

Ferroelectric Order of Parallel Bistable Hydrogen Bonds

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A new $\text{NH}\cdots\text{N}$ hydrogen-bonded ferroelectric crystal of $[\text{C}_6\text{H}_{12}\text{N}_2\text{H}]^+\text{ReO}_4^-$ (dabcoHReO₄) exhibits exceptional dielectric properties that result from the unique structure where all the bistable $\text{NH}\cdots\text{N}$ hydrogen bonds are parallel and directed exactly in the same sense. Consequently, the main structural origin of the spontaneous polarization of the crystal is the identical orientation of the asymmetric $\text{NH}^+\cdots\text{N}$ hydrogen bonds along [001]. This first observation of a ferroelectric with parallel arrangement of the $\text{NH}^+\cdots\text{N}$ bonded aggregates, gives temperature-independent and the highest spontaneous polarization ever reported for an organic or water-soluble substance.

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The polarizability of hydrogen bonds is one of their most characteristic features. Moreover, hydrogen bonds are formed by the most polar parts of molecules, and these polar groups are arranged and oriented in the crystal structures by the hydrogen-bonded motives. Thus these are the hydrogen bonds which potentially could contribute most to the spontaneous polarization and concurrent electro-optic, piezoelectric, pyroelectric, and other properties of the crystals. Materials with these properties are sought for their many applications in electronic devices [1]. However, to our knowledge, no structures have been known where the polarized hydrogen-bonded chains would directly contribute to the spontaneous polarization along the proton-donor to proton-acceptor direction. The $\text{OH}\cdots\text{O}$ hydrogen bonds do not form linear but zigzaglike aggregates. The characteristic feature of $\text{OH}\cdots\text{O}$ hydrogen-bonded ferroelectrics is the crucial role of proton ordering for the mechanism of the ferroelectric-paraelectric phase transition. However, the contribution from the proton itself to the crystal spontaneous polarization, \mathbf{P}_s , is minor. In the best-known example of hydrogen-bonded ferroelectrics, the KH_2PO_4 crystal, denoted KDP and commonly regarded as a typical *hydrogen-bonded ferroelectric*, the spontaneous polarization is approximately perpendicular to the $\text{OH}\cdots\text{O}$ bond [2]. Thus only a subtle offset of the H atom from the $\text{O}\cdots\text{O}$ line contributes to \mathbf{P}_s [3]. The disordering of the H atom between the donor and acceptor sites in the paraelectric phase averages the offset of the H atom perpendicular to the bond, and so compensates this contribution to the polarization of the crystal. The main component of the hydrogen bond polarization along the bonds is compensated in all these structures due to antiparallel or nearly antiparallel arrangement of neighboring hydrogen bonds.

Here we report the crystal structure of 1,4-diazabicyclo[2.2.2]octane perrhenate (dabcoHReO₄) built of straight and parallel aggregates formed by $\text{NH}^+\cdots\text{N}$

hydrogen bonds. The main components of \mathbf{P}_s derive in this crystal, apart from ionic displacements, from the parallel hydrogen bonds, and identical orientation of the polar cations. The ability of direct reversal of the $\text{NH}^+\cdots\text{N}$ chain polarization in dabcoHReO₄ offers a substance for direct evaluation of the contribution of hydrogen bonds to the overall spontaneous polarization of the crystal.

The dabcoHReO₄ crystals were grown from an equimolar aqueous solution of the perrhenate acid and dabco base. Slow evaporation at 280 K yielded colorless plates perpendicular to [100] and elongated along [001]. For dielectric measurements the samples were prepared in the form of 0.2–0.3 mm thick plates with silver paste deposited on the surfaces perpendicular to [100] (surface ca. 10 mm²) or [001] (ca. 0.5 mm²). Complex dielectric permittivity was measured with a Hewlett-Packard 4192A impedance analyser over the frequency range of from 100 kHz to 10 MHz. The dielectric hysteresis loops were recorded by a Diamant-Drenck-Pepinsky bridge method [4] at a frequency of 50 Hz. The spontaneous polarization was measured with a Keithley 6514 electrometer. A KUMA-4 diffractometer was used for dilatometric and preliminary x-ray structural studies. Single-crystal neutron-diffraction experiments were performed on the D9 four-circle diffractometer, $\lambda = 0.8404 \text{ \AA}$, at the ILL High-Flux Reactor in Grenoble.

At 298 K the dabcoHReO₄ crystal is monoclinic, space group Cm , $a = 10.043(2)$, $b = 9.143(2)$, $c = 5.3525(10) \text{ \AA}$, $\beta = 90.86(3)^\circ$, $V = 491.4(3) \text{ \AA}^3$, $Z = 2$, and $D_x = 2.456 \text{ g/cm}^3$. The crystal structure resembles those of the analogous ferroelectrics dabcoHBF₄ and dabcoHClO₄, both isostructural with orthorhombic $Pm2_1n$ space group [5]. But while in the dabcoHClO₄ and dabcoHBF₄ structures the consecutive chains of $\text{NH}\cdots\text{N}$ hydrogen-bonded dabcoH⁺ cations are arranged antiparallel, in dabcoHReO₄ they are all parallel with all the $\text{NH}\cdots\text{N}$ bonds directed in the same sense along the

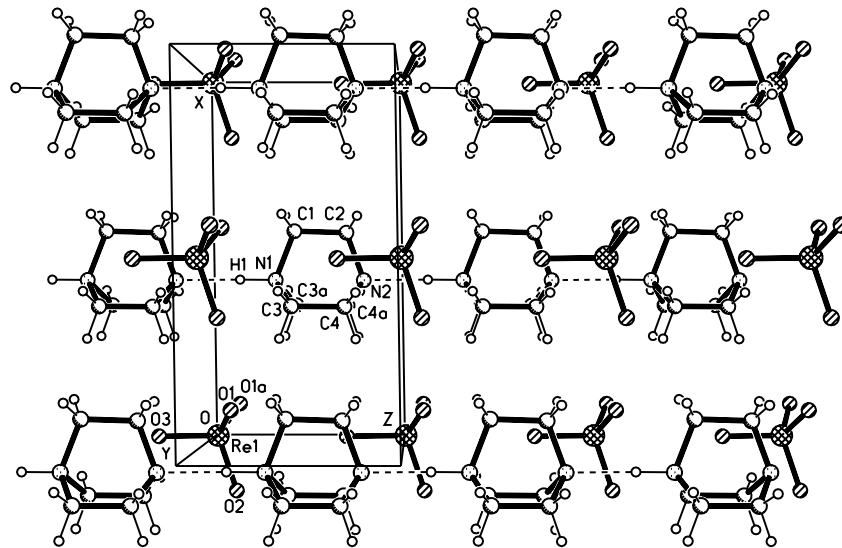


FIG. 1. Autostereogram [6] of the dabcoHReO₄ structure viewed down [100].

chains, as shown in Fig. 1. This feature is unique among crystals generally, not just for the crystals of dabco salts investigated so far or for the KDP-type ferroelectrics. Interestingly, in the structure of lithium hydrazinium sulfate (LiN₂H₅SO₄), historically the first NH⁺···N bonded crystal for which ferroelectric properties were considered [7], the hydrazinium cations are very weakly linked (N···N of 3.051 Å) into parallel zigzag chains [8]. Although LiN₂H₅SO₄ was shown not to be ferro-

electric [9], its ionic conductivity evidenced mobility of the protons even in such weak hydrogen bonds.

The unique parallel arrangement of the linear hydrogen-bonded chains in dabcoHReO₄ has multiple consequences. First, the orthorhombic symmetry is reduced to monoclinic and, although the unit-cell parameters are similar to those in dabcoHClO₄ and dabcoHBF₄, a monoclinic deformation of about 1° and a shear strain are generated (Fig. 2). However, the main difference from the isostructural dabcoHClO₄ and dabcoHBF₄ is in the properties of dabcoHReO₄ reported below. The existence of the Curie point in dabcoHReO₄ is evident in the temperature dependence of the real part of the dielectric permittivity along [100] (Fig. 3). The ferroelectric-paraelectric phase transition occurs at 374 K and is

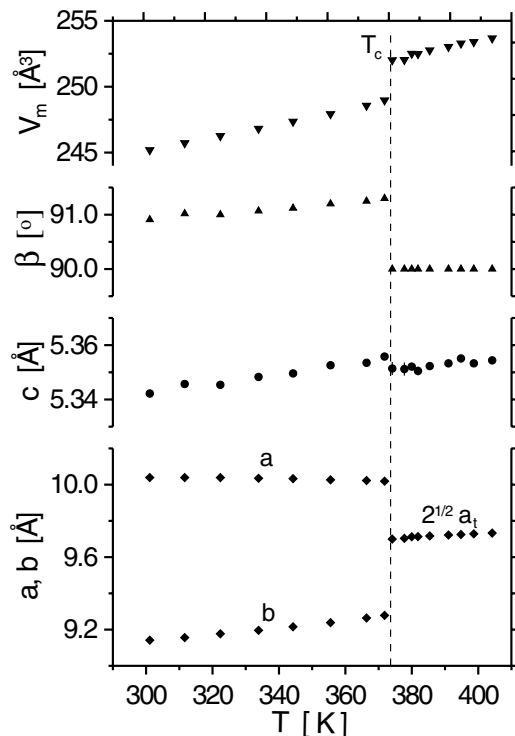


FIG. 2. The temperature dependence of the unit-cell dimensions in dabcoHReO₄: for the tetragonal phase above $T_c = 374$ K the lengths of [110] diagonal have been plotted.

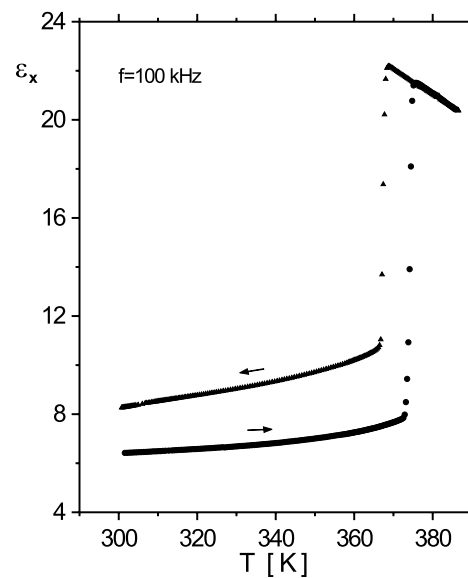


FIG. 3. Temperature dependence of the real part of the dielectric permittivity of dabcoHReO₄ along [100].

discontinuous, as is clearly seen from the shape of the anomaly and from the temperature hysteresis of 5 K (see also Fig. 4). A significant difference between the heating and cooling runs in the ferroelectric phase testifies that a multidomain ferroelectric structure is formed when the crystal returns from the paraelectric to the ferroelectric state.

Above T_c the crystal is tetragonal, as is clearly seen from the temperature evolution of the unit-cell parameters (Fig. 2); space group $P4/mmm$, and at 380 K $a = 6.858(1)$, $c = 5.356(1)$ Å, $V = 251.9(2)$ Å³, $Z = 1$, and $D_x = 2.395$ g/cm³. The unit-cell volume halves in the paraelectric phase. The cationic and anionic symmetries, C_{3v} and T_d , respectively, are inconsistent with the D_{4h} symmetry of the sites occupied by these ions in the tetragonal cell. Thus both ions must be disordered. Our structural determination showed that the disorder of the anions differs considerably from that observed in the isosymmetric paraelectric dabcoHClO₄ phase [5,10]. The cations show similar disorder in their orientation about the [001] axis. The Re atoms in dabcoHReO₄ are located at the D_{4h} -symmetric sites and the oxygens are orientationally disordered. In dabcoHClO₄ the chlorine of the perchlorate anion was disordered over two sites 0.543(10) Å apart along [001].

The DSC runs (Fig. 4) are characteristic of a discontinuous phase transition. The transition enthalpy of 4.14 kJ mol⁻¹ corresponds to the entropy change of 11.1 J mol⁻¹K⁻¹, which is close to $R \ln 4$ (R is the gas constant) fully confirming the order-disorder mechanism of the transition. The measured entropy change lower than the transition entropy calculated on the basis of the para- and ferroelectric structural models indicates that dabcoHReO₄ constitutes a strongly correlated system, similar to those of dabcoHClO₄ and dabcoHBF₄ [11].

The symmetry reduction of $P4/mmm$ to Cm classifies dabcoHReO₄ as a proper ferroelectric and improper ferroelastic [12]. For a $4/mmmFm$ species [13] the formation

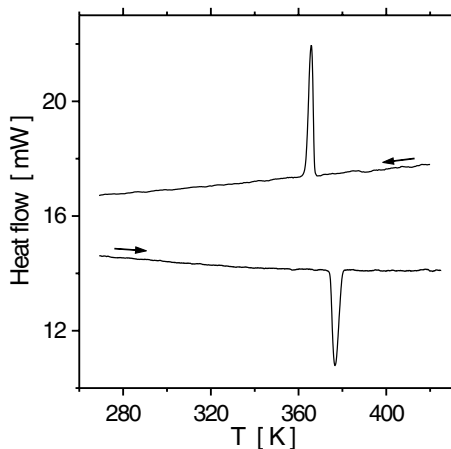


FIG. 4. The DSC signal of dabcoHReO₄ recorded with a Perkin-Elmer DCS-2 calorimeter at 10 K heating and cooling runs.

of eight ferroelectric and four ferroelastic states is predicted. But the dabcoHReO₄ crystals grown in the ferroelectric phase usually exhibited a single-domain state. In accordance with the symmetry of the ferroelectric phase \mathbf{P}_s can have two components, P_{sx} and P_{sz} , lying in the mirror plane m . Direct evidence of the ferroelectric properties of dabcoHReO₄ along [100] and [001] is provided by the hysteresis loops shown in Fig. 5. Because of a large coercive field, exceeding 30 kV/cm, the polarization of the crystals at room temperature is far from saturation. In both directions the coercive fields diminish with increasing temperature as can be deduced from the plots in Fig. 5, but the increasing conductivity of the samples precluded measurement of the loops in the vicinity of T_c . The temperature dependences of P_{sx} and P_{sz} were determined from the pyroelectric charges measured on the (100) and (001) surfaces as a function of temperature.

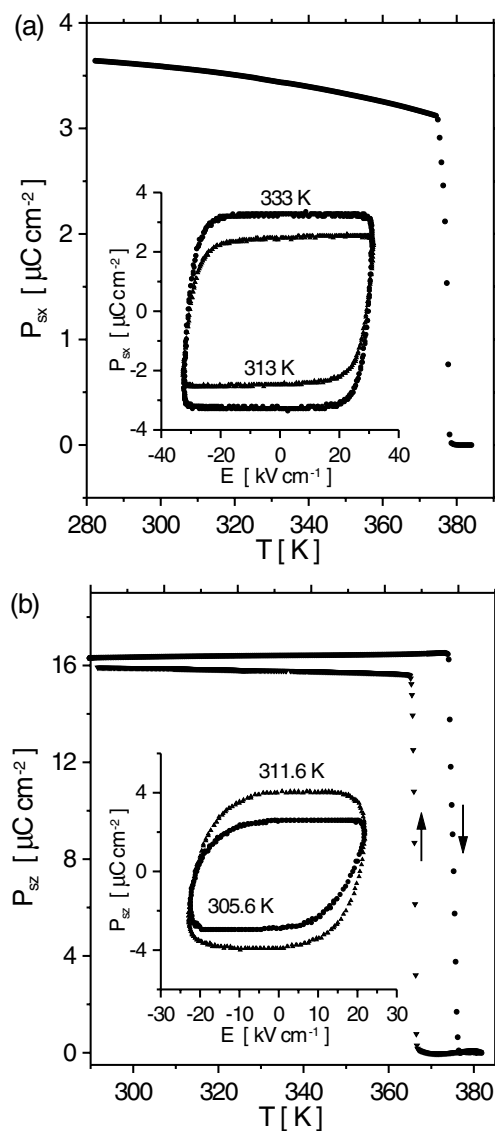


FIG. 5. Spontaneous polarization components P_{sx} (a) and P_{sz} (b). The insets show the hysteresis loops of dabcoHReO₄ along [100] and [001].

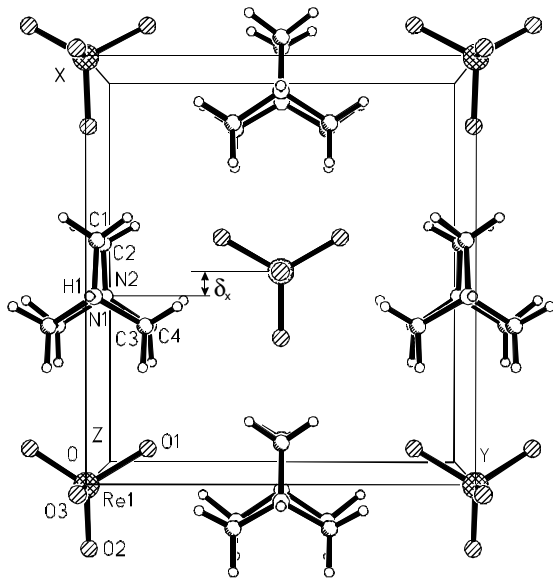


FIG. 6. The dabcoHReO₄ structure at 293 K viewed down [001]; δ_x indicates the ionic displacements along [100].

The magnitude of the P_{sx} component can be calculated using a simple point-charge model. At 295 K the cations and anions are displaced along [100] by $\delta_x = 0.553 \text{ \AA}$ (see Fig. 6), corresponding to P_{sx} of $3.62 \mu\text{C}/\text{cm}^2$, in excellent agreement with the experimental result of $3.6 \mu\text{C}/\text{cm}^2$ [see Fig. 5(a)]. However, the most striking feature of dabcoHReO₄ is the magnitude of P_{sz} [Fig. 5(b)] almost 5 times higher than P_{sx} . P_{sz} is weakly temperature dependent with almost constant value of $16.5 \mu\text{C}/\text{cm}^2$ over the entire temperature range between room temperature and T_c . Interestingly, unlike P_{sx} , on cooling the crystals from the paraelectric to the ferroelectric phase the sense and magnitude of P_{sz} were restored. This testifies that the crystals formed no antipolar domains in this direction, and suggests that the unique property leading to the formation of parallel H-bonded chains also prevents their antipolar arrangement that would be necessary within the domain walls. Two main contributions of P_{sz} are the polarization of parallel hydrogen bonds, and the relative displacements of the cations and anions along [001]. The onset of the long-range ordering of the protons arranges all dipole moments of the dabcoH⁺ cations in the same sense. The estimation of the dipole moment of the cation performed by the INDO method (intermediate neglect of differential overlap, as included in package Hyperchem 7.0) gave the value of $1.76 \cdot 10^{-29} \text{ C m}$ corresponding to a polarization of $7.2 \mu\text{C}/\text{cm}^2$. The contribution to P_{sz} of ionic displacements along [001] has been estimated as $12.8 \mu\text{C}/\text{cm}^2$, by assuming that the charges of the ions are located at N (1) and Re (1). The total value of P_{sz} is reduced by the opposite polarization due to the NH⁺···N bonds, estimated as $-3.5 \mu\text{C}/\text{cm}^2$. So P_{sz} is

between 16 and $17 \mu\text{C}/\text{cm}^2$, in a reasonable agreement with the experimental value. The measured values of P_{sx} and P_{sz} sum to the resultant magnitude of \mathbf{P}_s of $17 \mu\text{C}/\text{cm}^2$, with \mathbf{P}_s inclined by 12.3° to [001]. To our knowledge the spontaneous polarization of dabcoHReO₄ is the largest of the magnitudes observed in all known organic ferroelectrics and is also the highest among the water-soluble materials. Hitherto the largest polarization observed in this class of compounds was $15 \mu\text{C}/\text{cm}^2$ in the inorganic LiH₃(SeO₃)₂ [14].

In conclusion, the dabcoHReO₄ ferroelectric is unique in that the polarizability of bistable NH···N hydrogen bonds along P_{sz} contributes directly to the spontaneous polarization of the crystal, apart from the displacements of the ions along P_{sx} and P_{sz} , or from the molecular polarizability of the ions. Owing to the conjunction of these structural features, the dabcoHReO₄ crystal may compete with any ferroelectrics known for their highest spontaneous polarization. The intriguing, hardly temperature dependent polarization along the hydrogen bonds in dabcoHReO₄ is different from the polarizations generated by ionic displacements. This feature is advantageous for constructing molecular switches, and also explains the reliability of biological signal-transmitting or information-coding systems based on the transformations of hydrogen-bonded aggregates [15].

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