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Vapor pressure and specific electrical conductivity in the solid and molten H_2O - CsH_2PO_4 - CsPO_3 system – A novel electrolyte for water electrolysis at ~ 225 - 400°C

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Running head: CsH_2PO_4 for water electrolysis at ~ 225 - 400°C

Abstract

Cesium dihydrogen phosphate, CsH_2PO_4 (CDP) was studied for water electrolysis at ~ 225 - 400°C . In presence of sufficient humidity, CDP is structurally disordered and super-protonic conducting with conductivities reaching 0.2 - $0.25\text{ S}\cdot\text{cm}^{-1}$, when determined in suitable H-shaped sealed conductivity-cells. Freshly prepared $99.7\pm 0.3\%$ gravimetric pure CDP with correct X-ray diffraction and DSC diagram melted at $\sim 345^\circ\text{C}$. The vapor pressures, above CDP alone and mixed with 20 - $50\text{ mol}\%$ CsPO_3 or $13\text{ mol}\%$ H_2O , were determined in *sealed* ampoules up to 355°C by means of Raman spectroscopy based on internal reference-gases. Pressures up to $\sim 49\text{ bar}$ were estimated, much higher than previously expected. Conductivities were given as polynomials and plotted in solid and liquid states. Water splitting electrolysis $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ was demonstrated by Raman at $\sim 355^\circ\text{C}$ under a water pressure of $\sim 23\text{ bar}$ in a quartz cell with platinum electrodes, showing molten CDP to have significant potential for water electrolysis.

Keywords: CDP, ionic conductivity, H^+ conductor, phosphate-based electrolyte, elevated temperature pressure electrolysis

1. Introduction

Water electrolysis represents an attractive way to convert surplus electrical energy into chemical energy (hydrogen and oxygen) to balance the electric grid when an increasing fraction of the power input originates from fluctuating renewable sources such as solar and wind energy [1]-[2]. Using fuels such as synthesis gas and methanol in intermediate temperature solid electrolyte fuel cells at elevated temperatures has several advantages, among which the following can be mentioned: opportunity for better storage of excess energy, improved catalytic activity or possibility to replace noble metals with cheaper electro catalytic materials, more effective use of waste heat, and lower permeability through the electrolyte in comparison with current commercial polymer-electrolyte fuel cells (PEFCs) [3]-[4].

In all kinds of fuel cell and water electrolyzer systems the electrolyte is one of the most important features directly influencing performance. The magnitude of the specific proton conductivity is a key parameter that influences the system in several ways, such as operating temperature, permitted range of chemical composition, allowed humidity and associated water vapor pressure above the electrolyte.

We recently demonstrated that molten potassium dihydrogen phosphate (KH_2PO_4 , or KDP) could be a promising proton-conducting molten electrolyte for pressurized intermediate temperature water electrolysis, and observed a high conductivity ($\sim 0.30 \text{ S cm}^{-1}$ at 300°C) at pressures around 10 atm. [5]-[6]. However KDP is just one member of a whole family of proton-conducting electrolytes, salts with properties intermediate between a normal salts and acids, see e.g. [7]-[16].

Exceptional high conductivity ($\sim 2.2 \times 10^{-2} \text{ S cm}^{-1}$) has been discovered for solid cesium dihydrogen phosphate (CsH_2PO_4 or CDP) above its transition to a so-called superionic or “superprotonic” proton-conducting phase at about 230°C . The CDP crystal also undergoes a proton ordering ferro- to para-electric phase transition at low temperature, at about -119°C [17]-[23] that will not be considered here. The successful use of the CDP salt as a promising solid electrolyte was demonstrated in intermediate temperature fuel cells, sometimes with composite electrolyte membranes to stabilize the conductivity at temperatures up to $\sim 250^\circ\text{C}$ [12], [21], [24]-[44]. Thus CDP seems to be one of the most widely studied solid acid electrolytes. However, when CsH_2PO_4 is heated in air at atmospheric pressure *dehydration* takes place (it starts to lose weight) at about the same temperatures [4], [13], [45]-[48]. Under conditions of high humidity the transformation is reversible and water can be picked up again, but under dry conditions, the dehydration of CDP (Eq. (1)) proceeds to form polymerization products (hydrogen pyrophosphates and polyphosphates) at temperatures above $\sim 200^\circ\text{C}$ until complete decomposition to the metaphosphate CsPO_3 at still higher temperatures:

Since this dehydration reaction occurs in parallel with the transition to the superprotonic phase, the nature of CDP phases and the conduction mechanism has been much discussed over the last decades [4], [9], [12], [19], [21]-[23], [26]-[27], [33], [35], [38], [44], [46]-[63]. The phase diagram in the CsH_2PO_4 - CsPO_3 system was studied in e.g. refs. [19], [46]-[47], [55]. Stabilization of the superprotonic phase without any decomposition was demonstrated under appropriate humid conditions in e.g. crystallographic and electrochemical studies [4], [26], [53]. It was found that CDP

is stable in contact with Pt catalysts in oxidizing and reducing atmospheres up to at least 240 °C [12], [27], [46].

It was even proven that the CDP at high pressures (up 25 kbar) did not decompose prior to melting when heated up to ~460 °C [19], [22]-[23], [61]. Various melting points for CDP have been reported in the literature under different experimental conditions (pressure, confinement and water partial pressure) but the correct value is thought to be around 345-349 °C at pressures near ambient values [19], [38], [55], see Figure 1.

The crystal structure of CsH_2PO_4 (space group $P2_1/m$) at ambient temperature and pressure has a unique hydrogen-bond network [49] [64]. The lattice constants in this monoclinic paraelectric phase II are around $a = 7.912 \text{ \AA}$, $b = 6.383 \text{ \AA}$, $c = 4.882 \text{ \AA}$, $\beta = 107.73^\circ$, and each unit cell contains two formula units. The tetrahedral phosphate anions $[\text{PO}_4]^{3-}$ are linked via two kinds of partly disordered one-dimensional $\text{O-H}\cdots\text{O}$ hydrogen bonds forming layers of $[\text{H}_2(\text{PO}_4)]_\infty$ with room for Cs^+ cations at sites in between these layers (according to e.g. [17]-[18], [21]-[23], [65]-[67]).

Figure 1. Pressure – temperature phase diagram of CsH_2PO_4 based on data by Rapoport et al. [19]. Their results were obtained from DSC heating experiments of samples confined in pressurized Ni capsules. “Post mortem” X-ray powder diffraction experiments confirmed the absence of any decomposition of the CDP. The points and curves shown reproduce the author data (points and polynomials of the type: Temperature = an expression of pressure [19]. Positions for each author point were read manually pixel by pixel from an expanded plot relatively to the axis values by use of the open source GIMP 2.9.6 software (GNU Image Manipulation Program designed for the GNU Operating System from the Free Software Foundation, Inc. in Boston, MA, USA). The dotted-dashed curves obtained in this work fit better to the original data.

By heating CsH_2PO_4 above $\sim 228\text{--}231^\circ\text{C}$, the monoclinic structure (phase II) transforms to the cubic phase I that has been characterized as a CsCl-like structure in space group no. 221, $Pm\bar{3}m$, with $Z = 1$ and a lattice constant of $a = \sim 4.96 \text{ \AA}$, with one phosphate anion placed in the center of the cube and with Cs atoms at each corner (see Figure 2). This ‘superprotonic phase’ exhibits its superconducting properties after a sudden increase in the conductivity by three orders of magnitude, from about 10^{-5} to $2.2 \cdot 10^{-2} \text{ S cm}^{-1}$ [4], [7]–[9], [12], [21]–[22], [26], [46]–[47], [49]–[50], [61], [69]–[70]. The role of the phase transformation is thought to be to set the disordered hydrogen bond network free to easily transport protons. The oxyanion can take one of six possible orientations within the cube and therefore the hydrogen bonds can be formed in six possible ways. In this state the phosphate groups are linked together with hydrogen bonds of two different kinds: symmetric double minima and asymmetric single minimum bonds. The proton transfer is thought to happen rapidly via the hydrogen bonds and liberations or reorientation jumps of the $[\text{PO}_4]^{3-}$ anions influenced by phosphate group disorder [21], [26], [49], [53], [69]. Details of the mechanism for the high proton mobility are considered in several references involving many techniques including neutron scattering and nuclear magnetic resonance [12]–[14], [27]–[29], [36], [41], [51]–[52], [67], [68], [71]–[74].

Figure 2. The crystal structure of CsH_2PO_4 in the “superprotonic” phase I is well established with $a = 4.961(3) \text{ \AA}$ at 237°C [53] [22] and with $a = 4.9549(4) \text{ \AA}$ at 242°C [68]. The Cs^+ ions at cell corners are shown in violet. The yellow P ion in the middle of the cell is not visible. The four oxygen ions are disordered and red balls show their positions that are occupied with a 0.16667 probability. The hydrogen ions (not shown) are also disordered. The picture was created by use of single crystal data from [68] and the “CCDC Mercury program” from www.ccdc.cam.ac.uk.

An important role must also be played by the water present in humidified surroundings or by the containments obstructing the decomposition that would otherwise happen. Thus in many of the references, decomposition or dehydration of the CPD was considered and it was often noted that polymerization products were formed at higher temperature making the conductivity decrease as time elapsed [4], [22].

The decomposition has been claimed to be reversible, and a water pressure of, for example 0.3 atm. at 250°C should be sufficient to suppress dehydration for some time [4] [26]. It was reported that the conductivity of CsH_2PO_4 started to decrease when heated above 238°C and it was claimed to be due to the decomposition reaction (1) $\text{CsH}_2\text{PO}_4 \rightarrow \text{Cs}_2\text{H}_2\text{P}_2\text{O}_7 \rightarrow \text{CsPO}_3$ and that water saturation or high pressures were needed to avoid it [23], [46]–[47], [55], [61]. Taninouchi et

al. [46], [55] have directly related the onset Kelvin temperature of dehydration (T_{dehy}) to the water partial pressure ($p_{\text{H}_2\text{O}}$ in atm.) by means of extrapolated equations (Eq. (2)):

$$\log(p_{\text{H}_2\text{O}}/\text{atm.}) = A - B \times 1000 / T_{\text{dehy}} \quad (2)$$

where $A = (6.11 \pm 0.82)$ or (7.62 ± 1.18) and $B = (3.63 \pm 0.42)$ or (4.42 ± 0.56) are parameters.

Whether the “superionic conduction state” in CDP really exists is still questioned by some researchers: Could the high conductivity above $\sim 230^\circ\text{C}$ be a consequence of partial dehydration at the crystal surface? [51]-[52], [62]. It has been claimed that CDP does not undergo the superprotonic phase transition; instead a dynamically disordered hydrogen bond network might improve the protonic conduction, or a loss of water from the structure might raise the conductivity. However, we notice that many previous experiments were not performed at humidified conditions and many studies have shown the highly-conducting CDP phase to be poorly stable under reduced presence of water [4], [46]-[47], [53], [55]. Thus in a typical study, Bronowska [53] concluded from high temperature X-ray experiments in normal air that CDP crystal powders underwent a “reversible” transition at $\sim 231^\circ\text{C}$ to form $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ but *also* transformed to the superionic phase which however was unstable due to dehydration, soon leading to the formation of CsPO_3 ; but in a H_2O -saturated atmosphere much less decomposition was seen for the same CDP powders. In other words, the superionic phase of CDP seems to require a sufficient water vapor pressure over the salt, in which case the transition to the superionic phase takes place reproducibly.

Many ingenious chemical studies (such as substitution of H with D, Cs with Rb and P with As) have been performed to study and confirm the extreme conductive behavior in CDP and related substances, see e.g. [69], [75]-[79], but they will not be discussed here.

In the present work we investigate the relation between the vapor pressure of cesium dihydrogen phosphate and the electrical conductivity at elevated temperatures, up to *and above* the melting point. We report on the found conductivity properties of the superconducting phase and the *liquid* electrolyte, in a closed set-up in order to make sure that the solid and molten CsH_2PO_4 salt was intact during the measurements.

To our knowledge no one of the many earlier studies performed on the CDP salt, has focused on the protonic conduction properties in the *solid* state *at temperatures above approximately 300°C* , the reason probably being connected with the extensive problems of dehydration of the electrolyte with an insufficient water pressure over the CDP. We also studied the reversibility of the shift between the monoclinic and the “superionic conduction phase” at around $\sim 230^\circ\text{C}$. The main objective of this work was thus to see if the conductivity of the salt would be preserved after long-term tempering while keeping the salt under its own vapor pressure in rather full ampoules. The magnitude of the vapor pressure was not known, so we set out starting to use our newly established method of determining water vapor pressures over corrosive chemicals *versus* temperature by use of Raman spectroscopy [80]. We have previously used this method to study the water vapor pressure over molten potassium dihydrogen phosphate (KH_2PO_4) and determined the specific electrical conductivity, as well as demonstrated water electrolysis in the same system at $\sim 300^\circ\text{C}$ [5]-[6].

In the present study, the temperature dependence of the *vapor pressure* above CsH_2PO_4 was found to be much higher than presumed in the literature. We measured the level of specific electrical conductivity of CDP under its own vapor pressure, below and above the phase transition, between the monoclinic conductive phase (II) and the highly conductive cubic one (I), and of the liquid electrolyte melt under its own vapor pressure. We wanted to study what happens over longer periods of time and to see if it occurs reversibly at even higher temperatures where very high water pressures are necessary to avoid decomposition of the CDP salt. Rapoport et al. [19] claimed no decomposition to occur even at 550 °C and 20 kbar in fast experiments, and noted that it should be showing how well pressure can stabilize the compound. To our knowledge the long time stability has not been studied before. We also wanted, with the help of DTG analysis, to redetermine the melting point temperature of CDP. The earlier given values vary between a widely reported value of ~233 °C and up to ~346 °C, again as a result of the unnoticed dehydration decomposition at ambient water pressure and the associated formation of melting-point-depression “impurities” [19], [36], [46]-[47], [81], as shown in the phase diagram in [55].

2. Materials and Methods

2.1 Preparation of the salt

Crystalline CDP, CAS # 69089-35-6 is sensitive to conditions of preparation, as well as presence of micro-impurities and water. We prepared our samples, as described in most references, from H_3PO_4 (85 wt. % solution, CAS # 7664-38-2) and new Cs_2CO_3 (Cesium carbonate ReagentPlus®, 99%, CAS # 534-17-8), both provided by Sigma Aldrich. Cs_2CO_3 was dissolved in Milli-Q® water and slowly mixed with the H_3PO_4 acid in a mol ratio of Cs:P = 1:1. The solution was concentrated by evaporation where after methanol (MeOH, puriss. P.a., ACS reagent, CAS 67-56-1, provided by Sigma Aldrich) was added to the solution to precipitate crude CsH_2PO_4 . The yield was washed with methanol at least twice, since excess of H_3PO_4 dilutes in methanol (H_3PO_4 is soluble and CsH_2PO_4 is not). The resulting solid was left to dry and thereafter heated to 90 °C in a ventilated oven until the remaining water has evaporated. The formed crude CsH_2PO_4 was dissolved in Milli-Q® water and recrystallized in a petri dish at room temperature (~ 22 °C) by slow evaporation in a ventilated hood for several days. After that the salt was kept at 90 °C for one day to ensure complete dryness. The recrystallization ensured that residues of methanol, excessive acid or cesium solution which might have stayed between the crystallites were completely removed.

2.2 Verification of the composition

In order to verify the composition several portions with closely the same weight of recrystallized CsH_2PO_4 were weighed in platinum crucibles. These crucibles had previously been heated to red glowing in a flame and cooled in a desiccator filled with a Silica drying agent (CAS # 112926-00-8, P-code 100897613, provided by Fluka Analytical) to ensure constant weight. The crucibles with the CsH_2PO_4 portions were placed in an electric oven, gently heated to and kept at 800 °C for 4 hours, then cooled down to 200 °C and immediately placed in the desiccator. After weighing the crucibles the CsH_2PO_4 to CsPO_3 weight losses were compared. The solid residue average weight came out as 91.8 ± 0.4 wt. % of the initial compound, to be compared with the theoretical value 92.16 wt. %. From this phosphate gravimetry our CDP is therefore considered to be 99.7 ± 0.3 % pure. It is important to verify the composition of the synthesized CDP, because an excess of

phosphoric acid or Cs^+ ions could lead to formation of other compounds such as $\text{CsH}_5(\text{PO}_4)_2$ [34] [77], $\text{Cs}_8\text{P}_8\text{O}_{24}\cdot 8\text{H}_2\text{O}$ [81], and hydrates like $\text{Cs}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}$ [79] and $\text{Cs}_3\text{P}_3\text{O}_9\cdot \text{H}_2\text{O}$ [82] which did not seem to have happened in our case.

2.3 Measurements of the melting point

The melting point of our pure CDP was determined from Differential Scanning Calorimetry (DSC) analysis performed on hermetically sealed high-pressure sample crucibles of chrome nickel steel (AISI 316L) with similar lids both with gold-plated surfaces (product number 6.239.2-92.31.00) and reference containers. The crucible type was of bottom nominal width 6 mm, with a volume of 27 μl , with maximum internal pressure of 100 bar and a maximum temperature of 500 $^\circ\text{C}$. After filling with about 22 mg of salt, each crucible was closed with a sealing disk using a sealing press (product number 6.239.2-92.4), provided by the Netzsch Group. A Netzsch STA 409 PC (TG/DSC) instrument was used from room temperature to ~ 500 $^\circ\text{C}$. A dry argon or air atmosphere was used, i.e. without humidification but the crucibles were quite full ($>30\%$). A constant heating rate of 1 - 2 $^\circ\text{C}/\text{min}$ was used.

2.4 X-ray Powder Measurements

X-ray diffraction on the recrystallized CDP powder was performed with the help of a Huber D670 diffractometer using the Cu-K_α radiation line ($\lambda = 1.54056$ $\text{\AA}$) in the range of 3° to 100° in steps of 0.02° in 2θ .

2.5 Raman Vapor Pressure Measurements

Our method to determine the vapor pressure of a substance contained in a sealed ampoule has recently been described in detail [6]. *Note that precautions should be taken due to the risk of explosion whenever working with ampoules.* The water vapor partial pressure at a given temperature is obtained by use of Raman spectrometry whereby the presence and identity of water molecules in the gas (the vapor constitution) is measured quantitatively. In spite of the weak scattering strength, Raman spectroscopy is a favorable method to determine the content of gases trapped in voids, because the signals are species-specific and the intensities normally are linearly dependent on concentration (in the absence of resonance [83]).

Sampling. Nitrogen and methane ($>99.9\%$ pure gases) were obtained from AGA/Linde (Copenhagen S, Denmark). The Raman spectra showed no sign of trace impurities, confirming the gases to be clean and dry. The substance (here CDP) was placed in a home-made PyrexTM ampoule ($\sim 2\text{mm}$ wall thickness, ~ 16 mm internal diameter) that via rubber tubing and a stem was connected to a vacuum line. The used ampoules were wide to avoid signals from the walls and round to better resist high internal pressures. After evacuation (<0.1 Torr) the ampoule was filled with reference gas (typically nitrogen or methane). The reference gas needs to be inert and to have a strong Raman signal. The gas was typically added up to a predetermined pressure (0.5 bar) that was read off on a calibrated Bourdon manometer at ~ 22 $^\circ\text{C}$. Then the ampoule was sealed with a butane-oxygen torch flame. Enough CsH_2PO_4 was added to make the ampoule (cell) more than half full, so that minute changes in concentration by loss of water to the gas phase

during later heating could be minimized. By comparing the quantitative Raman signals from the vapor and the reference gas, partial pressures can be determined, because the species-specific signals (intensity of reference and water) are linearly dependent on concentrations; by variation of the temperature the pressure as a function of temperature was obtained.

Methodology. The method requires knowledge (or determination) of the precise Raman scattering ratios between the sought gas substance (water) and the reference gas, respectively. The approximate concentration in mol L^{-1} (n/V) of the reference gas can be calculated with a reasonable accuracy using the ideal gas law, $n/V = p/RT$. Here n is the number of moles, V is the estimated ampoule volume (~ 6 mL), p is the partial pressure, R is the gas constant ($0.083145 \text{ bar} \times \text{L} \times \text{mol}^{-1} \times \text{K}^{-1}$) and T is the absolute Kelvin room temperature. After sealing, the reference gas *concentration* stays constant whereas the *pressure* of course increases with T .

The water molecule is an asymmetric top with C_{2v} symmetry. It has a well-known Stokes Raman spectrum consisting of three active fundamental transitions: ν_1 (symmetrical O-H bond stretching), ν_2 (symmetrical H-O-H angle bending), and ν_3 (asymmetrical O-H bond stretching) [94]-[99]. Infrared absorption (ν_3) of water is very intense but has the problem of strong absorption for common window materials so IR cannot be used. The ν_1 band of water is relatively strong in Raman; the other ones are very weak. In the present case it means that the scattering ratios between the water ν_1 band (symmetric OH stretching at 3655 cm^{-1}) and the internal calibration gas reference (the ν_1 vibrational Q-branch of N_2 or CH_4) can be used to sample the water pressure. The Q-branch corresponds to a vibrational transition with no change in the rotational state; i. e. the J quantum number remains constant. These ratios have been previously found as 3.50 ± 0.03 for the H_2O band at 3655 cm^{-1} relatively to N_2 band at 2331 cm^{-1} and 0.40 ± 0.02 for H_2O band relative to the CH_4 band at 2917 cm^{-1} , respectively. The determinations were done on cells containing only water and nitrogen or methane in known amounts by measurements in our setup as explained in [6], [80]. The choice of nitrogen as internal inert reference calibration gas - unlike previously - has the risk of introducing errors due to nitrogen signals from the surrounding laboratory air, but the N_2 signal problem was avoided by placing a laser line narrow band pass filter in front of the laser line just prior to the sample. N_2 has the extra advantage that quartz ampoules can be used without risk of decomposition of the reference gas in the extreme heat needed for sealing silica. A more extensive description of the intensity calibration is given in [6], [80] and works cited there.

Measurements. Raman spectra were measured by use of a DILOR-XY 800 mm focal-length Czerny-Turner type spectrometer with 90° macro entrance and a $10 \times 10 \text{ cm}^2$ 1800 lines/mm plane holographic grating [84]. Excitation was done with laser light from a doubled Nd-YPO₄ Laser (wavelength 532 nm CW vertically polarized at a power setting of up to ~ 1.5 W). The cells were placed vertically to let the light pass horizontally. Light was collected with a wide achromatic lens (10 cm focal length). Rayleigh scattering was removed with a holographic Notch filter. A quarter wave plate was mounted before the entrance slit to depolarize the light, making the grating efficiency independent of the polarization of the light. Slit widths and lengths were set to $600 \mu\text{m}$ and 10 mm to obtain better signals at the expense of resolution [85]. The spectra were acquired with a multi-channel CCD detector (Horiba/Jobin-Yvon SynapseTM, 1024×256 pixels) with thermoelectric cooling (-69°C). The CCD signals were not calibrated for variation of the quantum efficiency versus wavelength. The gas spectral line intensities were measured 2 – 4 times with automatic removal of cosmic spikes. Integration times were between 20 and 1200 s, depending on

the signal strength, and the excitation beam intensity was kept at 1.5 W. The measurements were repeated and averaged in order to ensure reproducibility and obtain reliability. Measurements were done in a temperature range from $\sim 25^{\circ}\text{C}$ to $\sim 400^{\circ}\text{C}$; heating was achieved with a home-made insulated aluminum-bronze-core vertical-tube electrical furnace with four silica double layer windows [6], *protected with a net of steel because of the risk of ampoule explosion*. The gas or liquid/solid phase spectra were obtained by moving the ampoule holder up or down. Temperatures were determined with several 4-wire-Pt-100- Ω resistors to a precision better than $\sim 0.5^{\circ}\text{C}$ (the temperature inside the furnace was only precise to $\sim 2^{\circ}\text{C}$ due to gradients). The spectrometer cm^{-1} scale was calibrated with cyclohexane [86]. Other Raman experimental details (furnace, etc.) have been described elsewhere [87].

2.6 Details of conductivity cells

Four conductivity H-shaped cells similar to the ones used recently [5] were fabricated to determine the conductivity (σ) of the CDP substances. The cells were made from fused quartz glass by glass blowing. At first the bulb of a standard halogen lamp (PHILIPS type 7787XHP 36V/400W) was cut near the base and the tungsten spiral was cut over – thereby creating two electrodes for the first chamber. A similar operation was done for the second chamber. Details of the cell type and a picture can be found in a previous publication [5]. The tungsten electrodes were cleaned, etching off the WO_3 (formed during the glass blowing) by means of 20 wt. % aqueous HF overnight. Traces of WO_3 were removed by filling the cell with an equimolar amount of $\text{K}_2\text{S}_2\text{O}_7$ and K_2SO_4 , sealing under vacuum and heating to 440°C in a rocking furnace (details are given previously [5] [84]) followed by rinsing the electrodes with water in an ultrasonic bath. Same cell was in some cases used for repeated experiments, after washing out all solidified salt with water under ultrasonic agitation, rinsing with ultrapure water (resistivity = 18 $\text{M}\Omega\text{ cm}$), drying it in a heating cabinet at 80°C and then adding new stems and new chemicals.

The cell constant K for each cell was determined by measuring the resistance R_{KCl} for an aqueous KCl solution at a precisely known temperature near room temperature, according to the principles given by Jones and Bradshaw [88]. A standard solution was prepared following the ASTM Designation D1125–95 [89]: 3.734 g of high purity KCl, prepared by us as earlier described [90] was dissolved in 502.11 mL at 22.0°C of Milli-Q[®] water to form a 0.1 D solution of KCl. The *demal* (D) unit is used for concentration in electrolytic conductivity primary standards and is equal to the molar concentration at 0°C ; i.e. 0.1 D represents 0.1 mole of KCl in one cubic decimeter of the solution at 0°C . The obtained R_{KCl} value should be *dependent* of the electrolyte concentration, the temperature and the dimensions of the narrow capillary tube between the chambers of the cell and *independent* of the electrode areas and total amount of KCl solution used.

2.7 Conductivity measurement technique

The resistance of each salt or melt was obtained from an H-shaped cell, as described in our previous paper [5]. At first the materials that made up the sample were weighed and transferred quantitatively into the cell, which was sealed under vacuum (< 0.1 Torr). Then the cell was heated and equilibrated in a rocking furnace, similar to one previously used [5]. Equilibration was performed at first at $\sim 350^{\circ}\text{C}$ (above the melting point) for several days. Temperatures for each data point were determined with 4-wire-Pt-100- Ω resistors to a precision better than $\sim 0.5^{\circ}\text{C}$.

The impedance was measured with an automatic AC Wheatstone bridge potentiostat system (Princeton Applied Research VersaStat 4 with VersaStudio software) at an accuracy $\approx 0.1\%$. The electrodes of the cell were connected to the potentiostat via shielded electric wires using the 2-electrode input setup for the measurements (the pairs of chamber terminals were shorted in all the experiments as given: working electrode-sense electrode and counter electrode-reference electrode). The obtained impedance data were plotted as imaginary resistance versus real resistance curves for different frequencies of the applied alternating current supplied from the VersaStat 4 potentiostat. The resistance R_{sample} was read off as the real abscissa from the lowest point on each impedance curve. This point is used to determine the R_{sample} at the given temperature. Bubbles that might be present in the capillary and give a higher resistance were removed by rocking the furnace [5]. The conductivity of the sample (in units of S cm^{-1} at the particular temperature) is calculated from the obtained resistance via the relation $\sigma_{\text{sample}} = K/R_{\text{sample}}$. The cell constant $K = R_{\text{KCl}} \times \sigma_{\text{KCl}}$ has previously been determined for each cell (filled with solution of 0.1 M KCl solution after the ASTM D1125 standard [89]). K is rather independent of temperature because the fused quartz material hardly expands by heating, leaving the dimensions of the cell capillary rather unchanged (error less than $\sim 0.01\%$). The reproducibility for measurements performed at the same temperature was within 0.5-1 %, after minimizing the tendency of bubble formation. In some experiments the cell constant was re-determined after finishing the measurements. Other experimental details have been described elsewhere [91], [92].

2.8 Water Electrolysis Cell

A home-constructed electrolysis cell was used similar to the previous one [6]. The cell was made by glass blowing from fused quartz glass tubing (~ 14 mm O.D.) and a standard silica halogen lamp with vacuum-tight molybdenum-tungsten feed-throughs. Platinum electrodes were silver-welded to the internal feed-through tungsten spirals before more quartz tubes were added for later easy sealing. The cell was filled with CDP, attached to a vacuum line, evacuated, the N_2 reference gas added, sealed, and mounted to the holder with electric cables (silver contact wires isolated by alumina beads) and heated in the Raman furnace (see figures in [6] for details). After connection to a Princeton Applied Research VersaStat 3 potentiostat the setup allowed electrolysis *as well as* successive recordings of Raman spectra of the melt *and* the gas phases at high temperatures (and pressures) by use of the furnace elevation system. Electrolysis went on for many minutes with currents of about 5 to 100 mA. The furnace windows were covered with a *protective steel net because of the risk of ampoule explosion* [6].

3. Results and Discussion

3.1 Differential Scanning Calorimetry analysis data.

The behavior of CsH_2PO_4 upon heating under its own vapor pressure was studied by DSC in our hermetically sealed cells. A typical diagram is depicted in Figure 3. As expected two peaks were seen: A smaller peak at around 230°C , indicating the solid state $\text{II} \rightarrow \text{I}$ phase transition in the CDP salt, as previously reported in e.g. [8], [21], [35], [38], [47], [49]-[50], [56], and a larger peak at around 345°C , being the melting point signal. As noticed above previous thermal analysis results for CsH_2PO_4 varied, but for sealed and fully contained experiments most experimentalists have

agreed on results similar to what was found in this work. From the overview over already published DSC data it is evident that the behavior depends somewhat on the heating rate, and different results were found for e.g. 8.5 °C/min [93] and 2.5 °C/min [51] in open or closed crucibles. The dependence on heating rate, amount of humidity and enclosure is explained by the fact that equilibrium had not been achieved, and water was escaping from the salt at different speeds during the experiments. This is why we decided to perform the following vapor pressure and conductivity measurements with salts at pressurized conditions, placed in closed ampoules that were able to maintain the considerable water vapor pressures over the salts.

Figure 3. Differential Scanning Calorimetry plot for pure CsH_2PO_4 in a hermetically closed gold-plated crucible containing 22 mg of the compound in air. Heating rate 1 °C/min.

3.2 X-ray powder diffraction data.

X-ray powder diffraction data were obtained for our synthesized CsH_2PO_4 as shown in Figure 4. The results are given together with data on CDP from the ICSD crystallographic database, FIZ Karlsruhe in Germany, compound no. 200895. From this comparison it can be seen that there is a very good agreement between our data and the data by Matsunaga et al. [66], characterizing the identity of our material. The differences in intensity were probably caused by preferred orientation in the powder.

Figure 4. X-ray powder diffraction data on CsH₂PO₄ (Cu-K α radiation, $\lambda = 1.54056 \text{ \AA}$). Black curve: Result of our synthesized CDP. Blue curve: Calculated diagram for P2₁/m CDP phase II at room temperature, obtained by use of the “CCDC Mercury program” from www.ccdc.cam.ac.uk, based on single crystal data from the ICSD (Inorganic Crystal Structure Database) FIZ Karlsruhe, compound no. 200895 (originally published by Matsunaga et. al. [66]).

3.3 Raman spectroscopic measurements

Vapor pressure determination. The Raman spectra of the water vapor above CDP were recorded versus temperature for a number of more than half full sealed tube cells. The gas phase spectra have been recorded several times after equilibration for several hours at temperatures from ~ 25 to $\sim 350^\circ\text{C}$ for each cell. Methane or nitrogen has been added as internal calibration standards. Typical spectra are shown in Figure 5. The areas of the peaks were determined as indicated. In spite of the rather weak scattering strength, the Raman technique can determine the gas content in the cells, because the signal is species-specific and the intensity depends on the concentration at a rate determined by the known scattering cross section ratios for the molecules, here H₂O to CH₄ or H₂O to N₂. The spectra contain the well-known Q-branch rot-vib bands of the added nitrogen or methane (the ν str bands of N₂ at $\sim 2331 \text{ cm}^{-1}$ [100] or the ν_1 (A₁) sym str band of CH₄ at $\sim 2917 \text{ cm}^{-1}$ [101]) in addition to the Q branch rot-vib of the water molecules originating from the salt (the ν_1 sym str band of H₂O at $\sim 3655 \text{ cm}^{-1}$). The water band at $\sim 3655 \text{ cm}^{-1}$, see Figure 5, looks

like the H₂O spectra in the literature, see e.g. [94]–[99]. The relatively high pressures and temperatures broaden the bands by populating higher rotation-vibration (rot-vib) levels so that most spectral details remain unresolved, as discussed in detail in [6], [80].

The areas of the bands for several acquisitions (two or more sets of spectra) were integrated with use of the Labspec software. For the nitrogen or methane band envelopes, the areas were taken to range from ~ 2310 to ~ 2345 cm⁻¹ (S_{N_2}) or from ~ 2895 to ~ 2935 cm⁻¹ (S_{CH_4}), respectively, and for the water band the area was set to range from ~ 3610 to ~ 3676 cm⁻¹ (S_{H_2O}), as indicated in Figure 5. The water pressure was then calculated in the following way: By knowing e. g. the nitrogen pressure $p_{N_2}^0$ at the *ambient* Kelvin temperature T_0 , the water pressure p_{H_2O} at the actual experiment temperature T is given approximately by the ideal gas law as (eq. (3)):

$$p_{H_2O} = p_{N_2}^0 \times (T \times S_{H_2O} \times \sigma_{N_2}) / (T_0 \times S_{N_2} \times \sigma_{H_2O}). \quad (3)$$

S denotes the integrated Raman band signal area above the background for the molecules in play, here nitrogen and water. Similarly in the case of methane as the reference, the water pressure p_{H_2O} is given by eq. (4):

$$p_{CH_4}^0 = p_{CH_4}^0 \times (T \times S_{H_2O} \times \sigma_{CH_4}) / (T_0 \times S_{CH_4} \times \sigma_{H_2O}). \quad (4)$$

The scattering cross section ratios, $\sigma_{H_2O}/\sigma_{N_2}$ or $\sigma_{H_2O}/\sigma_{CH_4}$ between water and nitrogen or water and methane gas molecule Q-branch areas, as defined above, respectively, take values at around ~ 3.50 or ~ 0.40 , respectively, as determined previously [80], rather independently of temperature [94], although some deviations from these values were seen in older literature.

Figure 5. Typical spectra illustrating the principle of Raman spectroscopic quantitative determination of water (to the right) in sealed ampoules with nitrogen (to the left) or methane (in the middle) as reference gasses. The spectra were recorded with a 532 nm green laser under carefully experimental settings of the spectrometer to let accurate band areas, S_{water} and $S_{reference}$

be determined. The used integration ranges were from ~ 2310 to ~ 2345 (N_2), from ~ 2895 to ~ 2935 (CH_4), and from ~ 3610 to ~ 3676 cm^{-1} (H_2O). This allowed values for the ratio between the area ($S_{\text{H}_2\text{O}}$) of the water band relative to the reference area (S_{N_2} or S_{CH_4}) to be calculated. From this the water pressure was calculated as explained in the text.

A summary of the water vapor pressure results for five CsH_2PO_4 sealed Raman cells, quantified by CH_4 or N_2 intensity calibrations, are given numerically in Table 1 and shown graphically in Figure 6.

It is clear from Figure 6 that very similar results are obtained independent of whether nitrogen or methane are used as references for the pressure measurement. This indicates that the Raman spectroscopy pressure measurement technique is likely to be correct. A similar conclusion was reached when we studied the vapor pressure over concentrated phosphoric acid [80].

It is seen that the vapor pressure of CDP is much lower than for water at a given temperature; see the known vapor pressure curve of steam from the NIST Standard Reference Database [102] that is also included in Figure 6. The low CDP vapor pressure is to be understood as a high affinity for water to stay in the melt; it is being bound by strong hydrogen bonds.

On the other hand the CDP vapor pressure in general is much higher than what has been claimed in the literature, based on different indirect methods, see e.g. [4], [12], [21], [27], [46], [55], [103]. The formula reproduced as equation (2) has been claimed to be valid up to perhaps 315°C (according to Taninouchi et al. [46], [55]). When this formula was plotted with the A and B constants [46], [55] we obtained the two curves also included in Figure 6. It is clear that our measurements correspond to higher pressures. It indicates - to our belief - that it takes time for CDP to reach the equilibrium, presumably several hours in some cases. This might explain why literature values were found too low.

Also included in Figure 6 are the results from an experiment we made with a pressure cell with CsH_2PO_4 : CsPO_3 equal to 50 mol% : 50 mol%. The actual composition of the *liquid* phase in the 50 mol% : 50 mol % experiment is “not known precisely” because visual inspection showed that it is saturated with a solid (probably CsPO_3). The solubility of CsPO_3 is expected to be low and to vary with the temperature. It is interesting that the 50 mol% : 50 mol% curve is following about the same path as the curves of Taninouchi et al. [46], [55]: This might indicate that their samples have lost substantial amounts of water, or their extrapolation procedure has been based on assumptions that are not entirely valid, e.g. such as lack of equilibrium.

Table 1. Vapor Pressure Data from ampoules with pure CsH_2PO_4 , an electrolysis cell and a cell with $\text{CsH}_2\text{PO}_4:\text{CsPO}_3 = 50\% \text{ mol}: 50\% \text{ mol}$ (presumably CsH_2PO_4 saturated with CsPO_3 at the temperature).

CDP, CH_4 reference		CDP, N_2 reference		CDP, N_2 reference		CDP, N_2 reference	
Temp. °C	Pres. bar	Temp. °C	Pres. bar	Temp. °C	Pres. bar	Temp. °C	Pres. bar
25	0.0100	24	0.0062	24	0.0014	24	0.0068
99	0.1533	24	0.0072	24	0.0026	124	0.6482
101	0.1882	24	0.0054	150	0.7028	124	0.6155
175	0.8569	100	0.2880	150	0.8602	183	1.2211
175	1.0527	100	0.2411	200	1.1407	183	1.1289
225	2.2045	100	0.2645	200	1.1635	237.5	2.1783
225	1.4294	150	0.6427	225	1.5826	237.5	2.2189
225	1.8705	150	0.6358	225	1.4546	237.5	2.0577
250	2.2912	200	0.8236	225	1.4498	237.5	2.2717
250	2.2199	200	0.8316	250	2.2021	270	4.6286
250	2.3986	250	1.1917	250	2.2324	270	4.6820
300	10.5552	250	1.2413	250	2.2139	285	7.7666
300	10.1799	300	10.9211	275	5.3919	285	7.9473
324	17.9230	300	11.2687	275	5.2307	295	9.4607
325	18.8111	325	15.9085	275	6.6650	295	9.9002
326	18.0191	325	17.0292	275	5.9115	305	12.3005
		336	12.1081	275	5.8104	305	12.0803
		336	10.8433	300	9.1097	305	11.7479
		340	11.2125	310	13.2037	315	13.8865
		340	11.9260	310	13.6678	315	13.0463
CDP- CsPO_3 , N_2 reference				310	13.6326	325	17.0387
25	0			320	16.2841	325	16.4465
310	0.7738			320	16.9711	330	17.3501
311	1.1122	CDP electrolysis cell, N_2 reference		320	16.2551	330	16.6891
388	5.5946	355	23.015	325	18.5595	330	19.1948
392	5.6259			325	15.8813	330	15.4824
400	7.2452			330	14.4820	335	18.5185
410	8.8089					335	19.2922
410	9.0636

Figure 6. Vapor pressures in sealed ampoules versus temperature. The points represent our measurements. The curves show the standard vapor pressures of water from NIST [102] (full curve) compared with CsH_2PO_4 (narrow dotted) and CsH_2PO_4 : CsPO_3 , 50% : 50% by mol % (dashed, probably CsH_2PO_4 saturated with CsPO_3 at the temperature) as obtained by us. The establishment of equilibrium took several hours; if measurements were taken immediately after a stable temperature was reached, non-equilibrium lower results were obtained. Two curves of “partial pressure of water, $p_{\text{H}_2\text{O}}/\text{atm}$,” obtained via an extrapolation procedure by Taninouchi et al. [46], [55] are also given. Their latest determined wide dotted curve [55] is presumably better determined than their first dash-dotted one [46].

The narrow dotted and dashed curves for CDP and the CsPO_3 saturated mixture were calculated from the experimental points in Table 1 by using a linear fitting procedure on $\log_{10} p$ (in bar) plotted against $1000/T$, in the range 250–353 °C for the pure CDP data, and in the range 310–410 °C for the 1/1 molar mixture of $\text{CsH}_2\text{PO}_4/\text{CsPO}_3$ melt. The parameters for the fitted curves are presented in Figure 7.

Figure 7. Logarithmic fitting for data on the vapor pressure over pure CDP and for $\text{CsH}_2\text{PO}_4/\text{CsPO}_3$ 1/1 molar mixture (presumably saturated with CsPO_3 at the temperature). Also shown are circular points from Taninouchi et al. [55].

Raman on CDP versus temperature. We studied Raman spectra of the CDP substance versus temperature in the cells used for the vapor pressure measurements and got results as summarized in Figure 8. Similar spectra at low temperatures and up to $\sim 250^\circ\text{C}$ have already been obtained and much discussed in the literature [4], [25], [37], [70], [104]–[110]. Our Raman spectra looked much like the previous published spectra of confined CDP (large crystals, pellets or samples in sealed glass cells) at various temperatures. Typical CDP spectra can be seen in e.g. Figure 5(a) of reference [4], showing the spectral shifts and linewidth broadening of the internal modes versus temperature up to $\sim 260^\circ\text{C}$. As a new result, it was possible for us to record the spectrum of the melt and to observe a new line at $\sim 700\text{ cm}^{-1}$ originating from the formation of pyrophosphate ions (with P-O-P bridges), starting at temperatures higher than about 310°C . Such a spectral line, at $\sim 710\text{ cm}^{-1}$, has analogously been found when KH_2PO_4 was heated at high temperatures ($\sim 325^\circ\text{C}$) in closed cells [6]. Also a similar line was found and well documented for polycrystalline $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ at room temperature [70] but it was not present in NaH_2PO_4 [111].

Figure 8. Raman spectra of CsH_2PO_4 in sealed cells, as crystal powder and as molten electrolyte versus temperature. The inserted photo shows a cell just taken out of the furnace and with still molten CDP starting to freeze from the bottom. Up to about 300 °C the samples looked like powders. At higher temperatures the content looked like ice containing gas filled holes. Spectra with indications of indication of P-O-H bending and single water molecules were obtained in some instances (blue spectrum with a H-O-H stretching band at $\sim 3655 \text{ cm}^{-1}$, compare with Figure 5). was seen (at $\sim 1590 \text{ cm}^{-1}$). The melts showed broad features from ~ 2300 to $\sim 3600 \text{ cm}^{-1}$ that are characteristic of P-O-H stretching. Spectral bands below $\sim 1500 \text{ cm}^{-1}$ are due to the phosphate ions. Polyphosphate ions giving rise to bands at around 700 cm^{-1} (P-O-P bridge stretching) are seen in the molten transparent mixtures when the temperature was high enough ($\sim 325 \text{ °C}$). The pressure was dangerously high inside the cells and explosions occurred.

The superionic plastic phase of CDP contains characteristic broad bands because of the phase disorder with rapid reorientation of the H_2PO_4^- and O-H^- anions, involving breaking of some hydrogen bonds ($\text{P-O}\cdots\text{H-O-P}$) and creating other ones and thus causing the Raman bands to be broad [53], [70]. The high temperature line-broadening of CDP was first reported by Romain and Novak [70]. By virtue of the intensive broad band envelope from ~ 2300 to $\sim 3600\text{ cm}^{-1}$ the spectra also indicate a considerable amount of water bound in the melt, even at high temperatures. The salt apparently has a “thirst” against water. The broad envelope band at ~ 2000 to $\sim 3600\text{ cm}^{-1}$ is due to the dynamically disordered hydrogen bond network like in the CDP cubic phase. This structure is thought to be responsible for the high proton conductivity and for the high affinity between the salt and the water. When quenching the melt large crystals resulted, but the quartz or Pyrex glass also tended to develop cracks and to explode. The solid crystals had spectra similar to original CDP and no water soon remained in the gas phase. The easy and fast crystallization means that the water already is much available inside the CDP liquid at high temperature and moving quickly around (superconductivity) because otherwise there would not be time for the observed formation of coarsely grained crystals.

3.4 Conductivity measurements

We determined the conductivity of CsH_2PO_4 at higher temperatures than previously. An experimental series was made with four conductivity cells: One filled with pure CDP and also cells containing CDP with more and less water (a mixture of CDP and frozen H_2O and two mixtures of CsH_2PO_4 and CsPO_3). The compositions are given in Table 2. After adding the chemicals to the cells and sealing under vacuum the compositions are known *at room temperature*. But after heating to higher temperatures various amounts of water are taken up by the solid or lost to the gas phase. The composition of the condensed phases must depend on the amount of water in the gas phase and thus on the temperature. It means that compositions in principle should be corrected at each temperature. Approximate corrected compositions were estimated by use of the ideal gas law.

As an example for cell 1 (pure CDP at e.g. $300\text{ }^\circ\text{C}$, 573 K), the pressure p of water over the salt was approximately 11.2 bar, estimated by use of the results in Figure 6. The volume V was about 12.4 mL, and we can thus estimate how much water (n mol) should be lost to the gas phase: $n = pV / RT = (11.3 \times 0.0124) / (0.083 \times 573)$ mol. This amount of water must be subtracted from the CDP amount and added to the CsPO_3 amount to calculate the corrected composition.

The *formal* composition is conveniently given as the molar composition ratio ($\text{CsPO}_3/\text{H}_2\text{O}$) of added amounts. Thus a molar ratio of 1 would correspond to pure CsH_2PO_4 . A ratio of 2 would be $\text{CsH}_2\text{PO}_4 + \text{CsPO}_3$ (a molar ratio of 1 CsH_2PO_4 to 1 CsPO_3) and so on. For other compositions, the ratio was lower or higher than 1 depending on addition of water or CsPO_3 to the cell, respectively, according to Equation 1.

The steam partial pressures in the cells 1 and 4 were determined from Figure 6 directly, but for cells 2 and 3 the gas pressures needed to be determined by extrapolation / interpolation, see Table 2 and Figure 9.

Table 2. Compositions of the $\text{CsH}_2\text{PO}_4\text{--CsPO}_3\text{--H}_2\text{O}$ salt mixtures in the four conductivity experiments, given formally (total mass added) and with account for evaporated amounts of water at 300 and 400 °C at equilibrium in accordance with Equation (1).

Cell number	Mass of added CDP, g	Mass of added CsPO_3 or H_2O , g	Formal composition ratio $\text{CsPO}_3/\text{H}_2\text{O}$ at 25 °C	Estimated ^a gas pressure in cells, bar		Volumes ^b , mL		Estimated condensed ^c ratio, mol			Figure no.
								$\text{CsPO}_3 / \text{H}_2\text{O}$		CDP: Addition	
				300 °C	400 °C	total	condensed ^c phase	at 300 °C	at 400 °C	at 300 °C	
1	36.527	0	1.00	11.2	49.0	25.0	12.6	1.0187	1.0733	98.17 : 1.83	12
2	21.811	H_2O : 0.288	0.86	12.7	54.9	23.5	8.0	0.8888	0.9913	88.88 : 11.12	15
3	11.374	CsPO_3 : 2.618	1.25	8.5	38.5	17.3	5.3	1.3062	1.4986	76.56 : 23.44	13
4	6.538	CsPO_3 : 5.996	2.00	0.6	7.15	12.9	4.3	2.0027	2.0757	49.93 : 50.07	14

^a See interpolation data in Figure 9.

^b Volumes were estimated from photographs of cells after quenching to room temperature in upright position.

^c Condensed means solid or liquid.

Figure 9. Lines to estimate the water vapor pressure over the condensed “CDP” phases in the conductivity cells. The estimation was based on assumed equilibrium in the cells and the ideal gas law. The vapor pressures p for the formal mole ratio $\text{CsPO}_3 / \text{H}_2\text{O} = 1.0$ (CsH_2PO_4) or 2.0

($\text{CsH}_2\text{PO}_4 + \text{CsPO}_3$) were read off from Figure 6. The vapor pressure for the other compositions were estimated from the linear expressions $p = a - b \times (\text{CsPO}_3 / \text{H}_2\text{O})$ shown, where $(\text{CsPO}_3 / \text{H}_2\text{O})$ is the known overall “formal composition ratio” given in Table 2.

3.4.1 Conductivity results Cell 1. The results for our conductivity cell 1 experiment with pure CDP are shown as open circle points in Figure 10 and Figure 11. These logarithmic plots show the conductivity (left ordinate scale $\log_{10} \sigma$) versus the reciprocal of the absolute temperature T times 1000 (abscissa $1000/T$). The data are detailed in Figure 10 and compared with most results of the literature in Figure 11. The literature data points were obtained by reading values off from highly magnified prints. Some of the prints show different logarithms of σ or σT and for these data we have calculated the corresponding $\log_{10} \sigma$ values for our comparative purpose.

Figure 10. Measured conductivity data (open circles) for pure CDP in cell 1 under its own vapor pressure (from approximately 2 to 49 bar) corresponding to $\text{CsPO}_3/\text{H}_2\text{O}$ mole ratios from 1.000 to 1.0733 in the temperature range of 25–400 °C, deduced from Table 2. The data are compared with previously published data for CDP from Ponomareva et al. [32], [36], [40], [113]–[114], Qing et al. [43], Jensen et al. [41], Ikeda et al. [69], Lavrova et al. [78], Martsinkevich et al. [115], Taninouchi et al. [47], Hatori et al. [116], Muroyama et al. [34], Haile et al. [12], Baranov et al. [7]–[9], [112], Otomo et al. [4], [26], and Ortiz et al. [51], [52]. Coordinates for each literature point were read manually pixel by pixel from expanded plots relatively to the axis values by use of the open source GIMP 2.9.6 software (GNU Image Manipulation Program designed for the GNU Operating System from the Free Software Foundation, Inc. in Boston, MA, USA). The “superprotonic” area of this plot is the upper left quarter where the temperature is above 228 °C and the conductivity above 0.02 S cm^{-1} .

Figure 11. Overview of conductivity data for CDP. Open circles are our cell 1 measurements under its own vapor pressure (from approximately 2 to 49 bar) corresponding to $\text{CsPO}_3/\text{H}_2\text{O}$ mole ratios from 1.000 to 1.0733 deduced from Table 2. The other data are most other previously published conductivity data for samples claimed to be CDP, see Ponomareva et al. [32], [36], [40], [113]-[114], Qing et al. [43], Jensen et al. [41], Ikeda et al. [69], Lavrova et al. [78], Martsinkevich et al. [115], Taninouchi et al. [47], Hatori et al. [116], Muroyama et al. [34], Haile et al. [12], Baranov et al. [7]-[9], [112], Otomo et al. [4], [26], and Ortiz et al. [51], [52]. Coordinates from the literature were read from expanded plots as explained in the caption of Figures 1 and 10 (by use of the GIMP 2.9.6 software). Some of the published plots were showing $\ln \sigma$ or $\log \sigma T$ and these data were converted to the values shown here. The “superprotonic” area of this plot is the upper left corner where $t > 228^\circ\text{C}$ and $\sigma > 0.02 \text{ S cm}^{-1}$.

In Figure 10 – 11 our results are shown for the conductivity of CsH_2PO_4 under its own water pressure which varied from approximately 2 to 49 bar depending on the temperature. Simultaneously the actual $\text{CsPO}_3/\text{H}_2\text{O}$ mole ratios for the composition of the condensed phase was estimated to vary from 1.00 to about 1.02. The free space over the condensed phase (solid or liquid) took up about half of the cell space. When compared to the conductivity results of the literature, see e.g. [12], [40], [43]-[44], [47], [52], [69], [78], [112]-[114], [116], it can be seen that our results are grossly on the same order of magnitude.

Limiting the discussion to the “superprotonic” part of the conductivity range (Figure 10) we see that measurements above ~ 300 °C are not available in prior literature and that the high conductivities that have been reported are leveling off. We think that the explanation is that CsH_2PO_4 - if not confined - decompose into mixtures of ortho-, pyro- and meta-phosphates that become less conducting, the higher the temperature and the lower the water vapor pressure. To maintain a high conductivity apparently requires very high water vapor pressures. These results are of interest because it is the first time that the conductivity of molten CsH_2PO_4 has been obtained. To measure the conductivity of the liquid requires a water pressure up to 49 bar which explains why it has not been done before.

The conductivity points in Figure 10, both for the “superprotonic” part up to the melting point around 345 °C and above under pressure follow approximately linear Arrhenius type curves, meaning that the σ data can be reproduced by eq. (5). The fitting constants are given in Table 3.

$$\text{Log}_{10} \sigma = A - B \times 1000/T \quad (5).$$

This linear dependency follows the usual elementary equation for ionic conductors [117], [118]. Discussion of such and other expressions are given elsewhere [91]. The constant A corresponds to the intercept of the line at $1000/T = 0 \text{ K}^{-1}$ (at infinite temperature). The slope B is related to the activation energy [8], [12]. Clearly the conductivity increases with temperature in the range studied here, and it is higher in the molten state.

Table 3. Conductivity expressions $\text{Log}_{10} (\sigma / (\text{S cm}^{-1})) = A - B \times 1000/T$ for different electrolyte compositions of solid and molten CDP phases, see equation (5). The formal compositions are given in Table 2. The R^2 value approaches 1 for a perfect linear fit.

Formal composition of electrolyte	State	Intercept A	Slope B, K	R^2
Cell 1 (Fig. 12) Pure CDP	Solid	1.87504 ± 0.00674	1.83133 ± 0.00372	0.99976 (60 points)
	Molten	0.34037 ± 0.05035	0.62403 ± 0.0326	0.92648 (30 points)
Cell 2 (Fig. 15), added H_2O 14.42%	Solid	1.60919 ± 0.11759	1.55978 ± 0.06341	0.98693 (9 points)
	Molten	0.32517 ± 0.1647	0.64892 ± 0.10589	0.859 (7 points)
Cell 3 (Fig. 13), added 19.99% of CsPO_3	Solid	4.0734 ± 0.16399	3.0143 ± 0.09121	0.99363 (8 points)
	Molten	1.71515 ± 0.05371	1.53681 ± 0.03435	0.99453 (12 points)
Cell 4 (Fig. 14), added 49.88% of CsPO_3	Solid	4.31843 ± 0.23902	3.22063 ± 0.13147	0.98845 (8 points)
	Molten	2.84835 ± 0.13858	2.48053 ± 0.08807	0.99 (9 points)

Our conductivity data from Figures 10 and 11 are shown in Figure 12 and two lines are fitted to the points for the two different states: The range below 345 °C represents the regime with “superprotonic” conductivity, and at above 345 °C the salt is molten. As indicated by the dashed arrows the measurements were performed progressively in steps of 2 °C, with at least 40 minutes between each measurement. For each measurement series it was experimentally checked that longer time intervals of equilibration gave identical values. The measurements proved to be very reproducible, and the results did not change significantly after cooling and reheating of the cell (down to and above ~220 °C).

Figure 12. Details of measurements of specific electrical conductivity of CsH_2PO_4 (cell 1). We estimate that water has escaped from the condensed phase to form a CDP- CsPO_3 mixture of molar ratio $\text{CDP} : \text{CsPO}_3 = 98.17 : 1.83$ at e.g. 300 °C (see Table 2). Dashed lines with arrows indicate the progression of the measurements, starting with the filled triangles and then heating with the open ones. The length and position of the dashed lines indicate the segment, which was used for fitting. Solid lines show the fitting lines given in Table 3 for the molten ($t > 345$ °C) and the solid ($t < 345$ °C) regimes.

3.4.2 Conductivity results for cells 3 and 4. These cells, 3 and 4, containing new pure CsH_2PO_4 with direct addition of CsPO_3 (Table 2), were made, sealed and examined, in order to study the conductivity of the system as in a situation where more water has been lost, to simulate CDP measurements in open cells. In this way data were obtained proving the decrease in conductivity of $\text{CsH}_2\text{PO}_4 - \text{CsPO}_3$ condensed mixtures when water is lost. The data are presented in Figures 13 and 14. The studied compositions and temperature ranges are specified in the Figure captions and Table 2. The fitting results are reported in Table 3.

Theoretically the mixture in Figure 14 should give $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$, but the conversion is probably limited because CsPO_3 is a stable compound (m.p. around 735°C [47] [55] [119]) and it does not dissolve easily. Two supplementary simple ampoules were made with CsH_2PO_4 : $\text{CsPO}_3 = 50 : 50$ and $60 : 40$ mol%. Based on separate X-ray diffraction observations we estimate a solubility of CsPO_3 at around 60:40 mol % on the CDP: CsPO_3 basis at 400°C and a *post mortem* proven presence of a $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ phase [120], [121].

3.4.3 Conductivity results Cell 2. We also made a cell 2 containing extra water, and the conductivity data for that cell 2 is shown in Figure 15. This figure shows conductivity measurements with water added to the CsH_2PO_4 . The excessive amount of water was added as ice, weighed and frozen with liquid nitrogen as described in [80]. Studied compositions and temperature ranges are specified in the Figure captions. The water vapor pressure of this experiment depended markedly on the temperature and there must have been a considerable risk of cell explosion at the elevated temperatures [6].

Figure 13. Measured specific electrical conductivity of the CDP- CsPO_3 mixture of cell 3 of estimated molar ratio CDP : CsPO_3 at 300°C of 76.56 : 23.44 (see Table 2). Solid lines show the fitting lines given in Table 3 for the molten ($t > \sim 325^\circ\text{C}$) and the solid ($t < \sim 325^\circ\text{C}$) regimes. Dashed lines with arrows show progression of measurements, starting with the filled triangles to premelt the system up to $\sim 400^\circ\text{C}$ and then cooling, followed by re-warming with the open ones, and finally second cooling with the open squares.

Figure 14. Measurement of specific electrical conductivity of a saturated CDP-CsPO₃ mixture (cell 4) vs. temperature, having an estimated CDP : CsPO₃ molar ratio of 49.93 : 50.07 at 300 °C, (see Table 2). Dashed arrows show progression of measurements. Solid lines show fitted linear expressions (Table 3).

Figure 15. Specific electrical conductivity measured vs. temperature for cell 2, a CDP-H₂O mixture of an estimated molar ratio CDP : H₂O at 300 °C of 88.88 : 11.12 (see Table 2). Solid lines represent linear fittings (Table 3). Dashed arrows indicate how progression of measurements went on. The reason for the dip in conductivity at the melting point is not known.

As expected the conductivity increases with temperature in our closed cells (slope B in positive in Table 3). It is however clear that in order to obtain the preferred high conductivity, the water vapor pressure has to be *much* higher than the 0.3 – 0.4 bar often mentioned in the previous literature [12]. If the water pressure is low water tends to leave the CDP electrolyte to form CsPO_3 via eq. (1). The result of adding CsPO_3 to CsH_2PO_4 is shown in Figure 13 and 14, and the conductivity clearly decreased, the more the more CsPO_3 was added.

3.5 Conductivity prediction in the $\text{CsH}_2\text{PO}_4 - \text{CsPO}_3 - \text{H}_2\text{O}$ system

Obviously one would desire to predict the conductivity as a function of temperature as well as compositions. We present here a way to perform such a prediction:

1. First perform linear fittings to calculate values of A and B in Eq. (5) on the basis of the data in Figures 10-13 (shown in Table 3).
2. Then from the values of A and B construct a diagram of the conductivity as a function of composition and temperature, as shown in Figure 16.

In Figure 16 trends of changes in conductivity, depending on the composition of the melt, are shown projected to "0" in $\text{CsPO}_3/\text{H}_2\text{O}$ content ratio. Non-linear polynomial curve fitting was applied to make projections to the "0,0" point. The equation used was a cubic type of function, eq. (6),

$$\sigma = A_1(t) + B_1 \times X + C_1 \times X^2 \quad (6)$$

where σ is the conductivity in S cm^{-1} , t is the temperature in $^\circ\text{C}$ and X is the total molar content ratio of $\text{CsPO}_3/\text{H}_2\text{O}$. The resulting parameters for fitting this model to our measured data at different temperatures and compositions can be found in Table 4. It must be emphasised that measurements of the conductivity in the region for molar ratios of $\text{CsPO}_3/\text{H}_2\text{O}$ below the value 1 are limited due to the practical problem that quartz cells in the used technique cannot stand pressures much higher than what we used. This is why we only have the point at the origin.

It was also an objective to determine analytical expressions for the conductivity versus temperature. Such information is essential for the optimization of the high temperature water electrolysis application of the electrolyte.

Figure 16. Dependence of the conductivity of melts in the $\text{CsH}_2\text{PO}_4 - \text{CsPO}_3 - \text{H}_2\text{O}$ electrolyte as a function of composition at different temperatures, projected to “0” in the $\text{CsPO}_3/\text{H}_2\text{O}$ content.

Table 4. Fitting parameters, of use for data in Figure 16, obtained at different temperatures.

Temperature	250 °C	300 °C	350 °C	400 °C
	Value and Standard error	Value and Standard error	Value and Standard error	Value and Standard error
$A_1(t)$	0.00193 ± 0.01236	$-6.04037 \times 10^{-4} \pm 0.0132$	0.00273 ± 0.01961	-0.00163 ± 0.02333
$B_1(t)$	0.0493 ± 0.02476	0.10242 ± 0.02635	0.35849 ± 0.03894	0.41629 ± 0.04544
$C_1(t)$	-0.022 ± 0.01175	-0.03847 ± 0.01252	-0.16125 ± 0.01848	-0.16507 ± 0.02111
Reduced χ^2 ^a	1.55066×10^{-4}	1.76568×10^{-4}	3.89456×10^{-4}	5.50744×10^{-4}
Adjusted R^2 ^a	0.3293	0.79802	0.95392	0.95628

^aHow well a model describes a set of observations is described as a goodness of fit. The reduced chi-square value (χ^2) is often used as a goodness of fit parameter. The adjusted R-square value (R^2) accounts for the goodness of fit when several parameters are in play.

4. Proof of Water Electrolysis by Raman Spectroscopy

It was considered important to demonstrate experimentally that water electrolysis indeed could be done. We made an electrolysis cell as described in the experimental section, filled it with CsH_2PO_4 and N_2 , and heated it to a high temperature ($\sim 355^\circ\text{C}$) to let a melt be formed. It proved possible to successfully supply potential differences of about 1.6 – 2.2 V to the cell. This caused currents of about 0.1 mA to pass through the cell *via* its two coiled platinum wire electrodes (areas $\sim 2.5\text{ cm}^2$). Electrolysis was performed 8 times in periods of each 800 seconds duration. Resistances were about $20\ \Omega$ and current densities were on the order of 40 mA/cm^2 . When currents were passing through the CDP liquid, formation of small bubbles could be seen at the electrodes, with more gas coming from the negative electrode, and more the higher the current. Gas phase Raman spectra were recorded in between the electrolysis periods, see Figure 17. It was difficult to get good gas spectra because of the protective net and the short path length of the cell, but without any doubt the spectra showed formation of new characteristic sharp bands. As expected [6] the bands are assignable to H_2 hydrogen S rotational bands (up to 1500 cm^{-1}), and oxygen and hydrogen rot-vib Q-branch bands at $\sim 1555\text{ (O}_2\text{)}$ and $\sim 4156\text{ cm}^{-1}\text{ (H}_2\text{)}$, in addition to gas phase bands from the formed water and the added N_2 reference, see also Figure 5 and Table 5 [97]-[98], [100], [122]-[123]. These bands were not present before start of the electrolysis. In this way the splitting of water, into 2 H_2 and O_2 molecules can indeed be demonstrated. No other gases seemed to appear during the electrolysis, but a weak CO_2 signal was seen, possibly originating from soot from the welding of Pt-electrodes to the W-pins.

The amount of H_2 relative to O_2 seems to be near the expected 2 to 1 ratio. The O_2 signal is being so small in Figure 17 because of the known small Raman scattering cross section of O_2 relative to that of H_2 . Note that the situation is complicated by the hydrogen presence as both para- H_2 and ortho- H_2 , see e.g. [124].

The relative stability of the $2\text{ H}_2 + \text{O}_2$ molecular mixture towards reformation of water, for 14 hours without electrolysis at a temperature of 285°C , possibly is due to lack of gas contact with the platinum electrodes which were covered by the solidified melt. Simultaneous presence of water molecules in the gas and in the superconductive phase might reduce the speed of the direct recombination reaction $2\text{ H}_2 + \text{O}_2 \rightarrow 2\text{ H}_2\text{O}$. And if this reaction occurs, the only thing happening will be formation of water vapor that adds not much new to the spectra. However, the observed simultaneous presence of H_2 and O_2 molecules in the gas phase and thus the water splitting remains a fact.

Figure 17. From below: Four typical Raman spectra of the gas phase of the electrolysis cell with CDP and 0.5 bar of N_2 reference gas, obtained during electrolysis of CsH_2PO_4 at 355 °C. The cell sitting in its holder after the experiment is shown in the inserted photo. The blue color is thought to come from W(V,VI)-compounds formed from the pins during the electrolysis. The top spectrum shows the gas phase after stop of electrolysis and leaving the cell at 285 °C over-night. The long blue spectrum shows the gas after cooling to ~185 °C. The pronounced bands are labeled with wavenumber values and are due to H_2 rotational transitions, and CO_2 , O_2 , N_2 , H_2O and H_2 vibrations. The gas spectra are weak because of the protective steel net around the experiment. A 532 nm laser running at ~2 W was used during recording of the spectra.

Table 4. Raman bands (cm^{-1}) observed in the gas phase during and after electrolysis.

This work at high temp. / cm^{-1}	Literature at room temp.	References	Assignment
355.6	354.4	[122], [123], [125]	para H_2 rot 0 $\rightarrow$ 2
588	587.0	[122], [123], [125]	ortho H_2 rot 1 $\rightarrow$ 3
815	814.4	[122], [123], [125]	para H_2 rot 2 $\rightarrow$ 4
1035	1034.7	[122], [123], [125]	ortho H_2 rot 3 $\rightarrow$ 5
1246	1246.1	[123], [125]	para H_2 rot 4 $\rightarrow$ 6
1447	1447.3	[123], [125]	ortho H_2 rot 5 $\rightarrow$ 7
~ 1486	~ 1489	[97], [98], [100]	Strongst CO_2 line, formed from C + O_2
~ 1555	~ 1555	[97], [98], [100]	Q branch of oxygen (O_2)
~ 2331	~ 2331	[97], [98], [100]	Q branch of added N_2
~ 3655	~ 3655	[97], [98], [100]	Q branch ν_1 sym str band of H_2O
~ 4073	4073.7	[125]	rot-vib Q branch H_2 5 $\rightarrow$ 5
~ 4103	4102.6	[125]	rot-vib Q branch H_2 4 $\rightarrow$ 4
~ 4126	4125.9	[125]	rot-vib Q branch H_2 3 $\rightarrow$ 3
~ 4144	4143.5	[125]	rot-vib Q branch H_2 2 $\rightarrow$ 2
~ 4156	4155.2	[125]	rot-vib Q branch H_2 1 $\rightarrow$ 1
~ 4163	4161.2	[125]	rot-vib Q branch H_2 0 $\rightarrow$ 0

Conclusions

CsH_2PO_4 (CDP) was prepared and investigated for use as a rather high-temperature liquid electrolyte for splitting water to hydrogen and oxygen. The melting point of our CDP was found to be at around 346°C , confirming several quite old careful measurements by e.g. Rapoport et al. [19]. Also many researchers have previously claimed CDP to be dependent on the surrounding partial pressure of water, and this tendency was confirmed in our experiments.

We have determined the vapor pressure above CDP by means of a recently developed Raman method. The pressure is considerable at higher temperatures, reaching perhaps values as high as 23 bar at 355°C (Figure 6). These pressures are considerably higher than claimed in previous reports. It was therefore realized that experiments must be conducted in closed cells or under otherwise confined circumstances.

The pressure of water above CsH_2PO_4 at elevated temperatures is thus much higher than earlier thought. Along this rationale we have determined the conductivity of CDP, and attempted to obtain reliable corrected data for the conductivity of CDP at very high temperatures, up to about 400°C (Figure 10-11). At these rather high temperatures we have obtained record high conductivities of molten CDP approaching values of perhaps $\sim 0.3 \text{ S cm}^{-1}$, when saturated under its own vapor pressure or confined.

These conductivity values cannot be measured in an open system and sealed systems had to be used. In order to make accurate measures of e.g. the electrical conductivity the salt has to be kept under its own vapor pressure to avoid decomposition into mixtures of pyro- and orthophosphates.

Furthermore the conductivity of the salt - in its superprotonic and molten states - does not vary much if a moderate part of the orthophosphate is replaced with pyrophosphate. In the superprotonic and molten states under pressure the ionic structure may not be affected very

much, and the protons may be travelling around very fast. If the salt loses water it will turn into a mixture of orthophosphate and pyrophosphate from which metaphosphates eventually will separate out and at even higher water losses the conductivity will be markedly reduced (figure 16).

We have - like previously for the KH_2PO_4 system [5], [6] - used Raman spectroscopy to demonstrate that electrolysis is possible whereby water molecules can be split to form only hydrogen and oxygen. We conclude that a new potentially high efficiency electrolyte has been found for intermediate temperature pressurized water electrolysis (at $\sim 350^\circ\text{C}$), with great perspectives for development of efficient water electrolysis. At such high temperatures it should be possible to find cheap and effective electrodes.

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Rapoport, 1978

I-II interphase

X	Y
0.24254	228.2727
1.43657	231
1.92164	233.8182
3.48881	236.4546
3.30224	238.6364
5.89552	242.3636
7.22015	247
7.0709	248.8182
7.74254	254.2727
9.19776	254.2727
9.12313	256.6364
9.5709	258.4546
11.10075	261.1818
11.10075	263.3636

Liq-I interphase

X	Y
0	346.0909
2.25746	366.5455
1.97761	369.1818
3.69403	377.3636
4.5709	385.8182
5.52239	392.8182
6.25	391.6364
6.58582	393.8182
6.21269	396.5455
6.69776	402
8.60075	409.3636
8.22761	413.4546
8.69403	414.0909
9.29104	417.8182
9.8694	421.5455
10.29851	421.5455
11.77239	426.8182
11.66045	429.5455
12.14552	431.0909
12.42537	429.9091
12.89179	436.4546
13.28358	434
13.58209	438.3636
14.45896	436.9091
14.8694	435.4546
15.20522	441.2727
15.52239	439.0909

FIG. 4. The phase diagram of CsH_2PO_4 to 45 kbar.

Data from this paper, Fig.10-11

1000/T	log conductivity
1.61838	-0.87211
1.6129	-0.60916
1.60449	-0.6308
1.60346	-0.62979
1.60888	-0.63975
1.60862	-0.64074
1.61394	-0.64756
1.61303	-0.64756
1.61303	-0.65045
1.6129	-0.65045
1.61838	-0.65807
1.61852 --	
1.62404	-0.66926
1.62893	-0.67656
1.62866	-1.07013
1.62959	-1.09569
1.63599	-1.11192
1.64029	-1.12371
1.64568	-1.13519
1.65139	-1.14821
1.65673	-1.15967
1.66223	-1.17025
1.66764	-1.18057
1.67364	-1.19287
1.67912	-1.20268
1.68492	-1.21332
1.69047	-1.22372
1.69635	-1.23486
1.70213	-1.24525
1.70809	-1.25539
1.71394	-1.26623
1.71954	-1.2768
1.72577	-1.28757
1.7319	-1.29851
1.73792	-1.30918
1.74414	-1.32083
1.74993	-1.33097
1.75623	-1.34206
1.76196	-1.35287
1.76866	-1.3649
1.77525	-1.37625
1.78174	-1.38766
1.78779	-1.39946
1.7942	-1.41096
1.80083	-1.42345

1.80734	-1.43559
1.81389	-1.44679
1.82083	-1.45681
1.82083	-1.4601
1.82749	-1.47244
1.83436	-1.48499
1.84111	-1.49583
1.84809	-1.51013
1.8546	-1.52165
1.86168	-1.53439
1.86846	-1.54676
1.87564	-1.55974
1.88271	-1.57281
1.89	-1.58749
1.89717	-1.59846
1.90422	-1.61126
1.91168	-1.62472
1.9192	-1.63857
1.9266	-1.65199
1.93405	-1.66556
1.94156	-1.67908
1.94913	-1.69254
1.95695	-1.70796
1.96464	-1.72074
1.97239	-1.7489
1.9802	-1.74951
1.98807	-1.76336
1.99601	-1.77865
2.00421	-1.79286
2.01207	-1.80796
2.02041	-3.29634
2.01654	-3.29634
2.00823	-3.29634
1.99402	-3.29634
1.97883	-3.29634
1.97883	-3.29634
2.0002	-3.29634
2.0014	-3.29634
2.0018	-3.29634
1.99322	-3.29634
1.97785	-3.29634
1.96967	-1.73536
1.96986	-1.73631
1.93555	-1.66704
1.89825	-1.59716
1.86098	-1.53162
1.86324	-1.53263

1.85598	-1.51906
1.84911	-1.5064
1.8423	-1.49363
1.83554	-1.48132
1.82849	-1.46337
1.82183	-1.45471
1.81472	-1.44123
1.80799	-1.42988
1.80148	-1.41758
1.79485	-1.40559
1.78875	-1.3936
1.78237	-1.38199
1.77573	-1.37043
1.76913	-1.3593
1.76243	-1.34788
1.75639	-1.33655
1.74993	-1.32694
1.74383	-1.31712
1.73807	-1.30622
1.73175	-1.2946
1.72563	-1.28356
1.71984	-1.27315
1.71394	-1.26202
1.7078	-1.25059
1.70184	-1.24033
1.69607	-1.22983
1.69019	-1.21907
1.68449	-1.20963
1.6787	-1.1978
1.67294	-1.18732
1.66722	-1.17601
1.66154	-1.16558
1.6559	-1.15668
1.65057	-1.14515
1.64514	-1.13393
1.63948	-1.12757
1.63399	-1.1172
1.63132	-1.10926
1.62866	-1.10252
1.62575	-1.09775
1.62285	-1.08874
1.62022	-1.07953
1.61773	-0.9591
1.61329	-0.67836
1.6072	-0.66556
1.60192	-0.6637
1.59655	-0.66183

1.59172	-0.65807
1.58655	-0.65618
1.5814	-0.64659
1.57604	-0.63877
1.57109	-0.63679
1.56629	-0.6328
1.5614	-0.62878
1.5563	-0.62268
1.55171	-0.61856
1.54655	-0.61441
1.54202	-0.61232
1.53704	-0.61021
1.53221	-0.6081
1.52765	-0.60384
1.52765	-0.60384
1.52277	-0.61441
1.52277	-0.61441
1.51826	-0.61441
1.51343	-0.61021
1.50898	-0.6081
1.50444	-0.60384
1.49993	-0.59954
1.49432	-0.59301
1.49098	-0.59081
1.48699	-0.59301
1.48236	-0.59081

Ponamoreva, 2017

X axis	Y axis
1000/T	log sigma
1.95833	-1.67411
1.96792	-1.69196
1.98162	-1.76339
1.98984	-1.78125
1.99897	-1.74554
2.00628	-1.76339
2.01724	-1.78125
2.02683	-1.79911
2.02957	-1.83482
2.03733	-1.81696
2.05833	-1.95982
2.06929	-2.17411
2.08025	-2.51339
2.09121	-2.92411
2.10217	-3.74554
2.11313	-5.64137
2.12409	-6.00149
2.13642	-6.06994
2.14737	-6.14137
2.17066	-6.26637
2.20628	-6.4628
2.24463	-6.67708
2.28299	-6.8378
2.34874	-7.17708
2.36381	-7.24851
2.40628	-7.44494

Fig. 2. Temperature dependencies of conductivity for CsH₂PO₄ (1) and (1 - x)CsH₂PO₄ - xH₃PO₄ at x = 0.01 (2); 0.03 (3); 0.05 (4) (cooling regime, 1 °C·min⁻¹ in air, RH = 15%).

Qing, 2015

X axis

1000/T

1.84363

1.8816

1.95118

2.0342

2.12005

2.21344

2.32123

2.43373

2.56439

Y axis

log sigma

-1.57176

-1.63426

-1.75694

-2.75231

-3.62269

-4.0787

-4.3588

-4.56481

-4.53009

Fig. 7. Temperature dependence of the conductivity of a pure CsH₂PO₄ pellet electrolyte, CsH₂PO₄/SiO₂-C composite electrolyte with 80 wt% CsH₂PO₄, and the CsH₂PO₄/epoxy composite electrolytes with different CsH₂PO₄ contents, under 30% H₂O/Ar atmosphere.

Jensen, 2014

X axis	Y axis
1000/T	log sigma
1.82468	-2.68163
1.8417	-2.33265
1.87617	-2.09796
1.89362	-2.05918
1.91191	-2.01633
1.93021	-2.08776
1.98426	-5.53673
1.98766	-5.57551
2.00851	-5.66531
2.02809	-5.75918
2.04936	-5.84286
2.07021	-5.93061
2.11489	-6.09796
2.20681	-6.47143
2.25702	-6.62449

Figure 4. Temperature dependence of conductivity of CsH₂PO₄, 6CsH₂PO₄/1ZrO₂ and 2CsH₂PO₄/1ZrO₂ samples. Air was saturated with water at 50°C.

Ikeda, 2014

X axis	Y axis	
1000/T	sigma	log sigma
1.864	0.028	-1.553
1.899	0.024	-1.616
1.935	0.021	-1.680
1.974	0.018	-1.748
1.997	0.016	-1.790
2.007	0.016	-1.810
2.013	0.015	-1.824

Fig. 15 Arrhenius representation of the conductivities of cubic $\text{Cs}_{1-x}\text{Rb}_x\text{H}_2\text{PO}_4$ and $\text{Cs}_{1-x}\text{K}_x\text{H}_2\text{PO}_4$ as functions of temperature.

Ponomareva, 2014

X axis	Y axis
1000/T	log sigma
1.826	-1.512
1.847	-1.556
1.866	-1.590
1.884	-1.632
1.904	-1.672
1.924	-1.708
1.943	-1.751
1.963	-1.793
1.985	-1.835
2.007	-1.877
2.028	-1.918
2.040	-1.951
2.050	-2.476
2.059	-2.949
2.073	-3.195
2.084	-3.668
2.119	-4.649
2.134	-5.097
2.143	-5.691
2.152	-6.258
2.167	-6.410
2.193	-6.476
2.218	-6.613
2.244	-6.715
2.272	-6.816
2.299	-6.909
2.327	-7.036
2.356	-7.112
2.387	-7.220
2.417	-7.355
2.448	-7.433
2.481	-7.611
2.512	-7.761
2.547	-7.865
2.582	-8.008
2.617	-8.127
2.653	-8.319
2.690	-8.480
2.729	-8.590
2.769	-8.742
2.810	-8.871
2.852	-8.956

Fig. 8. Arrhenius plots of conductivity for (1) CsH₂PO₄ and CsH₂PO₄-A composites: A = (2) SiO₂ [8], (3) SiO₂-0.07P₂O₅, and (4) SiO₂-0.25P₂O₅ [9] (relative humidity of 0.6 mol % H₂O).

Lavrova, 2013

Fig. 1. Temperature dependences of conductivity of the $(1-x)\text{CsH}_2\text{PO}_4-x\text{SrZrO}_3$ composites with different composition; the heating mode; 2°C/min ; air. For comparison, the data for the first heating of the $0.9\text{CsH}_2\text{PO}_4-0.1\text{SrZrO}_3$ sample are shown.

Martsinkevich, 2012

X axis	Y axis
1000/T	log sigma
1.957	-1.667
1.967	-1.698
1.986	-1.724
1.996	-1.741
2.006	-1.765
2.016	-1.782
2.026	-1.805
2.036	-1.827
2.057	-1.963
2.068	-2.180
2.079	-2.517
2.090	-2.927
2.101	-3.748
2.112	-5.636
2.123	-6.013
2.134	-6.082
2.146	-6.156
2.169	-6.278
2.205	-6.464
2.242	-6.674
2.280	-6.844
2.347	-7.173
2.361	-7.252
2.403	-7.450

Fig. 6. Proton conductivity of $\text{Cs}_{1-x}\text{K}_x\text{H}_2\text{PO}_4$; on cooling, 1–2 °C/min; in air.

Ponomareva, 2008, Fig. 2

Ponomareva, 2008, Fig. 3

Ponomareva, 2008, Fig. 3

X axis	Y axis			
1000/T	log sigma T	T	log T	log sigma
1.869	0.763	535.011	2.728	-1.965
1.871	0.911	534.377	2.728	-1.816
1.873	1.062	533.774	2.727	-1.666
1.876	1.141	533.183	2.727	-1.586
1.878	1.165	532.503	2.726	-1.561
1.880	1.163	531.965	2.726	-1.562
1.882	1.157	531.368	2.725	-1.568
1.884	1.153	530.772	2.725	-1.572
1.886	1.149	530.266	2.724	-1.576
1.888	1.145	529.525	2.724	-1.579
1.890	1.140	528.963	2.723	-1.584
1.893	1.134	528.235	2.723	-1.588
1.895	1.131	527.842	2.723	-1.591
1.897	1.125	527.195	2.722	-1.597
1.899	1.121	526.560	2.721	-1.600
1.901	1.117	525.994	2.721	-1.604
1.903	1.114	525.410	2.720	-1.606
1.906	1.110	524.769	2.720	-1.610
1.908	1.106	524.227	2.720	-1.614
1.909	1.103	523.763	2.719	-1.617
1.911	1.098	523.165	2.719	-1.620
1.914	1.093	522.395	2.718	-1.625
1.916	1.090	521.857	2.718	-1.628
1.918	1.086	521.340	2.717	-1.632
1.920	1.081	520.795	2.717	-1.636
1.922	1.076	520.232	2.716	-1.640
1.925	1.072	519.557	2.716	-1.644
1.927	1.068	519.015	2.715	-1.647
1.929	1.064	518.381	2.715	-1.650
1.931	1.060	517.851	2.714	-1.654
1.934	1.054	517.106	2.714	-1.659
1.936	1.051	516.467	2.713	-1.662
1.938	1.047	516.026	2.713	-1.665

Fig. 2. Temperature dependence of conductivity of CsH₂PO₄ at the heating rate of 1.2 K hr^{-1} . (a) Under Ar - 18 mol% H₂O atmosphere. (b) Under Ar - 23 mol% H₂O atmosphere.

Taninouchi, 2008, 23mol% H2O

X axis	Y axis			
1000/T	log sigma T	T	log T	log sigma
1.844	1.333	542.326	2.734	-1.401
1.846	1.306	541.675	2.734	1.428
1.849	1.294	540.849	2.733	1.439
1.851	1.278	540.376	2.733	1.454
1.852	1.260	539.832	2.732	1.472
1.854	1.245	539.288	2.732	1.487
1.857	1.240	538.644	2.731	1.492
1.859	1.237	538.011	2.731	1.494
1.861	1.232	537.431	2.730	1.498
1.863	1.229	536.913	2.730	1.501
1.865	1.223	536.254	2.729	1.507
1.867	1.219	535.637	2.729	1.510
1.871	1.213	534.478	2.728	1.515
1.873	1.209	533.855	2.727	1.519
1.875	1.204	533.293	2.727	1.523
1.877	1.200	532.643	2.726	1.526
1.880	1.195	531.995	2.726	1.531
1.881	1.191	531.497	2.726	1.534
1.884	1.187	530.811	2.725	1.538
1.886	1.184	530.266	2.724	1.541
1.888	1.179	529.594	2.724	1.545
1.891	1.174	528.864	2.723	1.549
1.893	1.170	528.185	2.723	1.553
1.895	1.166	527.665	2.722	1.556
1.897	1.161	527.156	2.722	1.561
1.899	1.158	526.638	2.722	1.563
1.901	1.154	526.082	2.721	1.567
1.903	1.150	525.498	2.721	1.570
1.905	1.146	524.954	2.720	1.574
1.907	1.143	524.372	2.720	1.577
1.909	1.138	523.889	2.719	1.581
1.911	1.134	523.300	2.719	1.585
1.913	1.130	522.741	2.718	1.588
1.915	1.125	522.164	2.718	1.593
1.918	1.121	521.474	2.717	1.596
1.920	1.117	520.786	2.717	1.600
1.923	1.112	520.099	2.716	1.604
1.926	1.106	519.186	2.715	1.610
1.930	1.097	518.040	2.714	1.618
1.937	1.084	516.279	2.713	1.629

Fig. 2. Temperature dependence of conductivity of CaH_2PO_4 at the heating rate of 1.2 K hr^{-1} . (a) Under $\text{Ar}-18 \text{ mol}\%$ H_2O atmosphere. (b) Under $\text{Ar}-23 \text{ mol}\%$ H_2O atmosphere.

Hatori, 2007

X axis		Y axis	
T	1000/T	sigma	log sigma
300.510	3.328	0.000	-7.090
302.420	3.307	0.000	-7.141
310.270	3.223	0.000	-7.136
316.290	3.162	0.000	-7.148
321.820	3.107	0.000	-7.142
329.310	3.037	0.000	-7.180
338.150	2.957	0.000	-7.214
341.530	2.928	0.000	-7.203
346.690	2.884	0.000	-7.203
351.600	2.844	0.000	-7.221
355.960	2.809	0.000	-7.234
361.550	2.766	0.000	-7.237
366.400	2.729	0.000	-7.234
373.220	2.679	0.000	-7.234
381.020	2.625	0.000	-7.225
388.940	2.571	0.000	-7.168
394.960	2.532	0.000	-7.152
399.070	2.506	0.000	-7.122
404.230	2.474	0.000	-7.093
408.770	2.446	0.000	-7.047
412.400	2.425	0.000	-7.007
416.760	2.399	0.000	-6.963
420.380	2.379	0.000	-6.910
423.390	2.362	0.000	-6.870
426.770	2.343	0.000	-6.818
430.640	2.322	0.000	-6.752
433.890	2.305	0.000	-6.693
437.510	2.286	0.000	-6.629
441.320	2.266	0.000	-6.556
445.680	2.244	0.000	-6.476
449.740	2.224	0.000	-6.401
454.160	2.202	0.000	-6.314
459.320	2.177	0.000	-6.213
461.890	2.165	0.000	-6.159
466.750	2.142	0.000	-6.064
470.920	2.124	0.000	-5.983
474.670	2.107	0.000	-5.896
479.340	2.086	0.000	-5.804
484.630	2.063	0.000	-5.701
487.750	2.050	0.000	-5.593
490.700	2.038	0.000	-5.499
494.560	2.022	0.000	-5.337
497.140	2.012	0.000	-5.197
499.850	2.001	0.000	-5.032

Fig. 1. Temperature dependence of electrical conductivity.

502.860	1.989	0.000	-4.851
505.930	1.977	0.000	-4.636
507.280	1.971	0.000	-4.503
508.630	1.966	0.000	-4.371
509.790	1.962	0.000	-4.241
511.270	1.956	0.000	-4.040
511.640	1.954	0.000	-3.932
512.130	1.953	0.000	-3.790
512.620	1.951	0.001	-3.271
513.110	1.949	0.008	-2.119
513.470	1.948	0.015	-1.839
514.220	1.945	0.019	-1.730
517.160	1.934	0.020	-1.694
520.360	1.922	0.021	-1.678
523.730	1.909	0.022	-1.652
527.300	1.896	0.023	-1.630
530.120	1.886	0.024	-1.614
533.008	1.876	0.025	-1.604

For Peer Review

Muroyama, 2007

X axis	Y axis
1000/T	log sigma
1.824	-1.463
1.889	-1.594
1.956	-1.704
2.026	-4.665
2.099	-4.776
2.181	-4.804
2.271	-4.886
2.360	-4.984
2.477	-5.086
2.599	-5.204

Fig. 3. Temperature dependence of the conductivity for MH_2PO_4 and $\text{MH}_2\text{PO}_4/\text{SiP}_2\text{O}_7$ -based composites (molar ratio: 1/2, $\text{M}=\text{K}, \text{Rb}, \text{Cs}$) under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere in the heating process.

Ponomareva, 2007

X axis	Y axis
1000/T	log sigma
1.909	-1.879
1.915	-1.898
1.934	-1.944
1.954	-1.972
1.971	-1.991
1.990	-2.019
2.032	-2.028
2.052	-2.056
2.074	-2.092
2.113	-2.138
2.141	-2.269
2.155	-2.464
2.163	-2.707
2.174	-3.079
2.186	-3.452
2.200	-4.363
2.211	-4.932
2.222	-5.435
2.236	-5.759
2.262	-5.862
2.286	-5.927
2.314	-6.280
2.325	-6.318
2.340	-6.368
2.356	-6.411
2.368	-6.458
2.379	-6.495
2.398	-6.522
2.414	-6.531

Fig. 1. The temperature dependencies of the conductivity of polycrystalline CsH_2PO_4 and $(1-x)\text{CsH}_2\text{PO}_4-x\text{SiO}_2$ composites with different SiO_2 content ($S_{\text{sp}} = 300 \text{ m}^2/\text{g}$, cooling regime $2\text{K}/\text{min}$, H_2O partial pressure $\sim 0.6 \text{ mol\%}$ in air).

Haile, 2006-2007

X axis	Y axis			
1000/T	log sigma T	T	log T	log sigma
2.150	-3.276	465.092	2.668	-5.943
2.142	-3.186	466.880	2.669	-5.855
2.135	-3.010	468.382	2.671	-5.680
2.130	-2.872	469.438	2.672	-5.543
2.126	-2.548	470.449	2.673	-5.221
2.122	-2.359	471.362	2.673	-5.032
2.117	-1.958	472.381	2.674	-4.633
2.113	-0.667	473.302	2.675	-3.342
2.108	0.333	474.330	2.676	-2.343
2.105	0.587	475.052	2.677	-2.090
2.101	0.683	476.035	2.678	-1.995
2.100	0.705	476.242	2.678	-1.973
2.086	0.724	479.377	2.681	-1.956
2.078	0.744	481.278	2.682	-1.939
2.069	0.756	483.407	2.684	-1.928
2.061	0.785	485.232	2.686	-1.901
2.049	0.811	488.159	2.689	-1.878
2.040	0.830	490.130	2.690	-1.860
2.031	0.846	492.283	2.692	-1.846
2.023	0.875	494.400	2.694	-1.819
2.015	0.891	496.309	2.696	-1.805
2.007	0.907	498.176	2.697	-1.790
1.998	0.926	500.401	2.699	-1.773
1.987	0.952	503.166	2.702	-1.750
1.979	0.962	505.378	2.704	-1.742
1.972	0.981	507.019	2.705	-1.724
1.962	0.990	509.621	2.707	-1.717
1.952	1.022	512.370	2.710	-1.687
1.942	1.045	515.027	2.712	-1.667
1.930	1.054	518.141	2.714	-1.660
1.923	1.087	520.052	2.716	-1.630
1.915	1.093	522.103	2.718	-1.625
1.907	1.106	524.421	2.720	-1.614

Fig. 4 Conductivity of polycrystalline CsH_2PO_4 under humidified air ($p(\text{H}_2\text{O}) = 0.4 \text{ atm}$) for two heating and cooling cycles.

Baranov, 2005

X axis	Y axis
1000/T	log sigma
2.499	-6.308
2.487	-6.308
2.442	-6.263
2.403	-6.263
2.357	-6.220
2.329	-6.181
2.307	-6.150
2.269	-6.031
2.244	-5.959
2.225	-5.900
2.174	-5.704
2.138	-5.582
2.123	-5.527
2.092	-5.418
2.076	-5.353
2.066	-5.308
2.056	-5.270
2.019	-5.095
2.007	-5.041
2.004	-5.019
1.997	-4.959
1.994	-4.900
1.992	-4.850
1.985	-4.654
1.985	-4.153
1.984	-3.854
1.983	-3.520
1.983	-3.131
1.982	-2.921
1.981	-2.828
1.981	-2.718
1.980	-2.470
1.979	-2.294
1.978	-2.181
1.977	-2.091
1.976	-2.017
1.974	-1.945
1.972	-1.866
1.971	-1.814
1.970	-1.728
1.967	-1.580
1.965	-1.523
1.958	-1.487
1.955	-1.487

Fig. 2. The temperature dependence of the ac conductivity in $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ mixed crystals at 1 MHz.

1.947	-1.473
1.943	-1.470
1.938	-1.463
1.918	-1.470
1.914	-1.470
1.910	-1.473
1.928	-1.613
1.937	-1.659
1.942	-1.690
1.945	-1.716
1.949	-1.747
1.953	-1.785
1.957	-1.835
1.958	-1.866
1.959	-2.396
1.959	-2.706
1.959	-2.752
1.959	-2.816
1.959	-2.943
1.959	-2.986
1.967	-3.017
1.976	-3.048
1.988	-3.095
1.999	-3.136
2.010	-3.162
2.025	-3.203
2.037	-3.234
2.045	-3.248
2.049	-3.258
2.056	-3.270
2.059	-3.279
2.063	-3.294
2.073	-3.317
2.077	-3.310
2.082	-3.329
2.088	-3.341
2.100	-3.363
2.102	-3.370
2.106	-3.427
2.107	-3.647
2.108	-3.938
2.109	-4.220
2.110	-4.527
2.112	-4.938
2.115	-5.391
2.120	-5.539
2.123	-5.604

2.128	-5.659
2.134	-5.704
2.144	-5.747
2.155	-5.802
2.166	-5.866
2.205	-6.079
2.287	-6.496
2.383	-6.866

For Peer Review

Otomo, 2005, 30 mol% H₂O

X axis	Y axis
1000/T	log sigma
1.747	-1.476
1.777	-1.554
1.805	-1.508
1.838	-1.630
1.871	-1.710
1.908	-1.775
1.943	-1.832
1.961	-1.852
1.976	-1.888
1.983	-2.412
2.022	-5.195
2.062	-5.243
2.106	-5.316
2.199	-5.446
2.354	-5.654

Fig. 3. Temperature dependence of CDP conductivity in a heating process. (a) 30 mol% H₂O/Ar-balance; (b) 90 mol% H₂O/Ar-balance; total pressure: atmospheric pressure.

Otomo, 2005, 90 mol% H2O

X axis	Y axis
1000/T	log sigma
1.745	-1.355
1.775	-1.434
1.805	-1.494
1.838	-1.550
1.872	-1.606
1.908	-1.669
1.944	-1.734
1.965	-1.776
1.984	-2.216
2.024	-5.033
2.063	-5.098
2.106	-5.091
2.151	-5.059
2.214	-5.020
2.266	-4.962
2.317	-4.882
2.374	-4.801

Fig. 3. Temperature dependence of CDP conductivity in a heating process. (a) 30 mol% H₂O/Ar-balance; (b) 90 mol% H₂O/Ar-balance; total pressure: atmospheric pressure.

Otomo, 2003,30mol%H₂O,lnsigmaT

X axis	Y axis				
1000/T	ln sigma T	log sigma T	T	log T	log sigma
1.912	2.348	1.020	523.059	2.719	-1.699
1.949	2.160	0.938	512.997	2.710	-1.772
1.988	1.976	0.858	502.919	2.701	-1.843
2.028	-6.064	-2.633	493.012	2.693	-5.326
2.070	-6.312	-2.741	483.019	2.684	-5.425
2.114	-6.524	-2.833	472.973	2.675	-5.508
2.207	-6.884	-2.989	453.029	2.656	-5.645
2.364	-7.368	-3.199	423.081	2.626	-5.826

Fig. 7. Temperature dependence of the conductivity of CsH₂PO₄/SiO₂ composite in 30 mol% H₂O/Ar on heating process. ●: Pure CsH₂PO₄; △: (1-x)CsH₂PO₄/xS1 at x=0.33; +: (1-x)CsH₂PO₄/xS2 at x=0.33; ○: (1-x)CsH₂PO₄/xS3 at x=0.33; ●: (1-x)CsH₂PO₄/xS3 at x=0.5.

Otomo, 2003, 30 mol% H2O(sigma)

X axis			Y axis	
t	1000/T	log conductivity	sigma	log sigma
250.000	523.150	1.911	0.008	-2.097

Fig. 2. Time dependence of the conductivity of polycrystalline CsH₂PO₄ at 250 °C with various humidity conditions. ●: Dry Ar; ▲: 3 mol% H₂O/Ar; ■: 30 mol% H₂O/Ar; ○: 90 mol% H₂O/Ar.

Otomo, 2003, 90 mol% H₂O(sigma)

X axis			Y axis	
t	1000/T	log conductivity	sigma	log sigma
250.000	523.150	1.911	0.014	-1.854

Fig. 2. Time dependence of the conductivity of polycrystalline CsH₂PO₄ at 250 °C with various humidity conditions. ●: Dry Ar; ▲: 3 mol% H₂O/Ar; ■: 30 mol% H₂O/Ar; ○: 90 mol% H₂O/Ar.

Ortiz, 1999

X axis

t	T	1000/T
89.907	363.057	2.754
100.000	373.150	2.680
108.972	382.122	2.617
120.140	393.290	2.543
125.140	398.290	2.511
130.140	403.290	2.480
135.187	408.337	2.449
140.280	413.430	2.419
145.234	418.384	2.390
150.187	423.337	2.362
155.234	428.384	2.334
160.140	433.290	2.308
165.187	438.337	2.281
170.140	443.290	2.256
175.140	448.290	2.231
180.187	453.337	2.206
185.093	458.243	2.182
190.187	463.337	2.158
195.093	468.243	2.136
200.140	473.290	2.113
205.093	478.243	2.091
210.000	483.150	2.070
215.140	488.290	2.048
220.093	493.243	2.027
225.187	498.337	2.007
230.187	503.337	1.987
245.187	518.337	1.929
250.327	523.477	1.910
255.327	528.477	1.892
260.327	533.477	1.874
255.327	528.477	1.892
250.374	523.524	1.910
246.262	519.412	1.925
240.327	513.477	1.948
235.327	508.477	1.967
230.234	503.384	1.987
225.280	498.430	2.006
220.093	493.243	2.027
215.187	488.337	2.048
210.093	483.243	2.069
200.093	473.243	2.113
190.140	463.290	2.158
180.093	453.243	2.206
170.093	443.243	2.256
160.140	433.290	2.308
150.234	423.384	2.362
140.234	413.384	2.419

Y axis

log sigma
-6.457
-6.187
-6.033
-5.760
-5.680
-5.593
-5.497
-5.407
-5.350
-5.277
-5.193
-5.120
-5.047
-4.960
-4.840
-4.690
-4.223
-3.960
-3.477
-2.633
-2.600
-2.547
-2.513
-2.483
-2.440
-2.400
-2.247
-2.150
-2.080
-1.997
-2.160
-2.280
-2.247
-2.197
-2.223
-3.103
-4.530
-4.527
-4.577
-4.670
-4.803
-4.773
-4.917
-5.197
-5.477
-5.660
-6.767

Fig. 6. Log of σ vs. T for the first (filled and open circles) and second (filled and open circles) heating-cooling cycles (filled and open circles - first heating-cooling cycle, respectively).

130.234	403.384	2.479	-6.930
120.187	393.337	2.542	-7.107
110.093	383.243	2.609	-7.223
100.000	373.150	2.680	-7.463
89.953	363.103	2.754	-7.800

For Peer Review

Baranov, 1989

X axis	Y axis				
1000/T	ln sigma T	log sigma T	T	log T	log sigma
1.893	2.801	1.216	528.175	2.723	1.507
1.903	2.756	1.197	525.505	2.721	1.524
1.918	2.702	1.173	521.388	2.717	1.544
1.927	2.658	1.154	518.868	2.715	1.561
1.940	2.598	1.128	515.412	2.712	1.584
1.950	2.557	1.110	512.791	2.710	1.600
1.961	2.509	1.089	509.884	2.707	1.618
1.971	2.473	1.074	507.241	2.705	1.631
1.980	2.432	1.056	504.932	2.703	1.647
1.996	-5.905	-2.564	500.979	2.700	5.264
2.023	-6.237	-2.708	494.208	2.694	5.402
2.049	-6.495	-2.820	487.975	2.688	5.508
2.076	-6.845	-2.972	481.758	2.683	5.655
2.097	-7.094	-3.080	476.788	2.678	5.759
2.132	-7.497	-3.255	469.124	2.671	5.927
2.163	-7.853	-3.410	462.410	2.665	6.075
2.205	-8.363	-3.631	453.585	2.657	6.288
2.226	-8.627	-3.746	449.177	2.652	6.398
2.247	-8.858	-3.846	445.031	2.648	6.495
2.275	-9.170	-3.982	439.506	2.643	6.625
2.308	-9.561	-4.152	433.212	2.637	6.788
2.360	-10.095	-4.383	423.723	2.627	7.010
2.388	-10.546	-4.579	418.817	2.622	7.201
2.422	-10.845	-4.709	412.907	2.616	7.325
2.457	-11.275	-4.896	406.991	2.610	7.505
2.488	-11.690	-5.076	401.927	2.604	7.680
2.524	-12.043	-5.229	396.129	2.598	7.827
2.561	-12.458	-5.410	390.449	2.592	8.001
2.594	-12.862	-5.585	385.560	2.586	8.171
2.629	-13.295	-5.773	380.309	2.580	8.353
2.694	-14.009	-6.083	371.226	2.570	8.653
2.735	-14.475	-6.285	365.624	2.563	8.848
2.755	-14.748	-6.404	362.925	2.560	8.964

FIGURE 1 Temperature dependences of the conductivity for some crystals of KDP-family

For Peer Review

Baranov, 1988

X axis		Y axis			
1000/T	ln sigma T	log sigma T	T	log T	log sigma
1.916	2.624	1.140	521.850	2.718	-1.578
1.955	2.429	1.055	511.464	2.709	-1.654
1.992	2.332	1.012	502.101	2.701	-1.688
2.024	2.244	0.974	494.157	2.694	-1.720
2.062	2.098	0.911	485.065	2.686	-1.775
2.094	-1.776	-0.771	477.646	2.679	-3.450
1.998	-3.932	-1.707	500.493	2.699	-4.407
2.019	-6.615	-2.872	495.363	2.695	-5.567
2.058	-7.034	-3.054	485.878	2.687	-5.741
2.100	-7.415	-3.220	476.302	2.678	-5.897
2.101	-7.415	-3.220	475.855	2.677	-5.897
2.127	-8.098	-3.516	470.126	2.672	-6.188
2.147	-7.922	-3.440	465.810	2.668	-6.108
2.188	-8.332	-3.618	457.105	2.660	-6.278
2.194	-8.780	-3.813	455.872	2.659	-6.471
2.227	-8.741	-3.796	449.115	2.652	-6.448
2.262	-9.122	-3.961	442.073	2.645	-6.606
2.298	-9.473	-4.113	435.155	2.639	-6.752

FIGURE 4 Temperature dependences of the bulk conductivity CDP in $\bar{a}(1)$, $\bar{b}(2)$ and $\bar{c}(3)$ -directions.