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Ferroelectric properties of pyridinium tetrafluoroborate

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The differential thermal analysis of a single crystal of pyridinium tetrafluoroborate was performed revealing two solid-solid phase transitions at 205 and 240 K. The real part of the dielectric permittivity was measured between 190 and 290 K. The large anomaly at the higher phase transition is interpreted as the Curie point of a new ferroelectric crystal.

Pyridine, a strong organic base, reacts easily with many acids to form an interesting family of pyridinium compounds. In solid salts the symmetrical, planar, heteroaromatic pyridinium cation is involved in interionic hydrogen bonds. Some pyridinium salts undergo solid-solid phase transitions at low temperatures, changing the cation dynamics. The pyridinium cation, held rigidly in the crystal lattice well below the phase transition, reveals orientational disorder at room temperature. Previous NMR studies have disclosed the dynamic character of this disorder as in-plane 60° reorientational jumps of the cation about its pseudohexad axis.[1,2]

Pyridinium tetrafluoroborate $C_5H_6NBF_4$ crystallizing in the trigonal space group $R\bar{3}m$, with $a = 5.626$ Å, $\alpha = 97.51°$ and $Z = 1$ undergoes a phase transition at 202 K.[3] Our ^{1}H and ^{19}F NMR study performed over a wide range of temperature yielded a quantative description of the molecular dynamics of both ions in both solid phases. The study indicated the existence of a coupling between stochastic reorientations of cations and anions at the phase transition.[4] This effect, probably driving the phase transition, has been discovered previously for a number of guanidinium salts.[5] To throw more light on the problem of order-disorder phase transitions and the relevant ion mobilities in pyridinium tetrafluoroborate we have undertaken the present study of dielectric properties and differential thermal analysis of a single crystal of the compound.

The differential thermal analysis (DTA) was performed by use of a homemade apparatus in order to confirm the existence of the phase transition and to examine its nature. Temperatures were measured using copper-Constantan thermocouples with an accuracy of ±1 K. The DTA results for heating and cooling at the rate of 2.5 deg/min are shown in Fig. 1. Two endothermic peaks appearing with increasing temperature at 205 and 240 K indicate clearly the occurrence of two solid-solid phase transitions. The exothermic peaks observed on cooling are only slightly shifted to lower temperatures. It is interesting to note that the heat anomaly which accompanies the higher transition is approximately twice as great as that revelant to the lower one. Distinct asymmetry of the DTA peak characterizes the higher temperature phase transition. An independent study by differential scanning calorimetry (DSC) performed for a polycrystalline sample by use of an Perkin-Elmer DSC 7 apparatus at the University of Ulm (Germany) confirms fully the results of the experiments described above.

Dielectric properties of the compound were studied between 190 and 290 K on a single crystal grown from an ethanol-water solution by evaporation method at room temperature. Complex dielectric permittivity was measured at frequencies between 10 kHz and 13 MHz using a Precision LF Impedance Analyser (Hewlett-Packard 4192A). Silver electrodes were deposited on the (001) surfaces of the crystal plate cut to the size of $5 \times 5 \times 1.7$ mm^3. The temperature of the crystal was measured with a copper-Constantan thermocouple to an accuracy of ± 0.2 K. The temperature dependence of the real part of the dielectric permittivity ε' taken at 10 kHz is shown in Fig. 2. A small maximum of ε' appears distinctly at the lower phase transition while a very large peak appears at the higher phase transition ($\varepsilon' \approx 1000$) indicating unusual dielectric behavior of the compound. A typical Curie-Weiss temperature dependence of $1/\varepsilon'$ is shown in Fig. 3. Similarly as for many ferroelectrics the low-temperature slope is about 3.7 times higher than the high-temperature one. The Curie-Weiss constant determined amounts to 10^3 K. This behavior and a very high value of the dielectric permittivity strongly suggests that

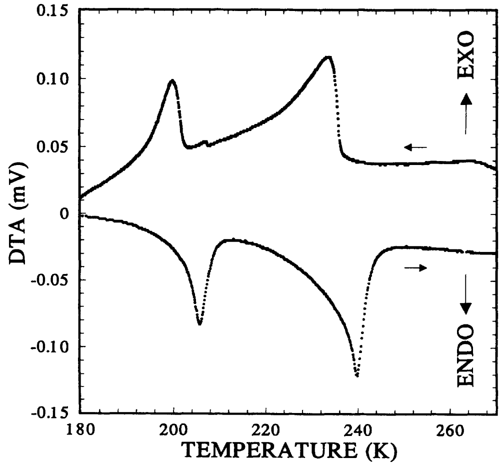

FIG. 1. DTA curves on heating and cooling (rate: 2.5 deg/min).

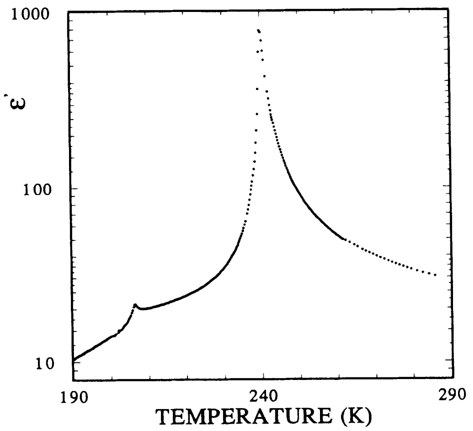

FIG. 2. Temperature dependence of the real part ε' of the dielectric permittivity taken at 10 kHz on heating.

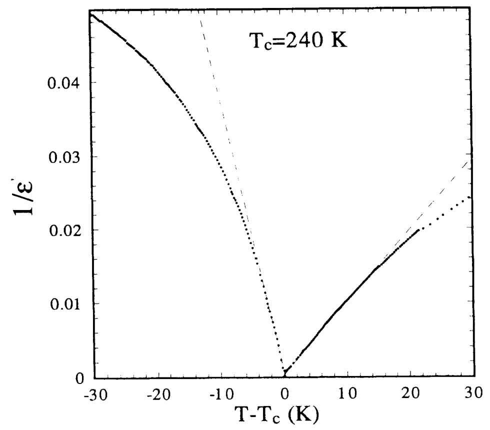

FIG. 3. Temperature dependence of 1/ε'.

the transition is ferroelectric-paraelectric in character. Thus it seems to be justified to define the high-temperature phase transition as the Curie point $T_c = 240$ K of a new ferroelectric crystal containing the pyridinium cation. The existence of the dielectric hysteresis loop corroborates the ferroelectric character of the compound below T_c. Preliminary measurements at 237 K indicate a high value of the coercive field of about 0.8 kV/cm and give a rough estimate of the spontaneous polarization of about 0.1 μC/cm^2. The coercive field rises strongly with lowering temperature. In a temperature range studied, the values ε' and ε'' appear frequency dependent. Very similar dielectric behavior has been observed for the polycrystalline pressed sample of the compound.

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