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# Study of the Phase Composition and Electrotransport Properties of the Systems Based on Mono- and Disubstituted Phosphates of Cesium and Rubidium

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## Abstract

A detailed study of the phase composition, transport and thermodynamic characteristics of the systems based on mono- and disubstituted phosphates of cesium and rubidium  $(1 - x)\text{MH}_2\text{PO}_4 / x\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Rb}, \text{Cs}$ ) within a wide range of compositions ( $0 \leq x \leq 1$ ) was performed. For these systems, new phases were identified, and their transport and thermal characteristics were determined. For cesium compounds, the new  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  salt was found at  $x = 0.5$ .  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  single crystals were synthesised and their crystal structure was determined for the first time, as well as thermodynamic characteristics and proton conductivity. It was shown that the compound does not have a superionic phase transition. In the rubidium system, a monophasic region at  $x = 0.25$  was found, corresponding to  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  compound. Its electrotransport and thermodynamic properties were investigated. It was shown that  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  has a phase transition at 252 °C to the high-temperature phase, which is characterised by high proton conductivity. For other mole fraction  $x$  values for  $(1 - x)\text{MH}_2\text{PO}_4 / x\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Rb}, \text{Cs}$ ), binary phase regions are realized; these two phases include the initial component, which dominates within this composition range, and the newly formed compound, which significantly affects the physicochemical properties of the system.

**Keywords:** mono- and disubstituted phosphates of cesium and rubidium,  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$ ,  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ , proton conductivity, solid electrolytes

## INTRODUCTION

The majority of acid salts like  $\text{M}_x\text{H}_y(\text{AO}_4)_z$ , where  $\text{M} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}, \text{Li}, \text{NH}_4$ ;  $\text{A} = \text{S}, \text{Se}, \text{As}, \text{P}$ , are characterized by the presence of phases with structural disordering of the network of hydrogen bonds, increased proton mobility, and high proton conductivity  $\sigma$  up to  $\sim 10^{-3} - 10^{-2}$  S/cm at 100–250 °C, which is comparable with the conductivity of melts [1, 2], so-called superionic phases. The compound with the highest conductivity,  $\text{CsH}_2\text{PO}_4$ , is promising for use as proton membranes in medium-temperature fuel cells

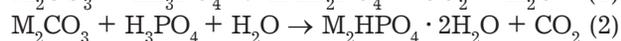
and other electrochemical devices [3]. As far as related salts based on disubstituted phosphates of cesium and rubidium are concerned, until recently the data on the composition of their crystal hydrates have been not quite correct, the characterization of their physicochemical properties has been incomplete, and their crystal structures have been established only recently [4–6]. At the same time, investigation of mixed systems  $(1 - x)\text{MH}_2\text{PO}_4 / x\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Rb}, \text{Cs}$ ) is of the fundamental scientific interest for the establishment of a connection between the structural features of the lattice and the parameters of proton

transfer, which may serve as the basis for understanding the mechanism of proton transport in acid salts, targeted regulation of the functional properties of compounds, and search for new highly conducting phases.

The goal of the present work was to analyse the data on the phase composition in the system of mono- and disubstituted phosphates of cesium and rubidium  $(1 - x)\text{MH}_2\text{PO}_4 / x\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Rb}, \text{Cs}$ ), comparison of electrotransport and thermodynamic properties of phases, revelation and characterization of new compounds. The paper is a generalization of a number of works carried out by the authors on this subject.

## EXPERIMENTAL

Compounds  $\text{MH}_2\text{PO}_4$  и  $\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Cs}, \text{Rb}$ ) were obtained by slow isothermal evaporation from the aqueous solution of  $\text{M}_2\text{CO}_3$  (Pure (Ch.) reagent grade) and  $\text{H}_3\text{PO}_4$  (chemically pure, Kh. Ch. reagent grade) at room temperature according to reactions



Synthesized mono- and disubstituted phosphates  $(1 - x)\text{MH}_2\text{PO}_4 / x\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  with different molar ratios of the components ( $0 \leq x \leq 1$ ) were thoroughly pestles in an agate mortar, pressed and heated for ~4 h at 55–60 °C. The heating temperature was chosen according to the thermal properties of initial salts and the temperature of the loss of crystal hydrate water in  $\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ . The experiment was carried out using the methods of X-ray phase analysis with a D8 Advance instrument (Bruker, Germany), differential thermal analysis with a STA 449 F/1/1 JUPITER thermoanalyzer (Netzsch, Germany), infrared spectroscopy with an Excalibur 3100 instrument (DigiLab, USA) and impedance spectroscopy with an IPU-1 instrument (Russia, the working frequency range 1 mHz – 3.3 MHz). The elemental composition was determined by means of energy-dispersive X-ray spectroscopy with the help of a Hitachi TM-1000 microscope (Japan), equipped with an INCA Energy XMax spectrometer. To measure conductivity, samples in the form of tablets (7 mm diameter, 2–3 mm thickness, relative density 96–98 %) were made from a mixture with a definite components ratio by pressing at 300 MPa and depositing silver electrodes. To suppress dehydration, measurements of the conductivity of rubidium samples were carried out at

high temperature in humidified argon flow, which was passed through a bubbler ( $T = 70\text{--}80$  °C), which corresponded to the partial pressure of water vapour  $P_{\text{H}_2\text{O}} \approx 0.3\text{--}0.56$  atm. The flow rate was measured with the gas mixture regulator UFPGS (Modern laboratory equipment, Russia). The rate of heating and cooling was 1 °C/min.

## RESULTS AND DISCUSSION

For  $\text{CsH}_2\text{PO}_4$  and  $\text{RbH}_2\text{PO}_4$  salts, the transitions into so-called superionic phase states were discovered at 230 and 276 °C, respectively (Fig. 1–3), while for potassium and sodium salts the transitions of that kind were not detected [7, 8]. The phase transition in  $\text{CsH}_2\text{PO}_4$  from the monoclinic ( $P2_1/m$ ) phase into superionic cubic phase ( $Pm\text{-}3m$ ) at 230 °C leads to the structural disordering of protons, an increase in mobility and an increase in productivity to  $6 \cdot 10^{-2}$  S/cm due to the participation of protons in the transfer process. The superionic phase  $\text{CsH}_2\text{PO}_4$  has a rather narrow temperature range of stability due to the dehydration process, which hinders its practical application.

Similar phase rearrangements but at higher temperatures proceed in  $\text{RbH}_2\text{PO}_4$ . The superionic phase of this compound exists within a narrower temperature range because of differences in the sizes of cations ( $R_{\text{Cs}^+} = 1.74$  Å and  $R_{\text{Rb}^+} = 1.61$  Å) [9]. Acid salts are characterized by the presence of a system of hydrogen bonds, which are rather strong for the systems under investigation, with a length of 2.4–2.6 Å. Accordingly, rather high activation energies (~0.9–1.1 eV) and low proton conductivity (less than  $10^{-6}$  S/cm) are observed in the low-temperature range. At room temperature  $\text{RbH}_2\text{PO}_4$  exists in the form of the tetragonal phase  $I\text{-}42d$ , which is transformed into the monoclinic phase  $P2_1/a$  within 90–130 °C; the transition temperature depends on the thermodynamic conditions of the experiment. The  $P2_1/a$  phase is stable up to 250 °C under normal conditions, then up to 320 °C slow dehydration takes place, with the formation of  $\text{Rb}_2\text{H}_2\text{P}_2\text{O}_7$  [10], which hinders the studies of salt characteristics in the superionic state. According to the phase diagram, to broaden the temperature range, the studies of the superionic phase are carried out under external pressure or increased humidity, in particular at the partial pressure of water vapour ~0.56 atm. It was established by means of powder diffraction and impedance measurement at increased

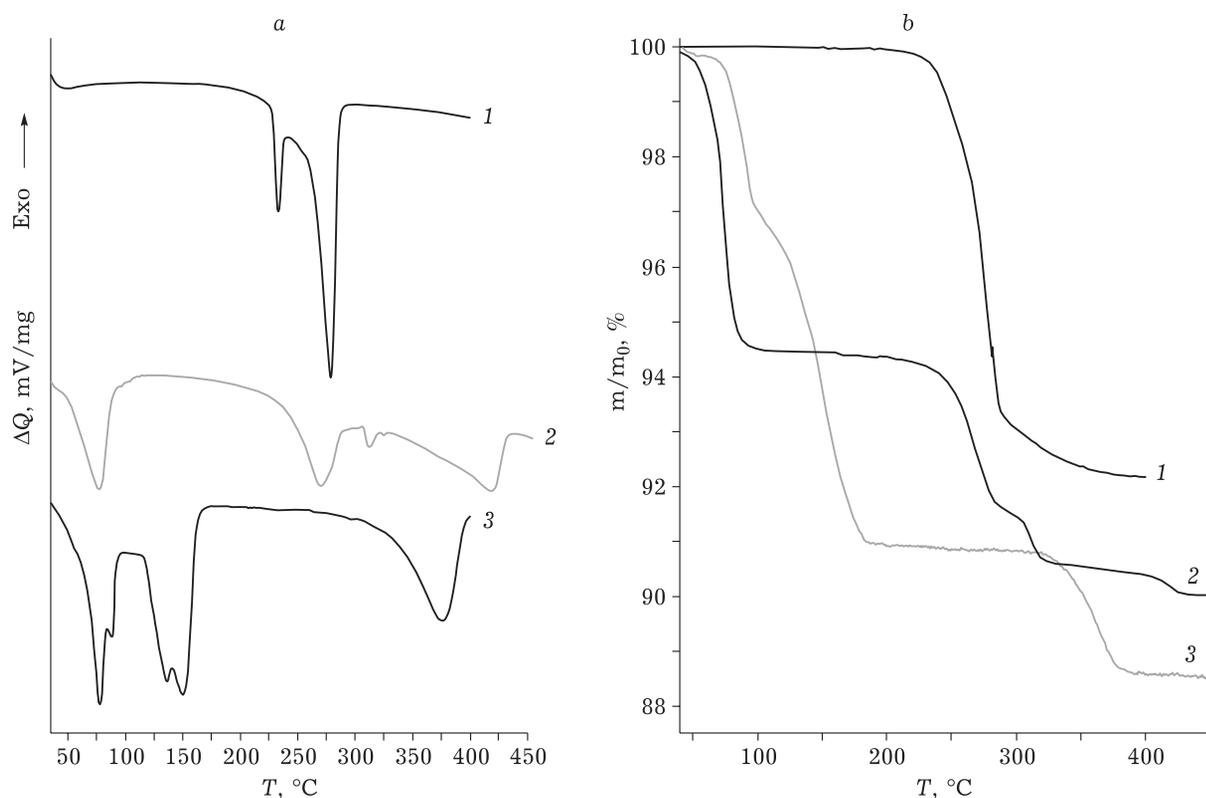


Fig. 1. Data of differential scanning calorimetry (a) and thermogravimetry (b) for the salts with the composition  $(1-x)\text{CsH}_2\text{PO}_4 / x\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , where the mole fraction  $x = 0$  (1), 0.5 (2), 1 (3).

pressure  $\sim 1$  GPa that the high-temperature phase of  $\text{RbH}_2\text{PO}_4$  belong also to the cubic system  $Pm\bar{3}m$  [11, 12].

It was established that, unlike for dihydrophosphates, disubstituted phosphates of cesium and rubidium do not have superionic phase transitions (see Fig. 1–3) [13]. It was demonstrated that they are crystallized from aqueous solutions in the form of dihydrates having the monoclinic crystal system  $P2_1/c$ . Thus, it was determined that the unit cell parameters for  $\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  are:  $a = 7.4764 \text{ \AA}$ ,  $b = 14.1898 \text{ \AA}$ ,  $c = 7.9535 \text{ \AA}$ ,  $\beta = 116.880 \text{ \AA}$ ,  $Z = 4$  [4]. It was dem-

onstrated that  $\text{Rb}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  is isostructural with  $\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ . Its structural characteristics, as well as the data for other salts, are presented in Table 1.

In spite of the isostructural appearance of  $\text{Rb}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , their thermal properties (see Fig. 1, 2) and electric transport characteristics (see Fig. 3) differ. Dehydration of  $\text{Rb}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , unlike for  $\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , starts at  $55 \text{ }^\circ\text{C}$  and is characterized by two stages, close in the rates to each other. After the loss of crystal water, further heating of  $\text{M}_2\text{HPO}_4$  salts ( $\text{M} = \text{Cs}, \text{Rb}$ ) results in the formation of pyro-

TABLE 1

Structural data for mono- and disubstituted cesium and rubidium phosphates,  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  and  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$

	ИГК	$a, \text{ \AA}$	$b, \text{ \AA}$	$c, \text{ \AA}$	$\beta, ^\circ$	$Z$	Reference
$\text{CsH}_2\text{PO}_4$	$P2_1/m$	4.8725	6.3689	7.9007	107.742	2	[14]
$\text{RbH}_2\text{PO}_4$	$I\bar{4}2d$	7.607	7.607	7.299	–	4	[15]
$\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	$P2_1/c$	7.4764	14.1898	7.9535	116.880	4	[4, 5]
$\text{Rb}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	$P2_1/c$	7.3640	13.6496	7.7341	118.176	4	[4]
$\text{Rb}_5\text{H}_7(\text{PO}_4)_4$	$Pnam$	28.570	10.277	6.090	–	4	[16]
$\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$	$Pbca$	7.4721	11.4369	14.8509	–	4	[17]

Note. Dash means that no data are known.

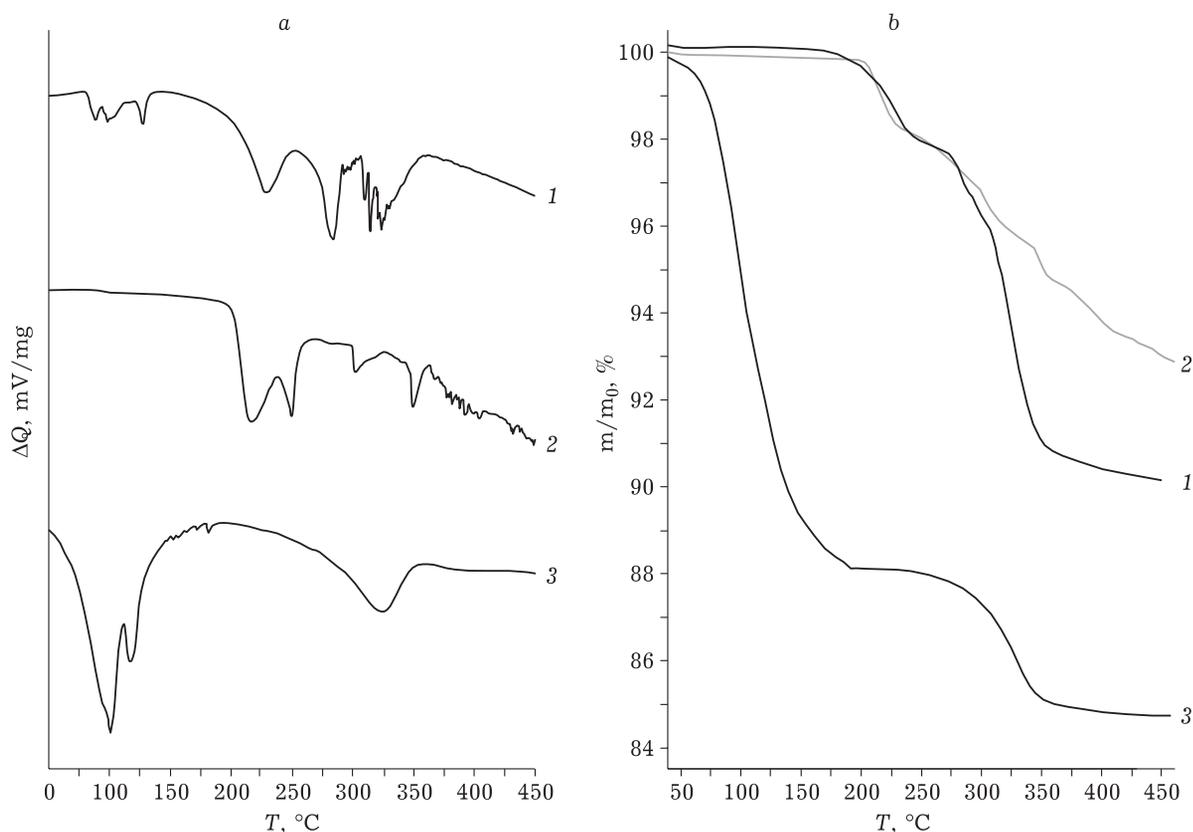


Fig. 2. Data of differential scanning calorimetry (a) and thermogravimetry (b) for salts having the composition  $(1-x)\text{RbH}_2\text{PO}_4 / x\text{Rb}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , where the mole fraction  $x = 0$  (1), 0.25 (2), 1 (3).

phosphate  $\text{M}_4\text{P}_2\text{O}_7$ . Mass loss due to the release of water molecules during heating fully corresponds to the theoretical values of dehydration stages

(Fig. 1, b, 2, b). The stability range of the formed salt  $\text{Rb}_2\text{HPO}_4$  is smaller by 70 °C than that for  $\text{Cs}_2\text{HPO}_4$ ; the latter salt is stable up to 320 °C. The

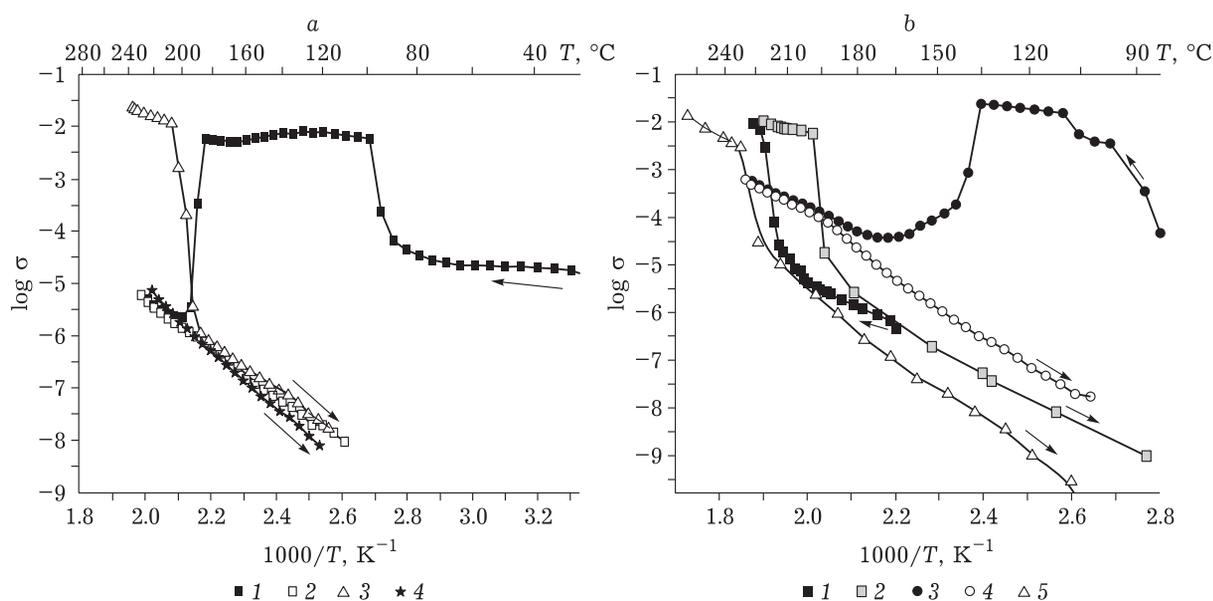


Fig. 3. Temperature dependences of proton conductivity  $\sigma$  (S/cm) at humidity 0.56 atm for salts of Cs (a):  $\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  - heating (1) and cooling (2);  $\text{CsH}_2\text{PO}_4$  - heating (3),  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  - cooling (4); and salts of Rb (b):  $\text{Rb}_3\text{H}_7(\text{PO}_4)_4$  - heating (1) and cooling (2),  $\text{Rb}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  - heating (3) and cooling (4),  $\text{RbH}_2\text{PO}_4$  - cooling (5).

difference in the thermal stability of salts is connected with the differences in ionic radii of rubidium and cesium, which causes changes in the length and strength of bonds.

The values of proton conductivity of dehydrated samples  $M_2HPO_4$  ( $M = Cs, Rb$ ) within temperature range 100–250 °C are close to each other and are  $10^{-8}$ – $10^{-4}$  S/cm with high activation energy  $\sim 1.2$  eV (see Fig. 3), which is connected with the presence of strong hydrogen bonds in the compounds [5]. In the investigation of the systems  $(1-x)MH_2PO_4 / xM_2HPO_4 \cdot 2H_2O$  ( $M = Rb, Cs$ ) within a broad range of compositions, a monophasic and diphasic regions were distinguished. The new formed phases were identified, their electrotransport and thermal characteristics were determined. For instance, in the cesium system, a monophasic region was revealed at  $x = 0.5$ , corresponding to the existence of a new, previously unknown compound having the composition  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$  (Fig. 4, a). The conditions for the growth of single crystals were determined, the elemental composition and content of crystal hydrate water in  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$  were studied; the crystal structure was established for the first time (Fig. 5). It was demonstrated that the compound crystallizes in the space group  $Pbca$  and is characterized by the three-dimensional network of hydrogen bonds; in addition to phosphate tetrahedrons, its formation involves two crystallographically identical water molecules. The equivalence of  $PO_4$ -tetrahedrons is characteristic of  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$ . This compound, similarly to  $Cs_2HPO_4 \cdot 2H_2O$ , does not have superionic phases, and the dependence of proton conductivity, its value and activation energy in the heating – cooling cycles are close for two salts (see Fig. 3, a). Dehydration of the compound with the loss of two water molecules occurs within 75–160 °C with the formation of  $Cs_3(H_2PO_4)(HPO_4)$ , which is stable up to 275 °C (see Fig. 1), and then is transformed completely into cesium pyrophosphate and metaphosphate,  $Cs_4P_2O_7$  and  $CsPO_3$ . The unit cell parameters of the formed anhydrous phase  $Cs_3(H_2PO_4)(HPO_4)$  were determined. It was demonstrated that it belongs to the monoclinic space group  $C2$  with unit cell parameters  $a = 11.1693$  Å,  $b = 6.4682$  Å,  $c = 7.7442$  Å and  $\beta = 71.822$  [17]. Unlike for crystal hydrate  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$ , the dehydrated form is characterized by low electroconductivity:  $(6 \cdot 10^{-6}) - 10^{-8}$  S/cm at 100–220 °C, with the activation energy of 0.91 eV, which is in agreement with the existence of strong hydrogen

bonds according to the data of IR spectroscopy (Fig. 6). Thus, for acid phosphates in the region of stretching and bending vibrations of OH groups involved in hydrogen bonds, three broad absorption bands are observed; as a rule, they correspond to O...O bond 2.4–2.6 Å long. For  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$ , the positions of the maxima correspond to 2790, 2350 and 1745  $cm^{-1}$  (see Fig. 6). The IR spectra of the crystal hydrates of these salts usually also contain a broad absorption band at  $\sim 3000$   $cm^{-1}$ , connected with the stretching vibrations of the molecules of structural water participating in the formation of the network of hydrogen bonds (see Fig. 6) [18, 19].

Investigation of the system within a broad composition range showed that, in addition to the monophasic region at  $x = 0.5$  there are two-phase regions at  $x \neq 0.5$ , corresponding at  $x < 0.5$  to the salts  $CsH_2PO_4$  and  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$  with different components ratios, while for  $x > 0.5$  –  $Cs_2HPO_4 \cdot 2H_2O$  and  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$ . In essence, these composition ranges may be considered as composition systems with thermal and electrotransport properties strongly affected by the formed new phase  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$ . It was demonstrated that the high proton conductivity with the superionic phase transition is characteristic of the composite systems at  $x < 0.5$  in the region of the existence of  $CsH_2PO_4$  and  $Cs_3(H_2PO_4)(HPO_4) \cdot 2H_2O$ . It was established by means of impedance spectroscopy that the low-temperature conductivity of the cesium system at  $x \leq 0.1$  increases by 3–5 orders of magnitude. At a temperature within the range 60–220 °C it reaches  $10^{-2}$ – $10^{-4}$  S/cm, which is connected with the composite effect on the basis of two related salts, structural disordering at the interface with the high proton mobility [20]. In addition, the protons of crystal hydrate water or adsorbed water also may take part in the transfer process thus making their contribution into an increase in the conductivity of the system.

In the course of investigation of the rubidium system within a broad composition range ( $0 \leq x \leq 1$ ), a monophasic region was discovered at  $x = 0.25$ , corresponding to the compound  $Rb_5H_7(PO_4)_4$  (see Fig. 4, b) [21] – the only known representative of the family of acid salts with the stoichiometry  $M_5H_7(AO_4)_4$ . Until recently, only the structural characteristics of this salt have been known, while the information on its thermodynamic properties and conductivity was absent. Known double phosphates  $Ca_2KH_7(PO_4)_4 \cdot 2H_2O$  [22] and  $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$  [23] can be related to the same

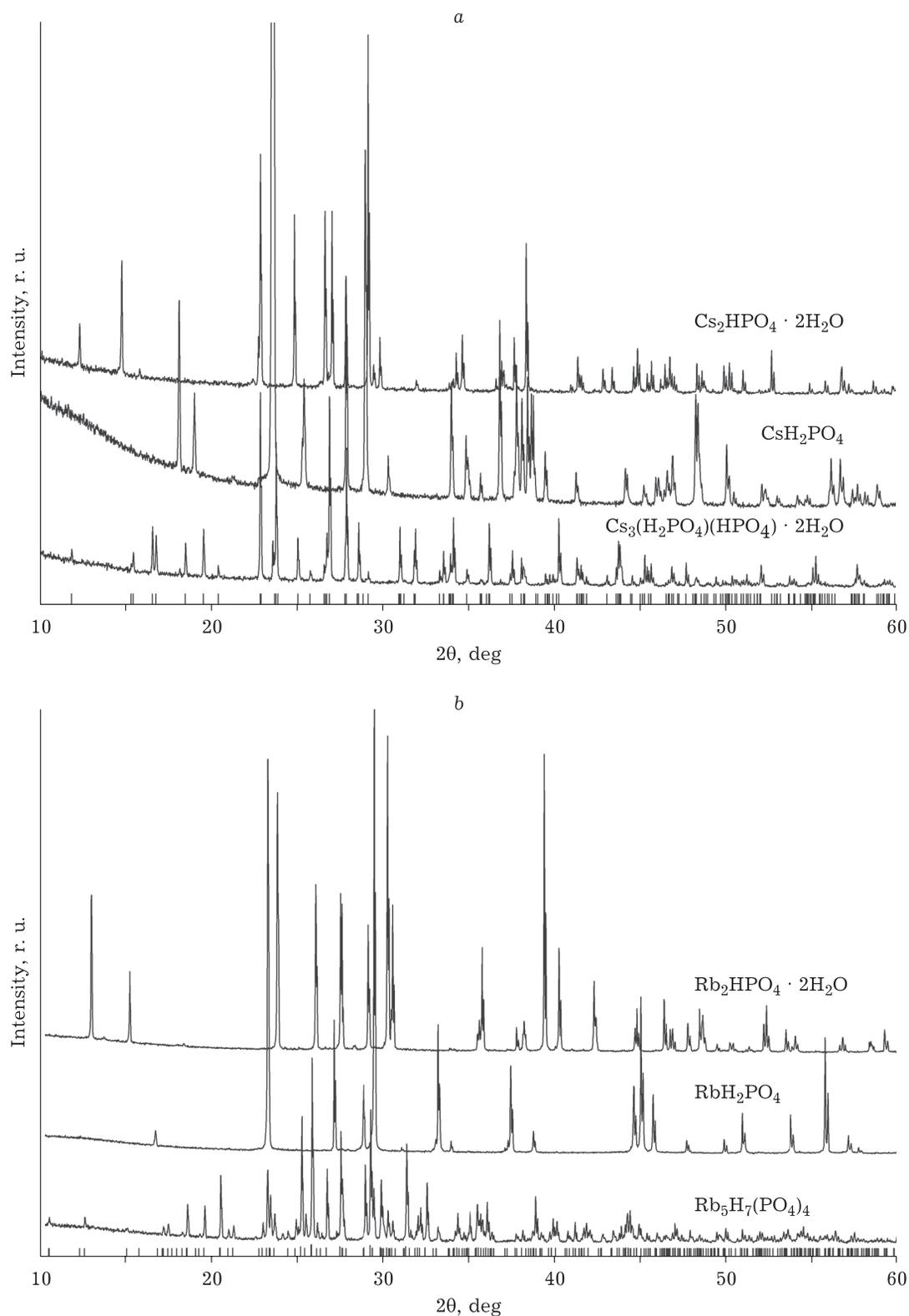


Fig. 4. X-ray diffraction patterns of the salts of Cs (a) and Rb (b). For comparison, theoretical dashed patterns of  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  (a) and  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  (b) are shown.

group, but these compounds are strongly different in their structure from  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$ : both Ca-containing salts are crystal hydrates and crystal-

lize in the triclinic system, while  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  relates to the orthorhombic system. Other compositions of the studied system correspond to the two-phase

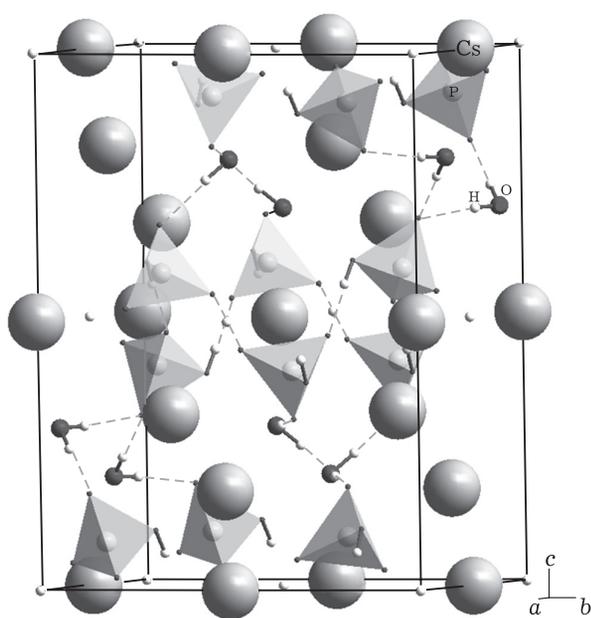


Fig. 5. Schematic image of the crystal structure of  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ .

region and to the existence of the salts of initial composition along with  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  in different ratios:  $\text{RbH}_2\text{PO}_4$  and  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  ( $x < 0.25$ ) or  $\text{Rb}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  ( $x > 0.25$ ) [21]. It should be noted that the proton conductivity of rubidium salts with different compositions is lower than that of the similar compounds in the cesium system. It is demonstrated for the first time that  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  undergoes a reversible phase transition at  $T_{\text{pt}} \sim 237^\circ\text{C}$  [24]. The range of stability of the high-temperature phase is about  $15^\circ\text{C}$ . According to the data of thermal analysis, slow decomposition of the salt occurs at usual humidity, which is connected with dehydration starting at  $200^\circ\text{C}$ . Under the conditions of high relative humidity ( $P_{\text{H}_2\text{O}} \approx 0.56$  atm), partial dehydration may be suppressed, and the phase transition may be observed. At a temperature of  $240^\circ\text{C}$ , it is accompanied by a sharp increase in conductivity up to  $10^{-2}$  S/cm – so-called superionic phase transition (see Fig. 2, 3, b). It is demonstrated that

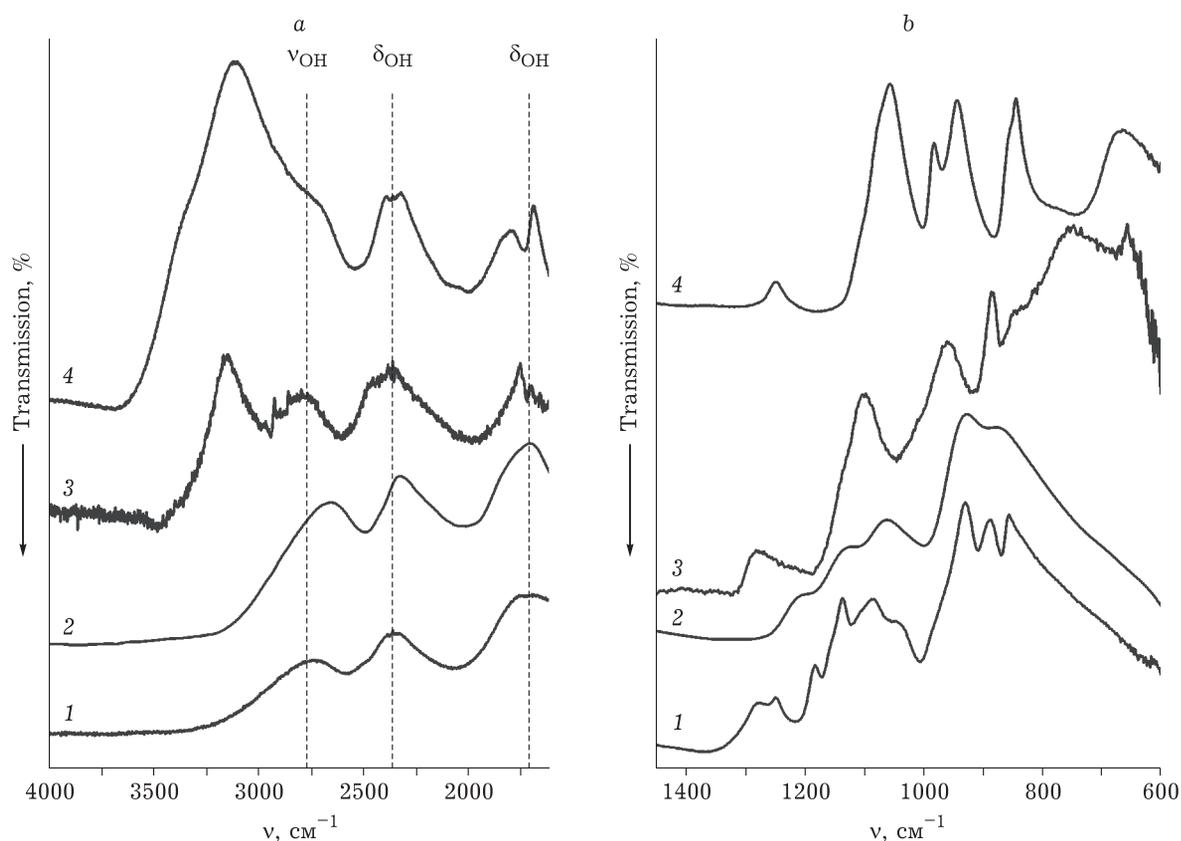


Fig. 6. Data of IR spectroscopy for the regions of hydrogen bonds (a) and phosphate tetrahedrons (b): 1 –  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$ , 2 –  $\text{CsH}_2\text{PO}_4$ , 3 –  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ , 4 –  $\text{Cs}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ .

the reverse transition of  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$  is slow, which may be connected with the structural rearrangement. A substantial hysteresis is pronounced for  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$ , which is typical for acid salts. The conductivity in the low-temperature phase does not exceed  $10^{-5}$  S/cm at  $T < 237$  °C, which is in agreement with the data of IR spectroscopy providing evidence of the presence of a network of strong hydrogen bonds in the structure. In addition, in the IR region corresponding to the vibrations of phosphate tetrahedrons in  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$ , unlike for other rubidium and cesium salts, we observe splitting of three intense bands:  $\nu_{\text{PO}} \sim 850, 1090 \text{ cm}^{-1}$  and  $\delta_{\text{OH}} \sim 1260 \text{ cm}^{-1}$  (see Fig. 6), which is the evidence of the deviation of tetrahedrons from the ideal shape and non-equivalence of phosphate tetrahedrons in the crystal structure of the compound [25].

## CONCLUSION

Thus, the phase composition, transport and thermodynamic characteristics of the systems based on mono- and disubstituted cesium and rubidium phosphates  $(1 - x) \text{MH}_2\text{PO}_4 / x\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Rb}, \text{Cs}$ ) were analyzed within a broad composition range ( $0 \leq x \leq 1$ ). New phases, previously unknown, were discovered in the studied systems; the proton conductivity and thermal characteristics of these phases were determined. In the cesium system, a new compound was discovered:  $\text{Cs}_3(\text{H}_2\text{PO}_4)(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  with  $x = 0.5$ ; its crystal structure, thermodynamic characteristics and proton conductivity were determined. In the rubidium system with  $x = 0.25$ , compound  $\text{Rb}_5\text{H}_7(\text{PO}_4)_4$ , was discovered. Analysis of the thermodynamic and electrotransport properties of this compound at increased humidity revealed the occurrence of a reversible superionic phase transition at 252 °C. For other  $x$  values, the phase composition  $(1 - x)\text{MH}_2\text{PO}_4 / x\text{M}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Rb}, \text{Cs}$ ) corresponds to the formation of composites based on two salts of the initial components, prevailing in the given composition range, and a new compound determining the physico-chemical properties of the system.

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