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Discovery of Ferroelectric Properties in Diammonium Hypodiphosphate $(NH_4)_2H_2P_2O_6$ (ADhP)

Przemysław Szklarz,* Michał Chański, Katarzyna Ślepokura, and Tadeusz Lis

Faculty of Chemistry, University of Wrocław, Joliot Curie 14, 50-383 Wrocław, Poland

Supporting Information Web-Enhanced

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A recent focus in material research is the hybrid organic—inorganic or metallorganic complexes. Among others, ferroelectric materials comprise a large group of compounds which are a subject of intense scientific investigations.[1−3] Ferroelectric crystals are widely applied, for example, in electronics in such devices as capacitors, sensors, transducers, or nonvolatile memories.[4] In large scale integration (VLSI) of electronic circuits, ceramic ferroelectrics are generally used. In the group of the classical ferroelectric crystals one of the ferroelectric substances discovered relatively early, namely, KDP (potassium dihydrogen phosphate), is still the component of many laser systems, used as a device for the multiplication of the primary harmonic. The electro-optic properties of KDP are used also in nonlinear Pockels cells. Ferroelectrics belonging to the KDP family were widely studied in the past also from the point of view of basic physics.[5,6] A large number of reports on KDP crystals, related to the phase transition physics, have been published. It is well-known, for example, that the mechanism of the ferroelectric phase transition in KDP is closely related to the proton dynamics in the hydrogen bonds.[7−9] Investigations on this type of oxygen ferroelectrics continue, but only a few novel crystals have been discovered in recent years. Although the field appeared thoroughly exploited, we have disclosed ferroelectricity in the ammonium salt of hypodiphosphoric acid ($H_4P_2O_6$). This acid was discovered by Salzer in 1877.[10] Until now only a few crystal structures of the hypodiphosphate compounds have been determined, and most of their physical properties are completely unknown. Thus, it was very surprising for us that the diammonium hypodiphosphate (ADhP) salt appeared to be ferroelectric.

Diammonium hypodiphosphate was prepared by addition of stoichiometric amounts of ammonium carbonate to an aqueous solution of hypodiposphoric acid obtained by the method described by Leininger.[11] Figure 1 shows DSC runs, on cooling and heating, for a polycrystalline sample of ADhP and its deuterated analogue in the temperature range between 160 and 220 K. The calorimetric results clearly reveal the existence of the solid—solid phase transition at 178/180 K (cooling/heating). The anomaly found is fully reversible with temperature. The shape of the DSC anomaly is characteristic of a second order phase transition. The small temperature hysteresis (±1.5 K) observed during cooling and heating runs may result from the finite scanning rate of 2 K/min or from the low heat conductivity of the sample. For the deuterated sample the respective phase transition was found at 200 K, that is, approximately 20 K higher in comparison to the nondeuterated sample. The shape of the anomaly for the deuterated compound is similar to that for the nondeuterated one.

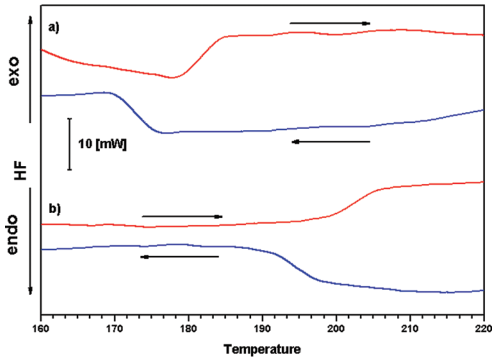

Figure 1. DSC runs (on cooling and heating) for (a) $(NH_4)_2H_2P_2O_6$ (DSC with the ramp rate of 10 K min^{-1}, sample mass 4.2 mg) and for (b) deuterated sample (DSC with the ramp rate of 10 K min^{-1}, sample mass 5.1 mg).

The single crystal X-ray diffraction studies were performed at two temperatures, 100 K (phase II) and 210 K (phase I). The crystal structure of ADhP was previously determined by Wilson[12] at room temperature, and our results are in accordance with his. ADhP crystallizes in the orthorhombic space groups $P2_1cn$ (No. 33) and $Pccn$ (No. 56) at 100 and at 210 K, respectively. The low temperature space group is polar (one of the glide **c** planes disappears at the **I** → **II** phase transition and therefore low temperature phase is described in nonstandard setting). The crystal is built of the separated hypodiphosphate $H_2P_2O_6^{2-}$ anions and a stoichiometric amount of the ammonium cations. The independent part of the unit cell of the phase **II** crystal along with the atom numbering scheme is shown in Figure 2a. The high temperature structure consists of one-half $H_2P_2O_6^{2-}$ anion and one NH_4^+ cation ($Z' = 1/2$). All atoms lay in general positions.

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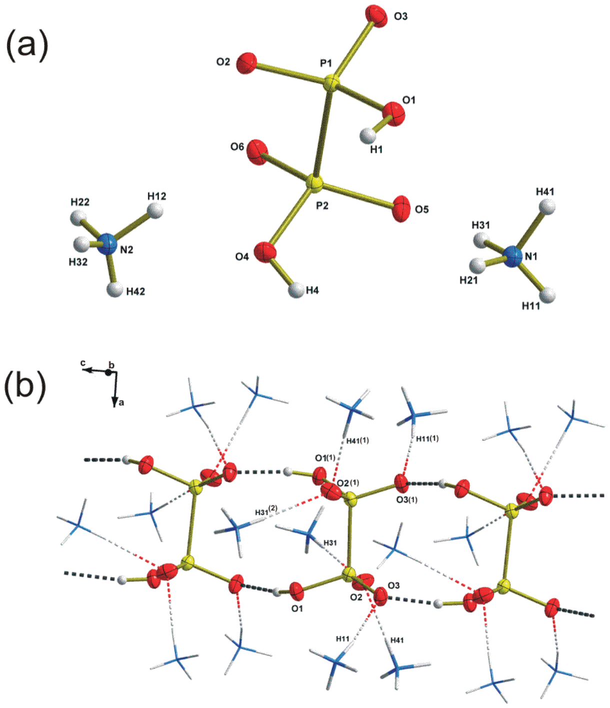

Figure 2. (a) Asymmetric part of the unit cell of $(NH_4)_2H_2P_2O_6$ crystal at 100 K. (b) Anionic ribbon of $H_2P_2O_6{}^{2-}$ with hydrogen bonded ammonium cations.

The centers of the P—P bonds lay on the 2-fold axis. In phase **II** the asymmetric part becomes twice as large as that in phase **I** and consists of one $H_2P_2O_6{}^{2-}$ anion and two $NH_4{}^+$ cations ($Z' = 1$). The appropriate bond lengths are in accordance with chemically expected values.[13,14]The structure of $(NH_4)_2H_2P_2O_6$ can be characterized by the presence of a three-dimensional hydrogen bond network. One can distinguish two types of hydrogen bonds: (1) the O—H···O bonds between hypodiphosphate anions, which form the infinite folded ribbons expanded along the *c*-axis, and (2) the N—H···O bonds between hypodiphosphate anions and ammonium cations, linking the anionic ribbons in the three-dimensional network. The $H_2P_2O_6{}^{2-}$ anions are arranged in the ribbons like "rungs of a ladder" (see Figure 2b). In phase **I** the P—P bonds are parallel to the crystallographic *ab* plane. The adjacent anions in the ribbon are tilted along the *b*-axis in opposite directions. The ammonium cations occupy the positions between ribbons and act as three-dimensional interaction networks (see Figure 2b).

The temperature dependence of the real part of the complex dielectric permittivity, ε', along the polar *a*-axis of ADhP was measured upon cooling at frequencies in the range between 125 Hz and 2 MHz. Figure 3a presents ε' vs temperature for the selected frequencies. The phase transition at 180 K manifests itself as a characteristic peak on the dielectric permittivity curve. The maximum value of the permittivity, $\varepsilon'_{\max}$, reaches 2000 at T_C. The behavior of the electric permittivity as a function of temperature strongly suggests the ferroelectric character of the **I** → **II** phase transition. In the vicinity of the critical temperature, T_C, both in the low and in the high temperature phase, no dispersion of the permittivity is observed in the frequency range applied. This suggests that the possible dielectric relaxation process could be observed at much higher frequencies. The Curie—Weiss relationship, $\varepsilon' = C_\pm/(T - T_C)$, in which $C_\pm$ denotes the Curie—Weiss constant, is well fulfilled over the temperature interval of approximately 10 K both above and below T_C (see inset in Figure 3a). The C_+/C_- ratio equal to 2.3 is quite close to the theoretical value expected for a second order paraelectric-ferroelectric phase transition ($C_+/C_- = 2$).

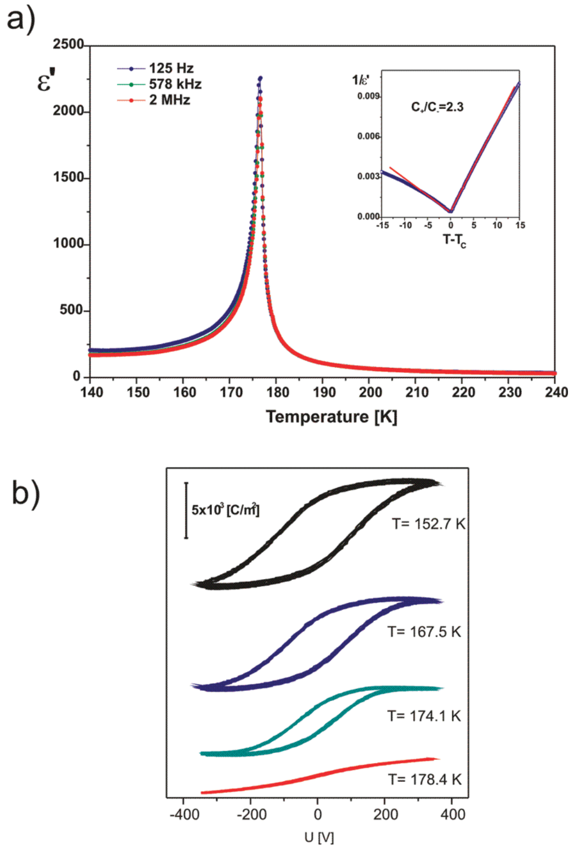

Figure 3. (a) Temperature dependence of the real part of the complex electric permittivity measured along the *a*-direction (on cooling). Inset: temperature dependence of $1/\varepsilon$ in the vicinity of T_C. (b) Hysteresis loops observed in various temperatures in phase II (sample thickness 0.8 mm).

To check the existence of spontaneous polarization in the phase **II**, which could be reversible in an external electric field, we performed hysteresis loop measurements. (The positive result of this measurement is crucial evidence of the ferroelectric character of phase **II** (Figure 3b). The obtained value of spontaneous polarization, equal to 4×10^{-3} C/m^2, is one order smaller than that for the KDP crystals.[15]

The results of the dielectric and hysteresis loop measurements performed for the ADhP crystal univocally indicate the ferroelectric nature of its phase **II** ($T < 180$ K). Taking into account that the group of the phosphate ferroelectrics of the KDP type is recognized very well, this novel diammonium hypodiphosphate is quite an unexpected discovery. Since the mechanism of phase transition in the KDP type crystals has been the scope of the numerous investigations for the last 70 years,[16] it seems desirable to compare the properties of this novel ADhP ferroelectric, described in this paper, to those of KDP and ADP. The main difference between crystals from the KDP family and ADhP is the mechanism of phase transition. In the former compounds the main contribution to the mechanism of the phase transition is ascribed to the order—disorder type. The hydrogen atoms in the

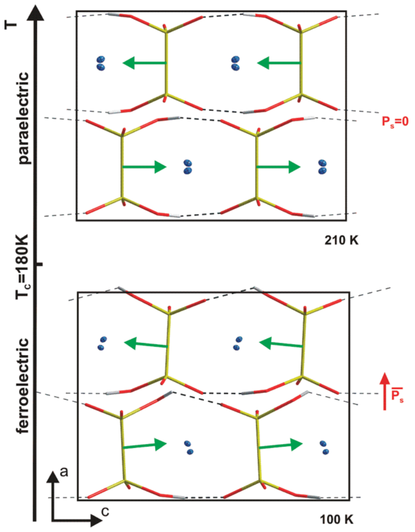

Figure 4. Ⓦ Mechanism of appearance of the spontaneous polarization during the phase transition **I**→**II** (green arrows denote permanent dipole moments of the anions, NH_4^+ cations are represented by blue ellipsoids, and hydrogen atoms of the cations are omitted for clarity). See also web enhanced object for animation.

O—H···O bridges in the paraelectric phase of KDP and ADP are disordered, and phase transition is accompanied by the ordering of these protons. On the other hand, careful analysis of the X-ray difference electron density maps for ADhP may indicate that all hydrogen atoms are ordered in both phases. To determine the hydrogen positions in the bridges, neutron diffraction measurements are necessary—they will be a subject of forthcoming experiments. Nevertheless, at the present stage of knowledge, it may be concluded that the slight change in the crystal packing during the phase transition may be responsible for the appearance of the polar properties of the crystal in the low temperature phase. From the X-ray results it may be merely concluded that no change in the proton dynamics is observed. The relatively small shift of the phase transition temperature in the deuterated sample, by approximately 20 K in comparison to the nondeuterated one, also indicates that hydrogen dynamics plays a minor role in the mechanism of the phase transition.

The comparison of the crystal structures of ADhP in the paraelectric and ferroelectric phases allows us to propose the probable origin of the appearance of the spontaneous polarization below T_C = 180 K. The $H_2P_2O_6^{2-}$ anions possess the permanent dipole moment, a vector of which is perpendicular to the P—P bond axis and is oriented toward a direction determined by the hydrogen atoms of the anion. In the paraelectric phase these vectors are oriented along the hypodiphosphate ribbons. Since the adjacent ribbons are oriented in the opposite directions, the permanent moments are canceled. After the phase transition, the $H_2P_2O_6^{2-}$ anions slightly change their orientations with regard to the *ab* plane. These reorientations occur in such a way that a nonzero component of the dipole moment appears in the *a* direction (Figure 4). One can distinguish another contribution to spontaneous polarization; this is an opposite mutual displacement of the centers of gravity of the NH_4^+ cations and $H_2P_2O_6^{2-}$ anions along the *a* axis. From this point of view the mechanism of the phase transition can be rather described as of the displacive type. Since ADhP shows ferroelectric properties in phase II, the mechanism of switching between two polar states by an application of the external electric field should be proposed. The applied external alternating electric field interacts with the macroscopic polarization vector and changes the orientation of the $H_2P_2O_6^{2-}$ anions with regard to the *ab* plane. After this reorientation a nonzero component of the dipole moment (and spontaneous polarization) changes its sign along the *a* direction (see web-enhanced object). A system in which such behavior is possible is expected to be characterized by a high polarizability. In other words, the interactions present in the system have to provide a cooperativity of the polarization reversal process. In the case of ADhP such an element is formed by the three-dimensional network of the hydrogen bonds.

In conclusion, the present work has opened an avenue for exploration of novel promising ferroelectrics based on hypodiphosphoric acid derivatives. Therefore, we would like to draw attention to this "long forgotten" acid and its almost uninvestigated salts as precursors for new polar materials.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures and crystallographic data tables (PDF) as well as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

Ⓦ **Web Enhanced Feature.** Two movies as described in the text and the Figure 4 caption.

■ AUTHOR INFORMATION

Corresponding Author

*Email: pszklarz@eto.wchuwr.pl.

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