

Article

Features of Phase Formation in the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ System and the Growth of the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ Crystals

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Abstract: In this paper, the conditions of phase formation in the system $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ are considered for the first time. The phase formation of $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ at $t = 50^\circ\text{C}$ has been studied extensively. The main concentration boundary conditions for this compound are considered for the first time. The solubility congruence of $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ is shown. Conditions and approaches for obtaining crystals by isothermal evaporation and saturated solution temperature reduction methods are considered. The results of obtaining $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystals with maximum dimensions of ~ 20 mm are presented.

Keywords: superprotonic crystals; phase equilibria; crystal growth



Citation: Komornikov, V.A.; Makarova, I.P.; Timakov, I.S.; Grebenev, V.V. Features of Phase Formation in the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ System and the Growth of the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ Crystals. *Crystals* **2023**, *13*, 1163. <https://doi.org/10.3390/cryst13081163>

Academic Editor: Heike Lorenz

Received: 15 June 2023

Revised: 21 July 2023

Accepted: 25 July 2023

Published: 26 July 2023



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1. Introduction

The consideration of the phenomenon of proton transport in the condensed state is probably impossible without considering such objects as crystals, and in particular, superprotonics. This group includes crystals of acid salts with the general formula $M_m\text{H}_n(\text{AO}_4)_{(m+n)/2} \cdot x\text{H}_2\text{O}$ ($M = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$; $A = \text{S}, \text{Se}, \text{P}, \text{As}$).

Superprotonic crystals attract the attention of researchers primarily due to the presence of order/non-order phase transitions in them. Such phase transitions occur at temperatures before melting and are accompanied by cardinal restructuring with an increase in the symmetry of the crystal. As a consequence of this restructuring, conditions for a directed proton diffusion in the crystal volume arise. Thus, during the phase transition, the conductivity in superprotonic crystals abruptly increases by several orders of magnitude and reaches values comparable with the conductivity in the melt (more than $10^{-3} \Omega^{-1}\text{cm}^{-1}$).

Experimentally, this phenomenon was first observed in [1,2]. By analogy with superionic phase transitions, such transitions have been termed superprotonic. At the same time, for the vast majority of the crystals belonging to the mentioned group, this phase transition is accompanied by an increase in the overall symmetry of the crystal [3].

The combination of high proton conductivity in solid state with moderate temperatures of phase transitions determines the prospects for the application of superprotonic crystals as proton-exchange membrane materials for various electrochemical devices [4–6].

Complex acidic cesium sulfate phosphates, along with CsHSO_4 and CsH_2PO_4 , belong to the family of superprotonic crystals. The results of the first systematic searching investigations of cesium sulfate phosphates are described in a series of works [7–10]. In these works, attention was mainly placed onto the structures of compounds and their conducting properties without the proper consideration of the conditions for obtaining crystals through a reproducible process. The study of phase formation in the system $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4$ from aqueous solutions [11] allowed us to obtain more reliable results. In particular, it was shown that the compounds $\text{Cs}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ and $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$ are separate double salts [12], although are very similar in structure, but are not the extreme members of the series of solid solutions as indicated in [8]. In addition, the existence of the

compound $\text{Cs}_5(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_2$ [13] was not confirmed. At the same time, the crystal $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$ [14], formally not belonging to the $\text{CsHSO}_4\text{--CsH}_2\text{PO}_4$ system, was found. Subsequently, thanks to precision structural studies, it was found that a more correct structural formula for it would be $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ [15].

One of the features of the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal is that it is the only superprotonic crystal that is formed from an aqueous solution in a non-conducting phase in cubic syngony. The $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal in the low-temperature state belongs to the $\bar{1}43d$ symmetry group with parameter $a = 14.5399$ (1) Å, $Z = 4$. In this structure, a hydrogen bond network is formed between SO_4 and PO_4 tetrahedra, in which the protons on the O--H...O bonds are arranged in one-minimum potentials. Such hydrogen bonding systems are typical of most superprotonic crystals, but in the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal, this hydrogen bonding system is three-dimensional even in the low-temperature state.

In addition, this crystal also exhibits a very moderate superprotonic phase transition temperature [16].

Studying the crystal structure of $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ and the peculiarities of its superprotonic phase transition would be impossible without obtaining single crystals of suitable quality. The conditions for obtaining single-crystal samples of $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ have not yet been described in detail. This is to be corrected in the present work.

Due to the fact that the crystal $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ is formed in a complex system ($\text{CsOH--H}_2\text{SO}_4\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$), the consideration of the concentration conditions of this crystal's crystallization is impossible when in isolation from the features of phase formation in this system.

Thus, the present work is devoted to: the consideration of some features of phase formation in the system $\text{CsOH--H}_2\text{SO}_4\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$, the determination of the concentration boundary conditions of $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal formation, and the conditions of its reproducible obtaining.

2. Experimental Part

To obtain single crystals of $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$, we used cesium hydrosulfate (CsHSO_4 , Rare Metals Factory LLC, Novosibirsk, Russia, 98+%) and cesium dihydrogen orthophosphate (CsH_2PO_4 , Rare Metals Factory LLC, 99%) without additional purification, as well as 85% phosphoric acid (H_3PO_4 , Acros Organics, 85+%, extra pure, SLR). In order to study phase formation, we used sulfuric acid (H_2SO_4 , Chimmed Group, 98% extra pure) and cesium sulfate (Cs_2SO_4 , Rare Metals Factory LLC, 98+%) in addition to the listed reagents.

The interaction between the components in the $\text{CsHSO}_4\text{--CsH}_2\text{PO}_4\text{--H}_2\text{O}$ system was investigated by the isothermal method under equilibrium conditions at 25, 50, and 75 °C. The temperature was maintained constant with the aid of a thermostat; the equilibrium time was 24 h. The equilibrium time in the solution was found by comparing the results of analysis on a cesium cation for samples selected with a step of 6 h.

Solubility isotherms were plotted by the Gibbs–Rosebom method, and the solid-phase composition was determined by the Schreinemakers method. Weights of materials were kept in a thermostat in round-bottom flasks 50 mL in volume; their mixing was implemented by the thermostat mixer drive (rocking gimbal).

Sampling of the liquid phase and solid residue was performed from the flasks located in the thermostat. At 25 °C, the liquid phase was sampled by a single-channel feeder with a removable plastic tip directly from the crystallizer. At 50 and 75 °C, the liquid phase was sampled in a similar way, but the removable plastic tip was previously heated to the thermostat temperature in this case. For each weight, solid residue samples were divided into two approximately equal parts so as to provide two solid residue samples for each liquid phase sample.

When determining the equilibrium time, the solubility of the compounds was analyzed by measuring (using the weighting method) the content of cesium (in the form of tetraphenylborates) in the saturated solution [17]. The content of phosphorus (PO_4^{3-} anion)

in the form of yellow phosphorus-molybdenum-vanadium heteropolyacid was determined by spectrophotometry [18].

The interaction between the components in the $\text{Cs}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ system was investigated similarly to the previous system at a temperature of 50 °C. For the analytical determination of component concentration, in addition to the procedure for the weight determination of cesium content, we used the weight determination of sulfate anion content according to the method described in [19].

X-ray diffraction analysis of polycrystalline samples and single crystals was performed at ambient temperature using Rigaku MiniFlex 600 diffractometer (Japan) (Cu K α source, continuous scanning mode—2 deg/min, in the 2θ range between 10 and 70° with an effective step size of 0.02°, no sample rotation, in the environment atmosphere).

Crystal growth was carried out by two methods: isothermal evaporation and controlled decrease in the temperature of the saturated solution.

The method of isothermal evaporation involved the preparation of a deliberately unsaturated solution, followed by a slow evaporation of the solvent and spontaneous formation of crystals. This method was used to obtain seed crystals.

The method of controlled decrease in the solution temperature aimed at obtaining a solution with a saturation temperature higher than room temperature. Then, a seed crystal was added to this solution, and the temperature of the solution was lowered in a controlled manner according to the corresponding program. The process was carried out in a sealed glass crystallizer with reverse stirring. The seed crystal was placed on a fixed platform.

3. Results and Discussion

3.1. Variety of Crystals in the $\text{CsOH--H}_2\text{SO}_4\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$ System

It is rather challenging to observe phase equilibria in the $\text{CsOH--H}_2\text{SO}_4\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$ four-component system, especially in the area with a high content of CsOH. Before proceeding to the description of the phase formation of the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal, it is necessary to examine the phase formation in the $\text{CsOH--H}_2\text{SO}_4\text{--H}_2\text{O}$ and $\text{CsOH--H}_3\text{PO}_4\text{--H}_2\text{O}$ systems at least schematically.

The system $\text{CsOH--H}_2\text{SO}_4\text{--H}_2\text{O}$ in the $\text{Cs}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ interval, studied by us in [20], contains the Cs_2SO_4 , $\text{Cs}_5\text{H}_3(\text{SO}_4)_2 \cdot y\text{H}_2\text{O}$ (where $y = 0\text{--}0.5$) and CsHSO_4 phases (listed according to the increasing proportion of H_2SO_4). The listed compounds are characterized by a congruent nature of solubility and fairly wide ranges of crystallization in mole percentages (Table 1, Figure 1).

Table 1. Concentration coordinates of the researched points and phase equilibria in the $\text{Cs}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ system.

Crys-n №	Composition of Liquid Phase, wt.% (Excluding Water).		Phase Equilibria
	Cs_2SO_4	H_2SO_4	
1	64.59	4.37	$\text{Cs}_2\text{SO}_4 \leftrightarrow \text{L}$
2	70.74	8.21	
3	71.54	10.43	$\text{Cs}_2\text{SO}_4 + \text{Cs}_5\text{H}_3(\text{SO}_4)_4 \leftrightarrow \text{L}$
4	72.61	13.11	$\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \leftrightarrow \text{L}$
5	69.18	15.33	$\text{Cs}_5\text{H}_3(\text{SO}_4)_4 + \text{CsHSO}_4 \leftrightarrow \text{L}$
6	69.43	18.80	$\text{CsHSO}_4 \leftrightarrow \text{L}$
7	59.31	19.63	
8	54.70	22.22	
9	48.68	24.49	

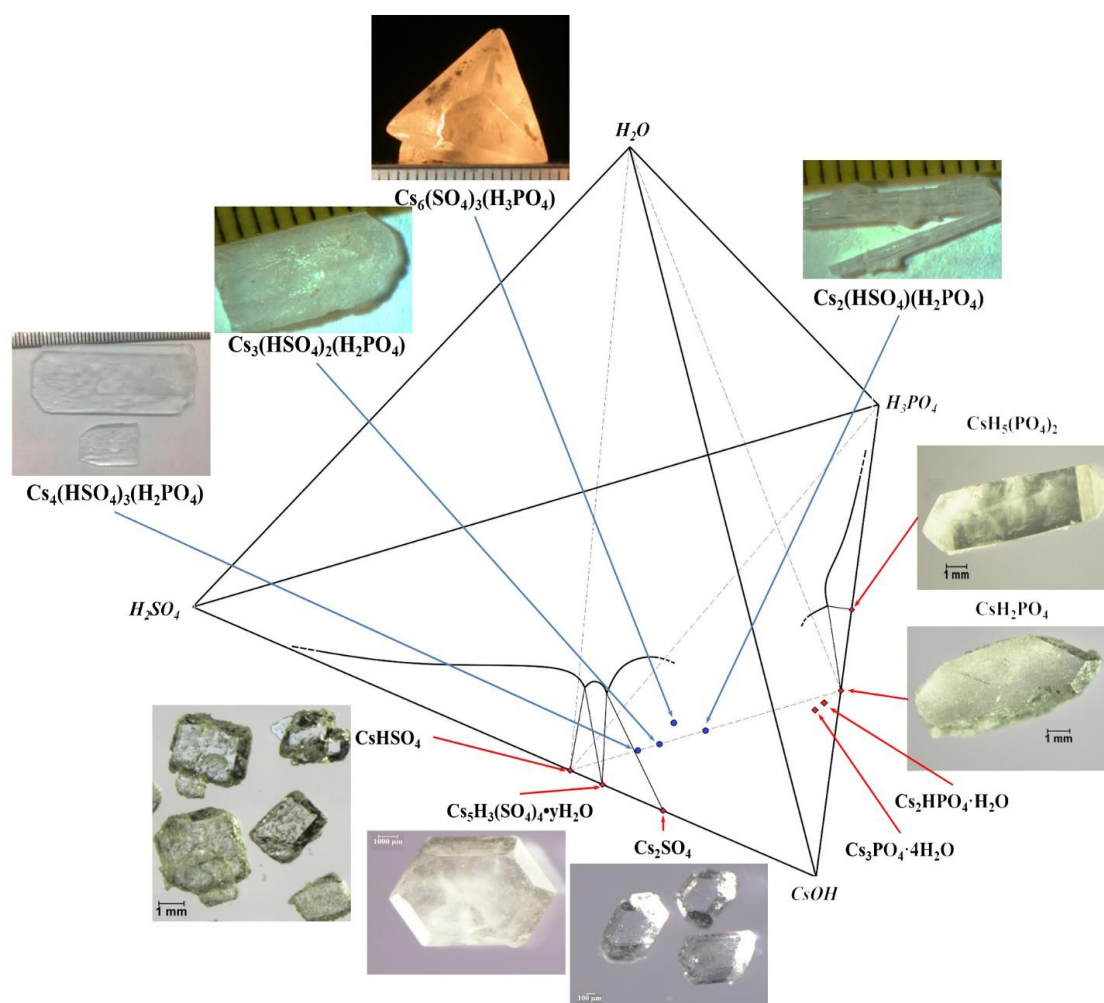


Figure 1. The variety of compounds in the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ system. The dotted line shows the $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4\text{-H}_2\text{O}$ pseudoternary cross-section and the choice of concentration coordinates for a simplified representation of the crystallization range of the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ compound. The photos show crystals of compounds obtained directly by the authors of this work.

The $\text{CsOH-H}_3\text{PO}_4\text{-H}_2\text{O}$ system is somewhat more difficult to analyze and display. In this system, we take into account the presence of the following compounds: $\text{Cs}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$, $\text{Cs}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$, CsH_2PO_4 , and $\text{CsH}_5(\text{PO}_4)_2$ (listed according to the increasing proportion of H_3PO_4). We managed to obtain the last two compounds from this list in the form of fairly large single crystals. These phosphates, as well as cesium sulfates, are congruently soluble and are characterized by rather wide crystallization intervals.

Immediately in the space of the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ four-component system, we studied the $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4\text{-H}_2\text{O}$ cross-section in great detail [11] (Figure 2, Table 2). Displaying this part of the phase diagram of the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ system is also complicated by the fact that, depending on the temperature, a different set of crystallization ranges for various compounds is observed in it. For instance, the $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ phases known from [9] and $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$ [11] crystallize in a limited temperature range. The $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ compound crystallizes from a stoichiometric solution ($\text{CsHSO}_4\text{:CsH}_2\text{PO}_4 = 1\text{:}1$) at a temperature below room temperature (about 12 °C). The $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$ compound crystallizes from a solution of the same composition in the temperature range of 15–40 °C, showing an incongruent nature of solubility. Finally, the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ compound crystallizes from the solution of the same composition at a temperature above 45 °C.

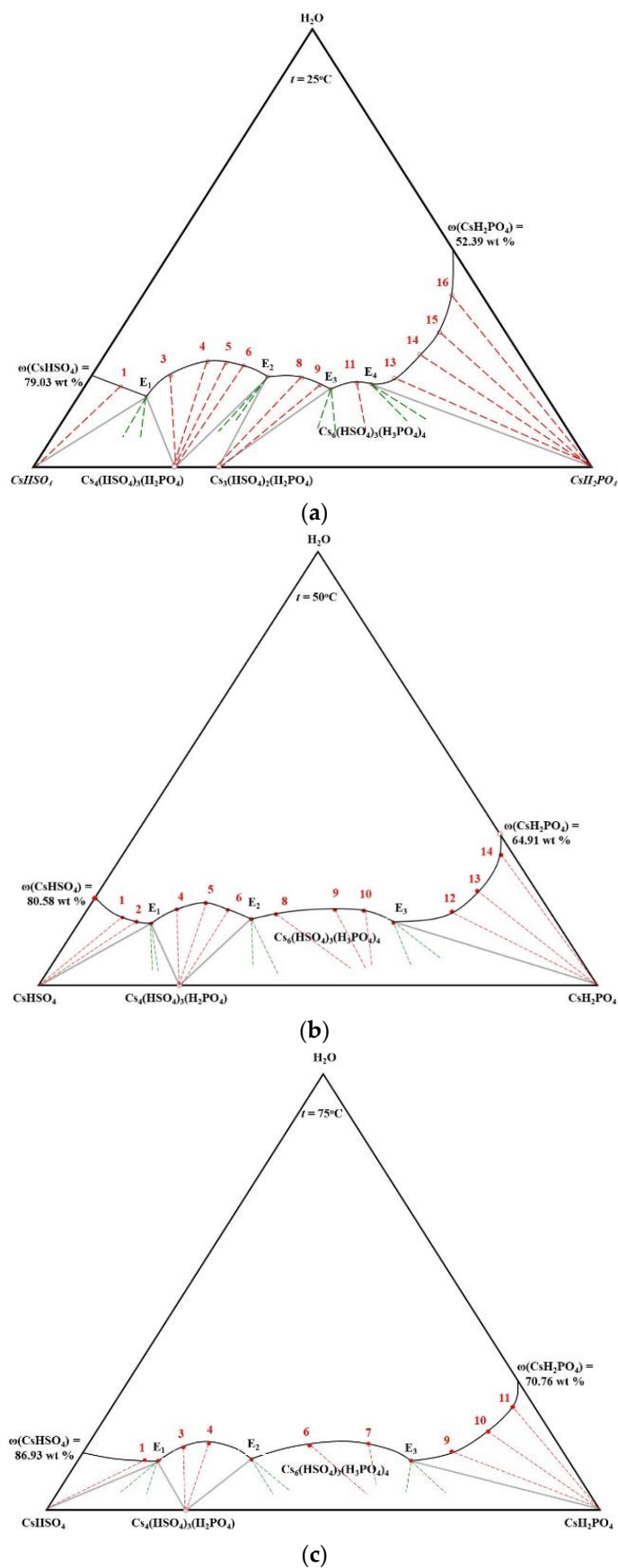


Figure 2. Phase equilibria in the CsHSO_4 – CsH_2PO_4 – H_2O pseudoternary cross-section at different temperatures: (a)— 25°C , (b)— 50°C , and (c)— 75°C .

Table 2. Concentration coordinates of the researched points and phase equilibria in the CsHSO₄–CsH₂PO₄–H₂O system at different temperatures.

25 °C			50 °C			75 °C		
Crys-n №	Composition of the Liquid Phase, wt. %.		Crys-n №	Composition of the Liquid Phase, wt. %.		Crys-n №	Composition of the Liquid Phase, wt. %.	
	CsHSO ₄	CsH ₂ PO ₄		CsHSO ₄	CsH ₂ PO ₄		CsHSO ₄	CsH ₂ PO ₄
CsHSO ₄	79.03	-	CsHSO ₄	80.58	-	CsHSO ₄	86.93	-
1	75.37	8.44	1	78.917	8.986	1	77.14	14.203
E ₁	73.72	11.67	2	77.865	10.311	E ₁	75.753	16.53
3	73.02	13.40	E ₁	76.586	12.807	3	69.747	21.321
4	62.31	24.75	4	66.644	20.062	4	64.553	27.91
5	56.83	34.93	5	65.194	22.323	E ₂	55.716	32.31
6	54.50	36.95	6	62.852	27.152	6	37.316	50.13
E ₂	54.19	36.65	E ₂	56.368	32.033	7	31.811	58.731
8	48.61	42.55	8	41.668	45.429	E ₃	29.067	61.92
9	42.66	53.09	9	28.724	61.703	9	22.47	65.375
E ₃	40.11	54.01	10	15.869	68.528	10	13.817	72.256
11	37.30	54.58	E ₃	14.479	68.827	11	9.771	76.561
E ₄	34.24	58.04	12	11.358	70.204	CsH ₂ PO ₄	-	70.8
13	24.39	52.69	13	7.18	69.73	CsH ₂ PO ₄ ↔ L		
14	17.54	53.93	14	2.87	69.07			
15	11.07	53.33	CsH ₂ PO ₄		-			
16	5.85	52.84						
CsH ₂ PO ₄	-	52.39						

Bold denotes concentration conditions for the points of noninvariant equilibrium.

The above analysis indicates the wide variety of known compounds formed in the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ system. Therefore, the correct display of all possible elements of the system (primarily the points of nonvariant equilibria, co-crystallization lines, solubility values) is quite complicated. Thus, in order to observe the crystallization conditions for a particular $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ compound, some simplifications must be made.

The first simplification of the display of crystallization fields in the system was the choice of a temperature of 50 °C, as this results in containing a smaller number of crystallization fields. The second simplification, which was made within the framework of this observation, was the choice of system components to display phase equilibria in the form of a tetrahedral diagram. For a simplified display of the crystallization phase field of the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ compound, we used the following initial components: $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ (Figure 3, Table 3). It is worth mentioning that the chosen initial components are a simplification and not an independent subsystem within a more complete system. This is due to the fact that one of the generatrices of the ternary systems, $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4\text{-H}_2\text{O}$, contains a phase crystallization branch that does not lie in the concentration plane of this system.

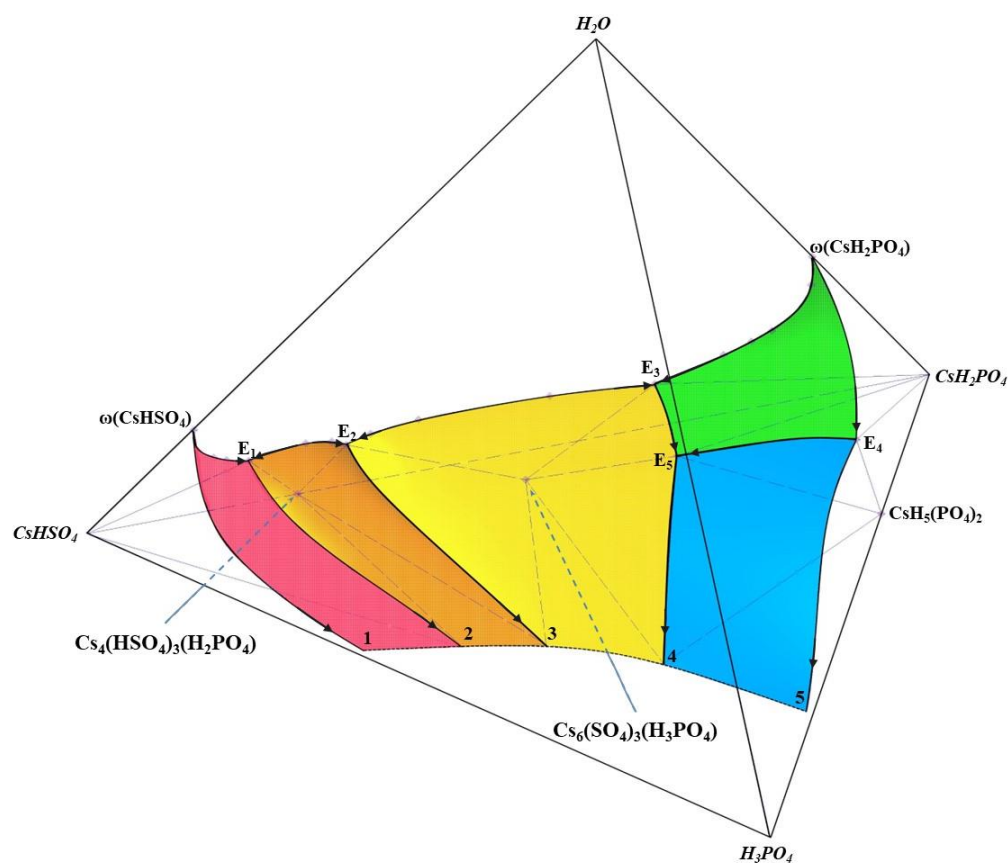


Figure 3. Phase equilibria in the $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ system as part of the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ system.

Table 3. Main elements of the $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ diagram.

Element	Description
$\omega(\text{CsHSO}_4)$	CsHSO_4 solubility at 50 °C, 80.6% mass
$\omega(\text{CsH}_2\text{PO}_4)$	CsH_2PO_4 solubility at 50 °C, 64.9% mass
E_1	$\text{CsHSO}_4\text{—}73.1$, $\text{CsH}_2\text{PO}_4\text{—}12.4$, $\text{H}_2\text{O—}14.5\%$ mass

Table 3. Cont.

Element	Description
E ₂	CsHSO ₄ —54.3, CsH ₂ PO ₄ —30.3, H ₂ O—15.4% mass
E ₃	CsHSO ₄ —28.8, CsH ₂ PO ₄ —56.6, H ₂ O—14.6% mass
E ₄	CsH ₂ PO ₄ —51.2, H ₃ PO ₄ —29.6, H ₂ O—19.2% mass
E ₅	CsHSO ₄ —22.3, CsH ₂ PO ₄ —45.8, H ₃ PO ₄ —18.2, H ₂ O—13.7% mass. Nonvariant equilibrium Cs ₆ (SO ₄) ₃ (H ₃ PO ₄) ₄ +CsH ₂ PO ₄ +CsH ₅ (PO ₄) ₂ ↔L
Line E ₁ -2	Equilibrium CsHSO ₄ +Cs ₄ (HSO ₄) ₃ (H ₂ PO ₄)↔L
Line E ₂ -3	Equilibrium Cs ₄ (HSO ₄) ₃ (H ₂ PO ₄)+Cs ₆ (SO ₄) ₃ (H ₃ PO ₄) ₄ ↔L
Line E ₃ -E ₅	Equilibrium Cs ₆ (SO ₄) ₃ (H ₃ PO ₄) ₄ +CsH ₂ PO ₄ ↔L
Line E ₄ -E ₅	Equilibrium CsH ₂ PO ₄ +CsH ₅ (PO ₄) ₂ ↔L
Line E ₅ -4	Equilibrium Cs ₆ (SO ₄) ₃ (H ₃ PO ₄) ₄ +CsH ₅ (PO ₄) ₂ ↔L
Line 1-2-3-4-5	Solid phase solubility in 100% H ₃ PO ₄
Surface ω(CsHSO ₄)-E ₁ -2-1	Crystallization range CsHSO ₄
Surface E ₁ -E ₂ -3-2	Crystallization range Cs ₄ (HSO ₄) ₃ (H ₂ PO ₄)
Surface E ₂ -E ₃ -E ₅ -4-3	Crystallization range Cs ₆ (SO ₄) ₃ (H ₃ PO ₄) ₄
Surface ω(CsH ₂ PO ₄)-E ₄ -E ₅ -E ₃	Crystallization range CsH ₂ PO ₄
Surface E ₄ -E ₅ -4-5	Crystallization range CsH ₅ (PO ₄) ₂

There are five crystallization fields for the compounds in the chosen coordinate system of the phase diagram components: CsHSO₄, Cs₄(HSO₄)₃(H₂PO₄), Cs₆(SO₄)₃(H₃PO₄)₄, CsH₂PO₄, and CsH₅(PO₄)₂. These regions of crystallization are delimited by a set of lines of monovariant equilibria (co-crystallizations). The main elements of this diagram are described in Table 2.

Thus, in the chosen concentration coordinates, during isothermal evaporation, the Cs₆(SO₄)₃(H₃PO₄)₄ compound is able to co-crystallize with the Cs₄(HSO₄)₃(H₂PO₄) compound, provided that the solution is lacking in CsH₂PO₄ and H₃PO₄ (line E₂-3). If CsH₂PO₄ is in excess, the Cs₆(SO₄)₃(H₃PO₄)₄ compound is expected to co-crystallize with CsH₂PO₄ (line E₃-E₅) until the composition of the solution reaches the E₅ point of nonvariant equilibrium. At this point, the co-crystallization of three compounds, Cs₆(SO₄)₃(H₃PO₄)₄, CsH₂PO₄, and CsH₅(PO₄)₂, will occur at once until water evaporates completely. If an excess of CsH₅(PO₄)₂ is created in the solution composition (which is equivalent to an excess of H₃PO₄), the E₅ point can be bypassed, and then co-crystallization will occur between the Cs₆(SO₄)₃(H₃PO₄)₄ and CsH₅(PO₄)₂ compounds (line E₅-4). All excesses in this case refer to the stoichiometric ratio of components relative to the Cs₆(SO₄)₃(H₃PO₄)₄ compound.

It should be mentioned that line 1-2-3-4-5 shown in Figure 3 and Table 2 is relative and was not determined experimentally. This is due to the complexity of conducting such an experiment (it is required to dissolve weighed portions of substances in a 100% H₃PO₄ melt in a dried atmosphere). At the same time, the results of such an experiment will not fundamentally affect the growth conditions of the Cs₆(SO₄)₃(H₃PO₄)₄ crystal.

A more complete description of the crystallization surface of the Cs₆(SO₄)₃(H₃PO₄)₄ compound (for instance, in the Cs₅H₃(SO₄)₄-CsH₂PO₄-H₃PO₄-H₂O or Cs₂SO₄-CsH₂PO₄-H₃PO₄-H₂O coordinates) will require the determination of the concentration coordinates of a far higher number of nonvariant points. For example, near the line of Cs₅H₃(SO₄)₄-CsH₂PO₄ compositions, there may be points of co-crystallization of the Cs₅H₃(SO₄)₄, Cs₄(HSO₄)₃(H₂PO₄) and Cs₂SO₄ phases, and only at 50 °C. Such a study is certainly beyond the scope of this work.

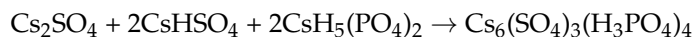
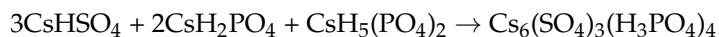
3.2. Growing a $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ Crystal from Water Solutions

The $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ compound crystallizes in a fairly wide phase area in the $\text{CsOH-H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ system. In addition, this compound has a congruent solubility pattern. These properties make the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal suitable for obtaining by lowering the temperature of a saturated solution. The disadvantage of the method of temperature lowering is, albeit positive, a rather weak temperature dependence of solubility. In particular, a decrease in the temperature of the solution in the range of 75–25 °C leads to a decrease in solubility by only ~4.5% mass. This solubility difference is equivalent to ~12 g of crystal in a 100 mL volume of solution. At the same time, at least 200 g of initial reagents will be required to prepare such a solution. That is, the efficiency of crystallization in relation to the used salt mass is no more than 10–15%.

It is also noteworthy that the resulting solutions have a very high density, so high that it is necessary to use a metal washer sealed in plexiglass as a platform for placing the seed crystal, because the fluoroplastic platform floats in this solution. Nevertheless, the $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal itself does not float in this solution. Given that the density of the fluoroplastic is ~2.2 g/cm³, and the X-ray density of the crystal according to [15] is 3.191 g/cm³, the density of the solution lies in the range of values 2.2–3.191 g/cm³.

A significant difficulty may be the need for a strict observance of the stoichiometric ratio of components in a rather complex solution. A saturated solution must contain a strict ratio of cesium cations to sulfate and phosphate anions, and all this at a fairly high level of acidity. If the stoichiometry is not observed, the composition of the solution during crystal growth (especially by the method of isothermal evaporation) will shift toward the co-crystallization lines mentioned in the previous section.

This difficulty can be overcome by using reliable weight forms of the initial reagents when preparing a saturated solution. These requirements are met by two formal synthesis reactions:



The result of growth from the solution prepared in this way is in the form of crystals, an example of which is shown in Figure 4.

The sample in Figure 4a in particular was obtained as a result of growth on a stationary platform with reverse stirring, from a saturated solution with a volume of ~200 mL in the temperature range of 45–40 °C. As a seed crystal, we used a small crystal obtained by spontaneous crystallization upon the evaporation of a solution at room temperature (an example is shown in Figure 4b). The resulting sample was characterized by a maximum size of ~20 mm and a weight of 3 g.

The single crystal obtained in this way is characterized by the X-ray diffractogram shown in Figure 5.

The $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$ crystal belongs to the cubic system, with the space group $\bar{1}43d$, which determines the equilibrium faceting of the crystal in the form of a trigonitetrahedron formed by the {hhl} family of faces. Noteworthy is the dependence of the ratio of the face areas within this simple form on the rate of obtaining a crystal. When obtaining a sample by methods of a temperature decrease in a saturated solution, i.e., in relatively short periods of time, the edges of the tetrahedron are clearly formed. In the case of crystal growth at a constant temperature, by a slow evaporation of the solvent over several months, the shape of the crystal approaches a spheroid (Figure 4b).

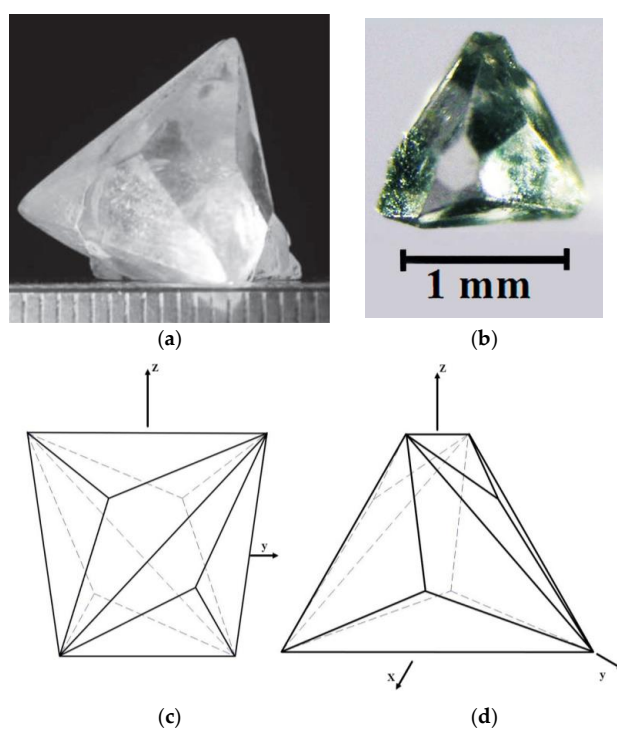


Figure 4. The grown crystals (a,b) and their corresponding faceting (c,d).

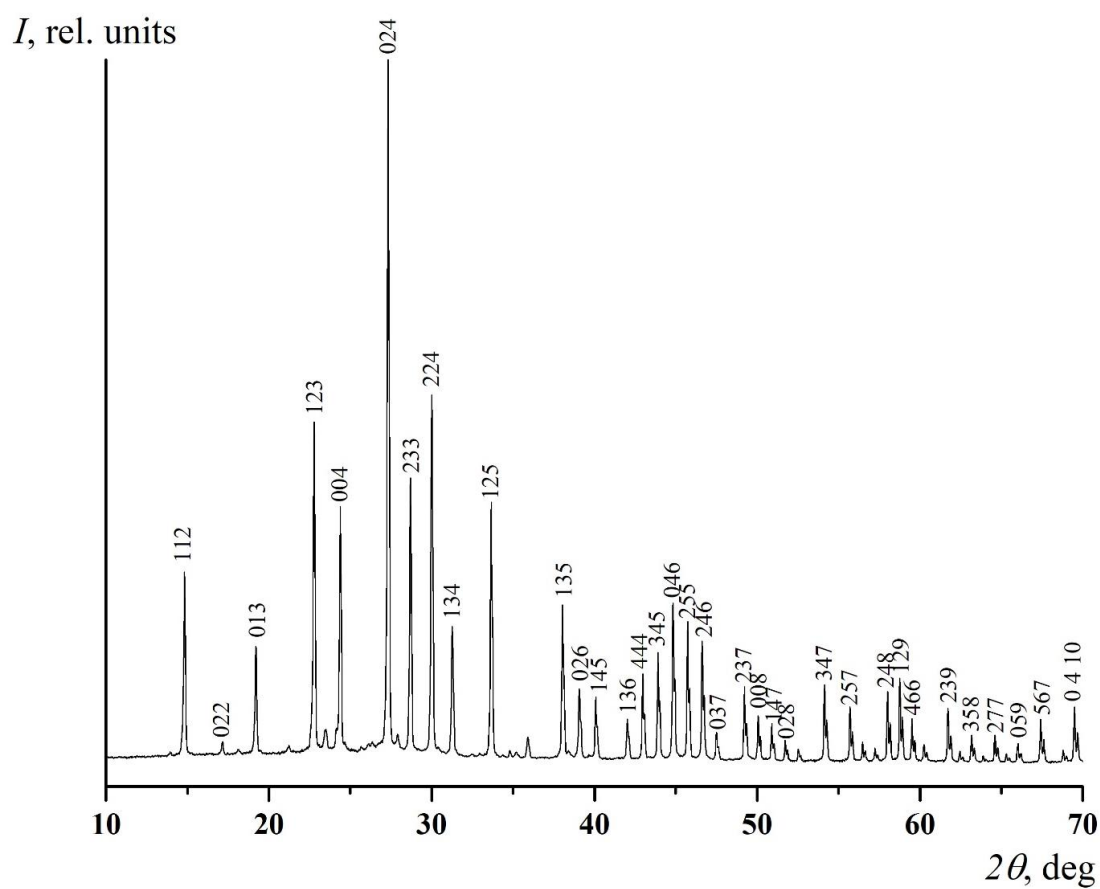


Figure 5. The obtained powder X-ray diffraction pattern of the grown crystal $\text{Cs}_6(\text{SO}_4)_3(\text{H}_3\text{PO}_4)_4$. The indexing was carried out in accordance with the data [15].

4. Conclusions

By summarizing the above results, we can conclude the following.

It is rather challenging to observe the overall concept of phase formation in the CsOH–H₂SO₄–H₃PO₄–H₂O system. It is much easier to study the crystallization range of a particular compound of interest using simplifying sections. The CsOH–H₂SO₄–H₃PO₄–H₂O system itself contains many different complex phosphate–sulfate, and no solid solutions were found in it.

It has been shown that Cs₆(SO₄)₃(H₃PO₄)₄ compound can be obtained in single-crystal form from water solutions. The methods of isothermal evaporation and lowering the temperature of the saturated solution have their advantages and disadvantages.

In the case of the isothermal evaporation method, the advantage is the ease of implementation and the completeness of the use of the initial reagents. The disadvantage, however, is the high sensitivity of the composition of the solution to deviation from stoichiometry and the likelihood of co-crystallization with other compounds.

The method of lowering the temperature of the saturated solution is attractive by maintaining the equilibrium composition of the mother solution throughout the entire growth process. Moreover, this method allows controlling the growth rate of the crystal and, accordingly, its quality and cut more accurately. The disadvantage of the method is the low efficiency of the use of initial reagents. Indeed, to obtain crystals weighing several tens (or hundreds) of grams, it is necessary to use hundreds (or thousands) of grams of initial reagents.

It is worth mentioning that there is a method of aqueous crystal growth that combines some of the advantages of both methods discussed above. This is a method of isothermal evaporation with feeding mother solution. It is also possible to obtain large crystals of good quality by this method while using the initial reagents more efficiently. This method alone is much more complex in instrumentation and is still sensitive to deviations from stoichiometry.

In general, the choice of the method for growing Cs₆(SO₄)₃(H₃PO₄)₄ crystals primarily depends on the purpose of their use. Small crystals of high diffraction quality for X-ray and synchrotron radiation experiments can be obtained by simple evaporation. For neutron diffraction or the study of physical properties, where larger crystals are needed, single crystal samples can be grown by lowering the temperature of a saturated solution.

Author Contributions: Methodology, V.A.K.; Investigation, V.A.K., I.P.M. and I.S.T.; Writing—original draft, V.A.K.; Writing—review & editing, I.P.M., I.S.T. and V.V.G.; Visualization, V.A.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: This work was performed within the State Assignment of FSRC “Crystallography and Photonics” RAS.

Conflicts of Interest: The authors declare no conflict of interest.

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