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# Ferroelectric order in highly disordered molecular-ionic crystals

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The ordering of the anionic sublattice at the coexisting high orientational disorder of the cationic sublattice produces spontaneous polarization in imidazolium tetrafluoroborate $[C_3N_2H_5]^+[BF_4]^-$. This ferroelectric crystal exhibits the Curie point at 297.0 K and undergoes two other polymorphic phase transitions at 213.6 and 187.8 K. In spite of its pentagonal ring the dynamically disordered polar cation is localized at a special position on the threefold axis of the highly symmetrical rhombohedral unit cell. Thus it does not contribute immediately to the spontaneous polarization which originates predominantly from the behavior of the distorted tetrahedral fluoroborate anion.

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The existence of spontaneous polarization reversible in an electric field, which is typical of ferroelectric ordering, has been proved recently in a family of molecular-ionic crystals of pyridinium salts.[1,2] In these hybrid organic cation-inorganic anion structures complex Coulomb, van der Waals and weak hydrogen-bonding interactions play essential roles. A number of pyridinium salts undergo polymorphic solid-solid structural phase transitions evidently related to the ordering of the cation or anion and to the changes in molecular dynamics. Ferroelectric order has been discovered in mesophases of pyridinium salts revealing at least two structural transformations. Centrosymmetric trigonal symmetry of the high temperature prototype phase determined for: pyridinium tetrafluoroborate, perchlorate and fluorosulfonate or centrosymmetric orthorhombic symmetry for perrhenate, periodate and fluorochromate, involve in all these compounds high orientational disorder of the pyridinium cation. Intense molecular dynamics of the cation can be described in terms of a model of rapid reorientation around the pseudohexad axis of the ring by 60° stochastic jumps among equivalent potential wells.[2]

The breaking of symmetry evidenced in mesophases leads to slowing down of the cationic and/or anionic motions and partial ordering of the ions responsible for the appearence of ferroelectricity. The unusual behavior of such molecular-ionic crystals has been studied by various physical methods.[3–10]

In order to generalize our findings and verify whether ferroelectric ordering can be created in other molecular-ionic systems with a different cation symmetry (pseudopentagonal instead of pseudohexagonal) but with expected similar dipolar interaction of organic cation with inorganic anion, we have synthesized and investigated imidazolium tetrafluoroborate. By use of differential scanning calorimetry, x-ray diffraction, $^1$H and $^{19}$F NMR relaxation, optical observation and dielectric spectroscopy we have investigated the existence of phase transitions, crystal and molecular structure, molecular dynamics and anticipated appearence of ferroelectricity in this new crystal.

Imidazolium tetrafluoroborate $[C_3N_2H_5]^+[BF_4]^-$ was synthesized for the first time by neutralization of the base dissolved in methanol with tetrafluoroboric acid. The salt was dried and ground to powder for the calorimetric, NMR and dielectric measurements. After recrystallization from distilled water the transparent single crystals grown from an isopropanol solution by a slow evaporation method at room temperature were selected for x-ray, optical and dielectric investigation. The differential scanning calorimetry DSC was performed using a Netzsch DSC 204 apparatus with a scanning rate of $10\,\mathrm{K\,min^{-1}}$. X-ray diffraction measurements were performed with a KUMA-4 diffractometer using Mo $K_\alpha$ radiation and $\omega$-$2\theta$ scan mode. The data were collected at 250 and 310 K. The structures were solved by direct methods using SHELXS-97 (Ref. 11) and refined using SHELXL-97.[12] The optical conoscopic investigation was performed using a NICON E600POL polarizing microscope with a Linkam hot stage. The temperature dependence of $^1$H and $^{19}$F spin-lattice relaxation time $T_1$ was measured by a saturation recovery method using a pulse NMR spectrometer operating at 60 MHz. The temperature of the sample was stabilized to $\pm 1$ K with a gas-flow cryostat. Measurements of dielectric permittivity were performed by use of a Hewlett-Packard 4192 A impedance analyzer at frequencies between 1 kHz and 10 MHz. The measuring ac electric field was $2\,\mathrm{V\,cm^{-1}}$. The temperature was measured with a copper-constantan thermocouple to an accuracy of $\pm 0.1$ K. A Diamant-Drenck-Pepinsky bridge (RADIOPAN MD2/1) was used to record the dielectric hysteresis loops at a frequency of 50 Hz.

The temperature dependence of the specific heat obtained from DSC experiment is shown in Fig. 1. Three solid-solid phase transitions are disclosed between 100 K and the melting point at 459.9 K. The transition between phase I and II takes place at 300.0/294.4 K (heating/cooling), between phase II and III at 213.6/200.0 K, and between phase III and IV at 187.8/140.5 K. The observed hysteresis effects point to the first order character of these phase transitions. The enthalpies of the respective transitions at heating are 10.5, 15.7, and $3.0\,\mathrm{J\,g^{-1}}$, the enthalpy of the melting equals to $26.0\,\mathrm{J\,g^{-1}}$. The corresponding entropy changes at the solid-solid phase transitions $\Delta S$ are 5.5, 11.5, and $2.5\,\mathrm{J\,mol^{-1}K^{-1}}$, and are very close to Rln2, Rln4, and Rln1.35 (R is the gas constant). These values strongly suggest the order-disorder mechanism of two higher temperature phase transitions II →I and III→II.

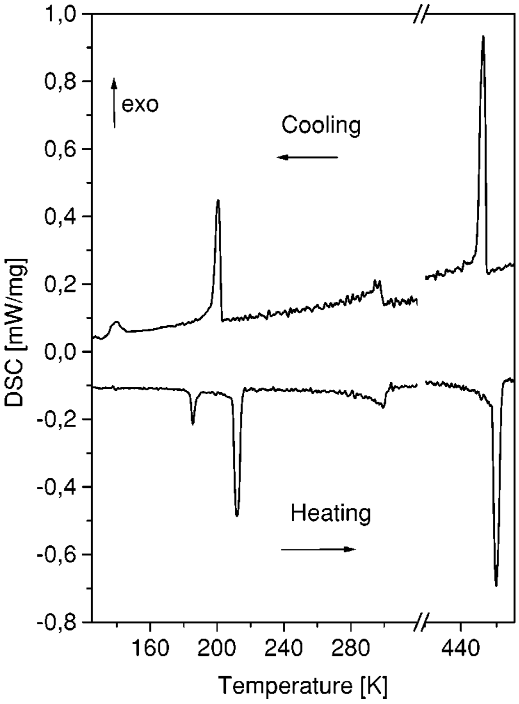

FIG. 1. DSC signal recorded at heating and cooling.

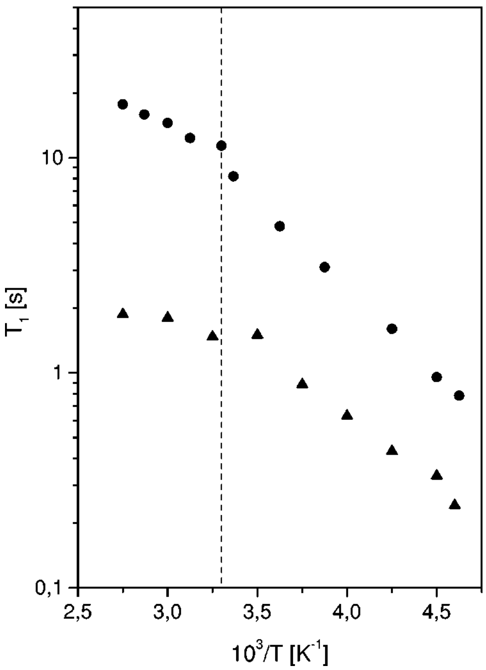

FIG. 2. Temperature dependence of the spin-lattice relaxation times $T_1^{\mathrm{H}}$(●) and $T_1^{\mathrm{F}}$(▲) at heating.

The x-ray determination of the crystal structure performed at 250 K shows that the crystal in phase II appears to be trigonal (noncentrosymmetric space group $R3$). The rhombohedral unit cell parameters are $a=5.384$ Å, $\alpha=94.72^\circ$, $Z=1$, volume $V=154.39$ Å$^3$, and $d_{\mathrm{calc}}=1.655\ \mathrm{g\,cm^{-3}}$. In high temperature phase I at 310 K the crystal remains trigonal with only slightly different rhombohedral unit cell parameters $a=5.437$ Å, $\alpha=94.93°$, $Z=1$, $V=158.83$ Å$^3$, and $d_{\mathrm{calc}}=1.630\ \mathrm{g\,cm^{-3}}$. Its space group $R3$ or $R\overline{3}$ is similar to that of the paraelectric phase of pyridinium fluoroborate.[13] It is worthy of note that in both phases the imidazolium cation localized at a special position on the [111] axis of the rhombohedral unit cell is highly orientationally disordered in the plane of its pentagonal ring. The cationic symmetry is inconsistent with the symmetry of the site occupied by the cation in the rhombohedral cell. Thus the cation must be highly disordered. The striking difference between both simple structures is related to the ordering of the tetrafluoroborate anion. In phase II the distorted tetrahedral $BF_4$ anion (one B-F bond 1.28 Å, three others 1.33 Å) is localized on the $C_3$ axis with 0.7 Å off-center boron atom position. In phase I there is an evident disorder of the $BF_4$ tetrahedron over two orientations and the boron position is on the average at the center of symmetry. One of the B-F bonds is oriented up or down along the $C_3$ axis. The single crystal conoscopic observation shows that both phases are optically uniaxial, which additionaly corroborates the trigonal symmetry evidenced by x-ray investigation.

The temperature dependence of the proton and fluorine spin-lattice relaxation time $T_1$ for both high temperature phases I and II is shown in Fig. 2. The observed change in the $^1$H spin-lattice relaxation time proves intense dynamics of the highly disordered imidazolium cations in both phases. The Arrhenius activation energy derived from the linear temperature dependence of $T_1$ for the cation motion in phase II equal to 16 kJ mol$^{-1}$ characterizes its rapid in-plane reorientation about the unusual pseudopentad symmetry axis. Since $T_1$ increases with temperature, according to the known BPP theory,[14] the correlation frequency for the cation motion must be higher than $10^{11}$ Hz. The II→I phase transition accelerates the reorientation rate of the disordered cation. The activation energy in phase I diminishes to 8 kJ mol$^{-1}$ due to the minute increase of about 3% in the volume of the elementary cell. The $^{19}$F spin-lattice relaxation time linearly increasing with temperature indicates intense dynamics of the fluoroborate anion in both phases II and I. The respective Arrhenius activation energies derived are 12 and 8 kJ mol$^{-1}$. The correlation frequency for this motion must be also higher than $10^{11}$ Hz. However, it is important to stress that the molecular motion in phase II has to be defined as the $C_3$ reorientation of the ordered fluoroborate anion jumping by 120° among equivalent potential wells, while in phase I the accelerated reorientation of the disordered anion is more complex.

The temperature dependence of the dielectric permittivity taken at 1 kHz measuring frequency is shown in Fig. 3. Clearly seen is a sharp jump in the permittivity at about 208 K corresponding very well to the first order solid-solid phase transition III→II disclosed in the DSC experiment. The most striking increase in permittivity corroborating the existence of the solid-solid phase transition II→I is observed at 297 K. The character of this change evidently points to the transition from the ferroelectric to the paraelectric phase. Its temperature has to be defined as the Curie point of a new ferroelectric crystal. The ferroelectric transition has probably a mixed order-disorder and displacive character.[15] It is tempting to argue that imidazolium tetrafluoroborate is the first precursor of the new family of ferroelectrics with heterocyclic aromatic

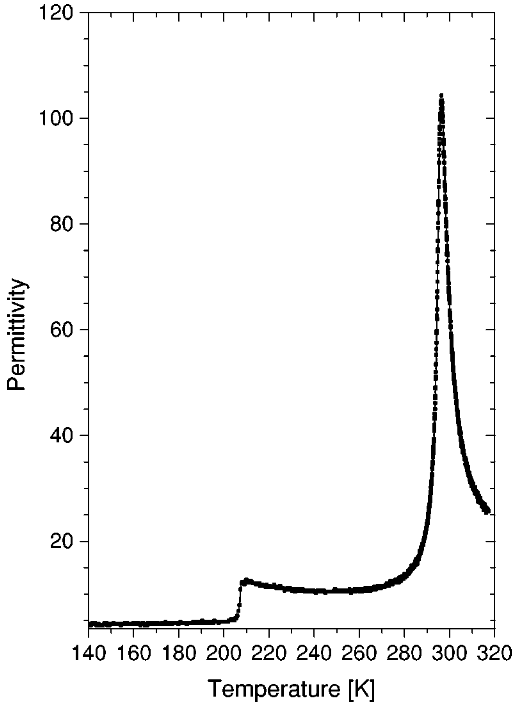

FIG. 3. Temperature dependence of the dielectric permittivity at 1 kHz measured along [111] at heating.

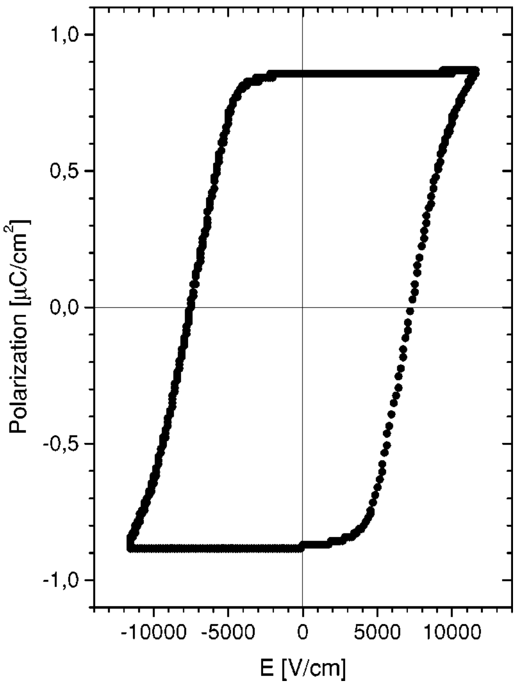

FIG. 4. Polarization vs electric field along [111] at 240 K.

cation of pseudopentagonal symmetry, highly disordered in the crystal lattice. The existence of a dielectric hysteresis loop shown in Fig. 4 is the crucial proof of the ferroelectric order in phase II, coexisting with a high disorder in the cationic sublattice. This cationic disorder remains in the high temperature paraelectric phase I accompanied therein by appearing disorder in the anionic sublattice. The high disorder of the imidazolium cations and thus of their permanent dipole moments in the ferroelectric phase averages to zero their contribution to the polarization of the crystal. The polarization originates decisively from the ordering and distortion of $BF_4$ anions. The rough estimate of the spontaneous polarization $P_s$ from the hysteresis loop yields a value of about $0.86\,\mu\mathrm{C\,cm}^{-2}$. The high coercive field increasing strongly with decreasing temperature characterizes this hard ferroelectric crystal. The origin of the ferroelectricity can be straightforwardly explained by calculating the magnitude of the spontaneous polarization. The permanent dipole moment of the distorted $BF_4$ anion estimated by Gaussian 98 amounts to 0.48 D. Hence, the spontaneous polarization along the [111] direction of the elementary cell is of the order of $1\,\mu\mathrm{C\,cm}^{-2}$ in good agreement with the value observed in the experiment.

In conclusion we have found a new crystal imidazolium tetrafluoroborate with high orientational disorder in both ionic sublattices in the high temperature prototype phase, but revealing ferroelectricity in the mesophase below 297 K, due to the ordering in the anionic sublattice. It appears to be the first known example of a molecular-ionic ferroelectric with the crystal structure comprising cations with heteroaromatic pentagonal rings.

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