

PROTON CONDUCTIVITY AND STRUCTURAL PROPERTIES OF $\text{CsH}_2\text{PO}_4 - \text{Ba}(\text{H}_2\text{PO}_4)_2$

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CsH_2PO_4 is one of the high conductive compounds in the family of solid acids of alkali metals $\text{M}_n\text{H}_m(\text{AO}_4)_p$, where $\text{M} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}, \text{Li}, \text{NH}_4$; $\text{A} = \text{S}, \text{Se}, \text{As}, \text{P}$ to be used as a proton membrane in intermediate temperature fuel cells. Its proton conductivity is $6 \cdot 10^{-2} \text{ Scm}^{-1}$ in superionic phase. The conductivity of CsH_2PO_4 in the low temperature phase (LT) ($\text{P2}_1/\text{m}$) is less than $10^{-6} \text{ S} \cdot \text{cm}^{-1}$ [1]. Homogeneous doping of CsH_2PO_4 by anions and cations improves usually electro transport properties of LT phase due to a formation of disordered solid solutions or stabilization of superionic phase at the lower temperatures [2,3]. The structural properties and proton conductivity of $\text{Cs}_{1-x}\text{M}_x\text{H}_2\text{PO}_4$ where $\text{M} = \text{Rb}, \text{K}, \text{Na}$, were investigated in details. The solid solutions isostructural to CsH_2PO_4 were formed with decreasing unit cell parameters [3,4]. The region of existence of $\text{Cs}_{1-x}\text{M}_x\text{H}_2\text{PO}_4$ solid solutions depends markedly on the size of substituting cation. A wide range of $\text{Cs}_{1-x}\text{Rb}_x\text{H}_2\text{PO}_4$ solid solutions up to $x=0-0.9$ was shown to exist; $\text{Cs}_{1-x}\text{K}_x\text{H}_2\text{PO}_4$ solid solutions were found at $x=0-0.3$ and at $x=0-0.2$ for Na^+ substituting cations. The isovalent substitution in CsH_2PO_4 was not investigated earlier and is of scientific interest as the disordered systems. Besides the proton conductivity of initial component $\text{Ba}(\text{H}_2\text{PO}_4)_2$ wasn't studied also.

The work was directed to the investigation of electrotransport, structural, thermodynamic properties of $(1-x)\text{CsH}_2\text{PO}_4 - x\text{Ba}(\text{H}_2\text{PO}_4)_2$ system in wide range of compositions, $x=0-0.4$, and to the study of proton conductivity of $\text{Ba}(\text{H}_2\text{PO}_4)_2$.

$\text{Cs}_{1-2x}\text{Ba}_x\text{H}_2\text{PO}_4$ were synthesized by prolong mechanical mixing of the stoichiometric quantities of CsH_2PO_4 and $\text{Ba}(\text{H}_2\text{PO}_4)_2$ and following heating $\text{Ba}(\text{H}_2\text{PO}_4)_2$ single crystals were synthesized from aqueous solutions. The investigation was carried out using IR and impedance spectroscopies and XRD, DSC, TGA analysis.

$\text{Ba}(\text{H}_2\text{PO}_4)_2$ single crystals were analyzed in detail by impedance spectroscopy. The measurements of the proton conductivity have been realized in different atmospheres (nitrogen, argon, air $\text{RH}=10\%$) and showed the significant effect of adsorbed water at $30-160^\circ\text{C}$. The anisotropy of proton conductivity was found in $\text{Ba}(\text{H}_2\text{PO}_4)_2$, which is caused by peculiar structural features of the salt: the presence of corrugated sheets of phosphate tetrahedra lying in the ac plane alternating with Ba^{2+} cations. The higher values of proton conductivity ($4 \cdot 10^{-9} - 1.5 \cdot 10^{-7} \text{ S/cm}$ at $60-160^\circ\text{C}$) were observed along the [100] crystallographic direction in comparison with [010]. The energy of activation of proton conductivity for $\text{Ba}(\text{H}_2\text{PO}_4)_2$ 0.8 eV was determined.

The X-ray diffraction data of $\text{Cs}_{1-2x}\text{Ba}_x\text{H}_2\text{PO}_4$ show the formation of solid solutions isostructural to CsH_2PO_4 ($P2_1/m$) at $x=0.03-0.1$ with small decrease of unit cell parameters. The reflexes of substituted CsH_2PO_4 are broadened and decreased in intensity. The proton conductivity of $\text{Cs}_{1-2x}\text{Ba}_x\text{H}_2\text{PO}_4$ increases more than three orders of magnitude in the low temperature phase and the superionic phase transition practically disappears with x . In contrast to substitution of monovalent cation, heterovalent substitution of CsH_2PO_4 includes the formation of Cs^+ vacancies in CsH_2PO_4 . The conductivity in superionic phase doesn't change up to $x=0.2$. The stability of high conductivity has been verified at high temperatures for the long term storage at the low relative humidity, $\text{RH}=10\%$. A mechanism of conductivity improvement includes the formation of Cs vacancies during heterovalent replacement which lead to phosphate tetrahedra reorientation and structural disordering of the salt up to its amorphization with x increase with weakening of hydrogen bond network. Significant changes of $\text{Cs}_{1-2x}\text{Ba}_x\text{H}_2\text{PO}_4$ thermal properties were revealed, which were in accordance with structural and transport characteristics.

With the growth of Ba^{2+} mole fraction, $x>0.10$ the solid solutions are not observed; the reflexes of $\text{Ba}(\text{H}_2\text{PO}_4)_2$ are appeared and two phases coexist, forming a composite system based on related salts. The heterophase high-conductivity systems was revealed in the range $x = 0.15-0.4$ with the maximum conductivity values at $x=0.1-0.2$. Superionic phase transition disappears with x increase. The further proton conductivity increasing takes place up to $x=0.25$ while the initial salts have the extremely low conductivity values (see figure). The mechanism of proton transport for $(1-x)\text{CsH}_2\text{PO}_4-x\text{Ba}(\text{H}_2\text{PO}_4)_2$ system in wide range of $\text{Ba}(\text{H}_2\text{PO}_4)_2$ is discussed. The high conductivity at $x>0.1$ deals with the formation of composite electrolytes based on related salts where the protons of water molecules adsorbed on the grain boundaries participate in the proton transport.

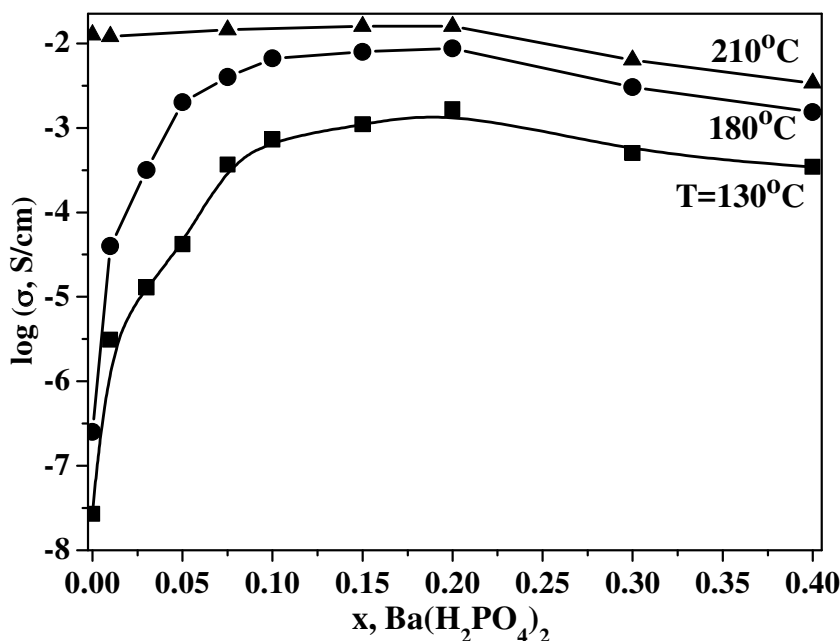


Figure. Isotherm of conductivity of $(1-x)\text{CsH}_2\text{PO}_4 - x\text{Ba}(\text{H}_2\text{PO}_4)_2$ at different x values.

The formation of composite systems with the optimal x values at 0.15-0.2 with the high proton conductivity $\sim 10^{-2}$ S/cm, chemically stable at a temperature of ~ 200 - 210 ° C in an atmosphere with low humidity was determined. It creates perspectives for the development of new functional highly conductive proton membranes for medium-temperature electrochemical devices.

The work was carried out with a partial financial support from the grant of RFBR n 15-08-08961

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