



**CsH<sub>2</sub>PO<sub>4</sub>** is not stable at 260 °C unless confined. Comments to article by C.E. Botez, I. Martínez, A. Price, H. Martínez, and J.H. Leal in *J. Phys. Chem. Solids* 129 (2019) 324-328

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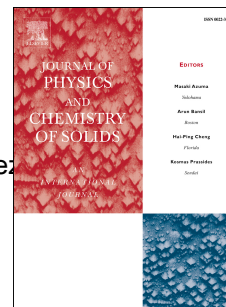
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# Journal Pre-proof

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**Short communication**

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**Abstract**

Botez, Martinez, Price, Martinez and Leal claim in J. Phys. Chem. Solids 129 (2019) 324-328 that superprotonic CsH<sub>2</sub>PO<sub>4</sub> (CDP) is stable in dry air at 260 °C. We discuss their observations and conclude that CDP is not stable unless sufficiently confined under a high humidity and high-pressure atmosphere, eventually formed from the sample itself. Temperature- and time-resolved impedance spectroscopy data show that a superprotonic CDP pellet measured in a hermetically sealed chamber holds a stable superprotonic conductivity of  $\sim 2 \times 10^{-2} \text{ S cm}^{-1}$  over a time span of 50 h at a temperature of 260 °C if the amount of sample is large enough and the container small and tight. Nyquist plots have confirmed the superprotonic nature of the conduction. X-ray diffraction data have revealed that CDP is present after the heating cycle to obtain superprotonic conductivity, but possibly CDP partly was decomposed to Cs<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> during the heating and was reformed reacting with water during the cooling.

**Key words:** Superconductivity; CsH<sub>2</sub>PO<sub>4</sub>; conductivity; phosphate-based electrolyte; high temperature

**Introduction.** Recently Botez et al. in a paper published in J. Phys. Chem. Solids 129 (2019) 324-328 reported on what they called the first observation of a stable superprotonic CsH<sub>2</sub>PO<sub>4</sub> (CDP) phase in the absence of high humidity and high pressure. From this statement, one might get the impression that CDP is stable in dry air at 260 °C. This is not the case. We discuss in the following our own observations

and conclude that CDP is not stable unless sufficiently confined under a high humidity and high pressure atmosphere, eventually formed from the sample itself. The temperature- and time-resolved impedance spectroscopy data by Botez et al. [1] have shown that a CDP pellet measured in a hermetically sealed chamber holds a stable protonic superconductivity of  $\sim 2 \times 10^{-2} \text{ S cm}^{-1}$  over a timespan of 50 h and at a temperature of 260 °C, but - as we calculate below - their amount of sample was large enough and their hermetically closed container was small enough to leave enough CDP to give the impression from Nyquist plots that the pellet was superconducting.

The protonic conductivities of CDP have been extensively studied by many researchers, at low temperatures and up to about 300 °C, as reviewed in our report on CDP properties [2]. In our report also we have included extensive measurements to even higher temperatures, up to  $\sim 400$  °C, by using a newly developed technique based on measuring CDP in homemade sealed quartz cells. By comparing to the many results in the literature we have observed that the superprotonic conductivity in CDP was found to start at various temperatures in a range of about 230 – 260 °C. The term superconductivity in CDP corresponds to a sudden jump in the conductivity (a superprotonic jump) from  $\sim 1 \times 10^{-5}$  to  $\sim 1 \times 10^{-2} \text{ S cm}^{-1}$ . Much discussion in the past has been concerned with the additional essential phenomenon that CDP is not stable versus heating, unless some way is provided to avoid decomposition, e.g. confinement of the sample or a humid atmosphere to reverse the decomposition reaction (1):



For an extensive review of many other previous results in the vast literature on the stability of CDP subject, we refer to Fig. 8 in [2].

Comparison of our results with the results by Botez et al. [1]. The recent results of Botez et al. [1] are shown in Fig. 1, together with our own results [2] on similar scales. The superprotonic jump and the melting of the CDP are clearly seen as discontinuities at  $\sim 230$  °C and  $\sim 346$  °C [2], and we observe that the results of Botez et al. [1] are on the same order of magnitude as are our own and many in the literature cited in [1-2].

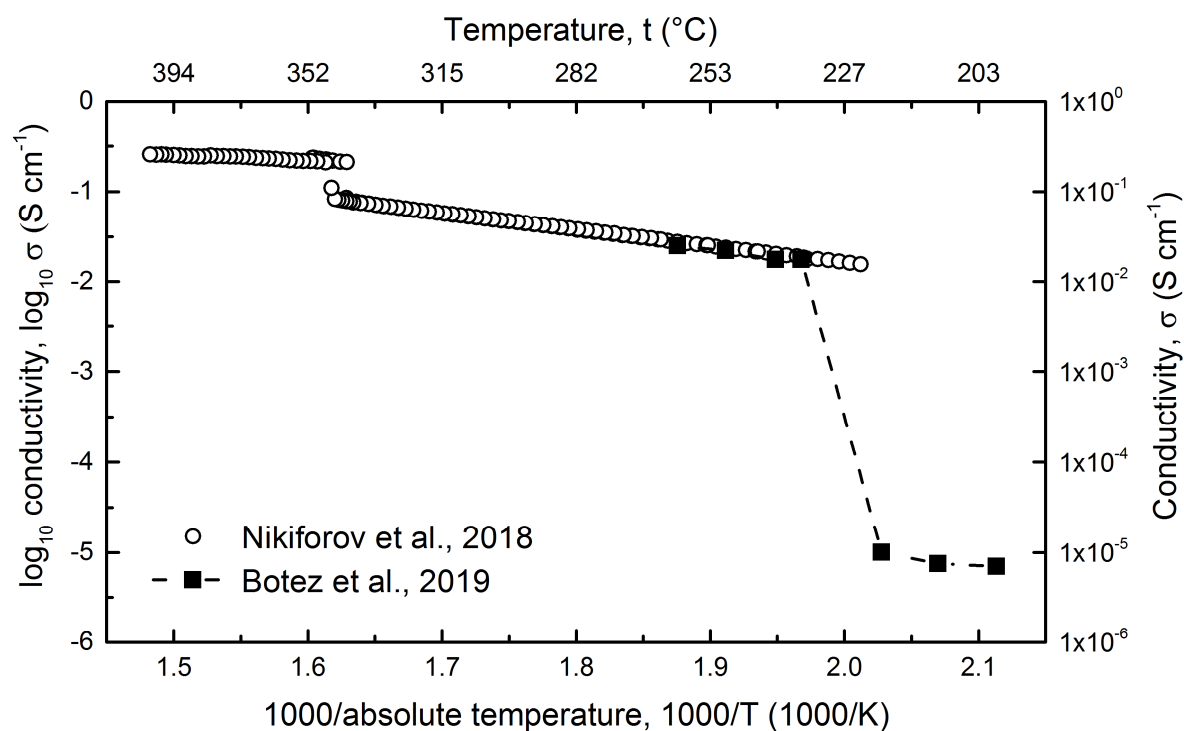


Fig. 1. Protonic conductivity of  $\text{CsH}_2\text{PO}_4$  at high temperatures, up to  $\sim 400^\circ\text{C}$ . Closed squares and open circles refer to results of Botez et al. [1] and Nikiforov et al. [2].

**Discussion.** Below we give a discussion and interpretation of the results of [1] and [2]. In their article Botez et al. [1] describe their methods and well characterize their CDP crystals and there is no doubt on the identities of the chemicals. A finely ground powder was used to make their CDP pellets of 1.3 cm in diameter ( $d$ ) and 0.25 cm in thickness ( $h$ ). The pellets were pressed at 0.65 GPa to obtain  $\sim 93\%$  of the theoretical CDP density ( $\sim 3.13 \text{ g/cm}^3$  at  $\sim 237^\circ\text{C}$  [3]). Silver paste was deposited on both pellet faces to serve as electrodes, and Pt wires were attached as measurement leads. The pellet was contained in a  $\sim 15 \text{ cm}^3$  hermetically sealed chamber, filled with dry air (22%rh). The chamber was placed inside a tube furnace. The proton conductivity was obtained from Nyquist plots measured by impedance spectroscopy recorded within a  $200^\circ\text{C} < T < 260^\circ\text{C}$  temperature range by use of a Solartron 1260 analyzer coupled with a ProboStat® sample holder. A 100 mV oscillating potential over a frequency range from 6 MHz to 1

Hz and a standard two-point, four-wire setup were applied to determine the pellet resistance that came out as  $\sim 7 \Omega$  at  $260 \text{ }^\circ\text{C}$  [1].

From these details we calculate the volume of the pellet to be  $\pi \times (d/2)^2 \times h = \pi \times 0.65^2 \times 0.25 \text{ cm}^3 = 0.3318 \text{ cm}^3$ . Their mass must then have been  $0.3318 \times 3.13 \times 0.93 \text{ g} = 0.963 \text{ g}$  or  $0.004189 \text{ mol}$  of CDP for a space filling of 93 %. According to our CDP vapor pressure measurements [2] done by Raman spectroscopy, the saturation water pressure at  $260 \text{ }^\circ\text{C}$  ( $533 \text{ K}$ ) must have been about 5 bar. The hermetically sealed chamber of volume  $(\sim 15 - 0.3318) \text{ cm}^3 = (\sim 0.015 - 0.0003318) \text{ L}$  should at equilibrium, according to the ideal gas law, contain  $\sim 5 \text{ bar} \times 0.01467 \text{ L} / ((0.0831 \text{ L bar mol}^{-1} \text{ K}^{-1}) \times 533 \text{ K}) = 0.001656 \text{ mol}$  of  $\text{H}_2\text{O}$ . Most of this water must have come from the CDP according to reaction (1).

Because dry air was used ( $\sim 15 \text{ cm}^3$  air of 22%rh at  $25 \text{ }^\circ\text{C}$  contains  $\sim 0.000004 \text{ mol}$  of  $\text{H}_2\text{O}$ , i.e. essentially nothing) it means that  $\sim 0.001656 \times 2 = 0.0033 \text{ mol}$  of CDP should be lost via reaction (1), leaving essentially  $0.004189 - 0.0033 = 0.0009 \text{ mol}$  of CDP or  $\sim 21\%$  of the starting mass. The situation at  $\sim 260 \text{ }^\circ\text{C}$  is sketched in Fig. 2.

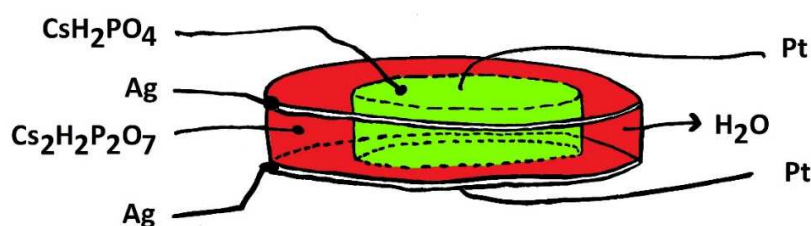


Fig. 2. Idealized diagram of the experiment by Botez et al. [1]. The silver paste layers on the top and bottom (shown transparent) are thought to obstruct the escape of the internal water, so that a 21-79% core-cladding structure will be formed by escape of water from the cylindrical surface. The red-brown area is the  $\sim 79\%$  cladding part of the CDP that has lost  $\text{H}_2\text{O}$  via reaction (1) to form  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ , leaving  $\sim 21\%$  of the CDP as the core of the pellet (green).

If we assume that the conductivity of solid  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$  at temperatures  $> \sim 230\text{ }^\circ\text{C}$  is small in comparison to that of the superprotonic CDP, we would predict that the resistance determined is an average of  $\text{CsH}_2\text{PO}_4$  and  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ . Only a fraction of the cross section (about 21%, the green core in Fig. 2) will be superconducting whereas the cladding part will conduct only moderately as  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ . The conductivity is inversely proportional to the cross section of the conductor, here the pellet. If the pellet area is  $A$ , the thickness is  $L$  and the resistance is  $R$ , then the average conductivity should be

$$\sigma = L / (R \times A) = h / (R \times \pi \times (d/2)^2) \text{ S cm}^{-1} = 2.69 \times 10^{-2} \text{ S cm}^{-1}$$

according to our calculation. But the effective superconducting part is less than the whole pellet, and therefore the CDP conductivity in reality must be corrected for the loss of the water. If the  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$  is only moderately conducting, the true value for CDP should be quite higher. The conductivity is reported as  $\sigma = \sim 1.5 \times 10^{-2} \text{ S cm}^{-1}$  at  $\sim 260\text{ }^\circ\text{C}$  in the abstract by Botez et al. [1], but rather it will be higher, perhaps up to  $\sigma = \sim 1.5 \times 10^{-2} \text{ S cm}^{-1} / 0.21 = \sim 7 \times 10^{-2} \text{ S cm}^{-1}$  if we assume  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$  to be essentially non-superconductive. But it must have quite some conductivity so that the apparent conductivity values for CDP in the various diagrams, e.g. in Fig. 3 and Fig. 5 of [1] for  $260\text{ }^\circ\text{C}$ , seem to be quite correct. Ideally, the CDP conductivity values should be corrected for this core/cladding effect. In extreme cases, the true value might be up to 10 times higher. On a  $\log_{10} \sigma$  logarithmic scale it means that the data values should perhaps have up to  $\log_{10} 10 = 1$  added to get true values for the CDP conductivities.

Accordingly we arrive at an understanding that the lack of use of corrections for the  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$  formation – or omission of the core /cladding effect as detailed above - is the reason for the wide scattering of the results found in the literature, as e.g. evidenced in Fig. 8 of [2].

Stability. The stability of the conductivity given as the "sealed in dry air" curve in Fig. 5 of Botez et al. [1] – according to our opinion – is a true result of the small volume of their applied container. If a larger container were used, the superconductivity would have

been lost. That experiment has already been done; see the "open atmosphere" curve in Fig. 5 of [1]. The stability of CDP conductivity requires containment.

Dynamic situation. The X-ray diffraction reported in [1] revealed limited dehydration of the CDP superprotonic phase when the pellet was examined after being cooled to down to room temperature. We take this to indicate that the formation of  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$  is quite reversible under the above-mentioned conditions. During cooling, reaction (1) goes back quite fast and the CDP is formed again.

We observed a similar reversible reaction by use of Raman spectroscopy when heating  $\text{KH}_2\text{PO}_4$  (KDP) in closed ampoules. The  $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$  was formed rapidly during heating of KDP and reacted fast back with the liberated water to reform KDP when the ampoules were cooled to room temperature, see [4]-[5]. We observed the same phenomena for CDP as described in [2].

Conclusion. When we read the main text and studied the values in the Figures of Botez et al. [1] we see values of  $\sigma = \sim 2 \times 10^{-2} \text{ S cm}^{-1}$  at  $T = 260 \text{ }^\circ\text{C}$ . This essentially means that the results of Botez et al. [1] and our values agree quite well as shown in Fig 1.

Superprotonic  $\text{CsH}_2\text{PO}_4$  (CDP) is reported to be a stable phase in the presence of high humidity and under a high pressure atmosphere formed from the sample itself. The temperature- and time-resolved impedance spectroscopy data reported by e.g. Botez et al. [1] have shown that the superprotonic conductivity of CDP pellets measured in a hermetically sealed chamber holds a  $\sigma \sim 2 \times 10^{-2} \text{ S cm}^{-1}$  protonic conductivity over a timespan of 50 h. That value was stable at a temperature of  $260 \text{ }^\circ\text{C}$  if the amount of sample was large and the container small and tight. Nyquist plots confirm the superprotonic nature of the conduction. X-ray diffraction data revealed that the CDP phase was present after the experiments to obtain superprotonic conductivity, but it is a likely possibility that the CDP during heating partly decomposed and reformed during the cooling part of the cycle.



The same principles described here apply to the conductivity experiments for composites of CDP with various fillers, as reported in other recent references, see e.g. [6] - [9].

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Highlights

- The stability of  $\text{CsH}_2\text{PO}_4$  at high temperature is discussed
- Confinement of  $\text{CsH}_2\text{PO}_4$  is necessary to obtain stability
- The super protonic conductivity at high temperatures of  $\text{CsH}_2\text{PO}_4$  requires confinement

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