrow{102\text{–}117°C} 2\alpha\text{-}CsZrF_2PO_4 \xrightarrow{721\text{–}723°C} Cs_2Zr(PO_4)_2 + ZrO_2;$$

$$CsH_2Zr_2F_2(PO_4)_3 \cdot 1.5H_2O \xrightarrow{76\text{–}145°C} CsH_2Zr_2F_2(PO_4)_3 \xrightarrow{320\text{–}460°C} CsHZr_2F(PO_4)_3 \xrightarrow{970°C} CsZr_2(PO_4)_3;$$

$$\beta\text{-}CsZrF_2PO_4 \cdot 0.5H_2O \xrightarrow{241\text{–}260°C} \beta\text{-}CsZrF_2PO_4 \xrightarrow[\text{crystallization}]{523\text{–}536°C} \beta\text{-}CsZrF_2PO_4 \xrightarrow{780°C} Cs_2ZrO_{1.5}PO_4 + ZrO_2.$$

Thus, at the molar ratio $PO_4^{3-}/Zr = 1.5$, new fluorophosphate zirconates, $CsH_2Zr_2F_2(PO_4)_3 \cdot 1.5H_2O$ and two modifications of $CsZrF_2PO_4 \cdot 0.5H_2O$, were isolated from solution, and a single-phase product, phosphate zirconate $CsZr_2(PO_4)_3$, was obtained by calcining acidic fluorophosphate zirconate.

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