Ferroelectric properties of pyridinium perchlorate

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Abstract. Polycrystalline pyridinium perchlorate has been studied over a wide range of temperatures by differential thermal analysis, proton NMR spectra and relaxation, and dielectric permittivity measurements. Two solid–solid phase transitions at 232 and 248 K have been revealed and the pyridinium cation reorientations in all three phases characterized. The higher transition appears to be the Curie point of a new ferroelectric compound.

1. Introduction

Quite recently we have found that a single crystal of pyridinium tetrafluoroborate undergoes two solid–solid phase transitions at 205 and 240 K. The higher transition appears to be the Curie point of a new ferroelectric crystal. A very high value of the real part of the dielectric permittivity characterizes this transition [1]. Our earlier ^{1}H and ^{19}F NMR study of the molecular dynamics of pyridinium cation $[C_5NH_6]^+$ and tetrafluoroborate anion $[BF_4]^-$ has disclosed the dynamic character of the ionic disorder above the Curie point as well as the existence of a coupling between stochastic reorientations of both ions at lower temperatures [2].

The present study of differential thermal analysis (DTA), proton NMR spectra and relaxation as well as dielectric properties of polycrystalline pyridinium perchlorate has been undertaken in order to verify whether ferroelectricity is a feature of more than one pyridinium salt. A similar structure of anions in isostructural guanidinium perchlorate and tetrafluoroborate [3, 4] motivated our choice of pyridinium perchlorate.

2. Experimental details

The pyridinium perchlorate $[C_5NH_6]^+[ClO_4]^-$ was prepared by allowing the base dissolved in 80% ethanol to react with perchloric acid. Upon neutralization of the chemically pure substrates the salt was recrystallized three times from ethanol and the pure product was dried and ground to powder. The samples for the NMR study were degassed by the usual freeze–pump–thaw technique and sealed under vacuum in glass ampoules. For dielectric measurements, pellets 0.15 mm thick and 20 mm^2 in area were obtained by pressing a polycrystalline powder.

The DTA was performed by use of a home-made apparatus described in [5]. The 15 mg polycrystalline sample was measured with heating and cooling rates of 2.5 K min^{-1}. The temperature of the sample was controlled using copper–constantan thermocouples; the accuracy was ± 1 K.

Measurements of the proton NMR second moment M_2 were carried out over a wide range of temperatures using a home-made wide-line spectrometer operating at a Larmor

frequency of 28 MHz. The second-moment values were calculated by numerical integration of the first derivative of an absorption line and corrected for a finite modulation amplitude. Mean values were obtained for about 20 curves registered at each temperature.

The temperature dependences of the proton spin–lattice relaxation time T_1 were measured by a $\frac{1}{2}\pi$–τ–$\frac{1}{2}\pi$ pulse sequence or by a saturation recovery method with home-made pulse NMR spectrometers operating at Larmor frequencies of 60 and 25 MHz. The accuracy of the measurements was at least $\pm 7\%$. The temperature of the sample was controlled by means of a gas-flow cryostat and monitored with a Pt resistor to an accuracy of about 1 K.

The dielectric properties were studied for the pressed polycrystalline pellets with silver electrodes deposited on the surfaces. The complex dielectric permittivity was measured by use of a precision LF impedance analyser (Hewlett–Packard 4192 A) at frequencies between 10 kHz and 13 MHz. The applied measuring AC electric field was 2 V cm^{-1}. The temperature was measured to an accuracy of ± 0.2 K with a copper–constantan thermocouple.

The hysteresis loop was measured with a Diamant–Drenck–Pepinsky bridge (Radiopan MD 2/1) at a frequency of 50 Hz on the same pellets which were used for permittivity measurements.
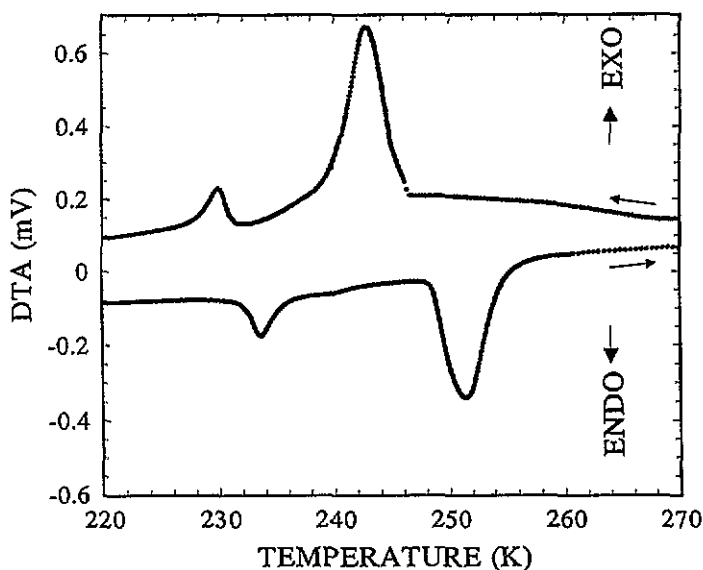

Figure 1. DTA curves on heating and cooling at a rate of 2.5 K min^{-1}.

3. Results and discussion

The DTA results presented in figure 1 reveal two endothermic peaks at 232 and 248 K. They evidently indicate the existence of two solid–solid phase transitions similar to those found in pyridinium tetrafluoroborate. A small but distinct hysteresis observed on cooling as well as the shapes of the DTA peaks indicate a first-order character of both transitions. The heat anomaly of the higher transition is about six times that of the lower transition.
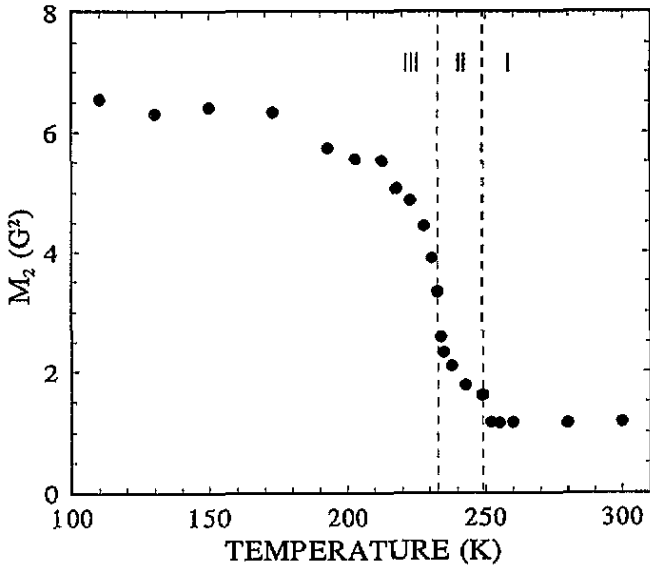
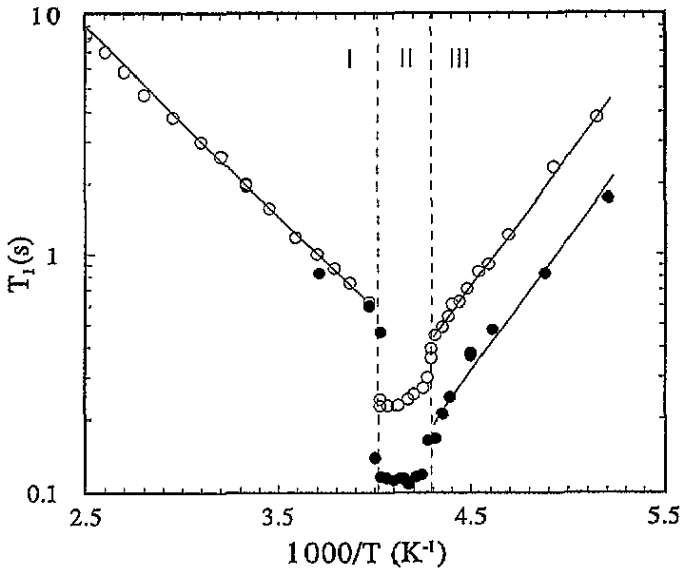**Figure 2.** Temperature dependence of the proton second moment.

Figure 3. Temperature dependence of the proton spin–lattice relaxation time at 60 MHz (O) and at 25 MHz (●).

In order to characterize the molecular dynamics of the pyridinium cation in all three solid phases detected, we performed a NMR study over a wide range of temperatures. The proton NMR spectra of pyridinium perchlorate registered between 110 and 400 K have allowed us to derive the second moments of the absorption lines shown in figure 2. The pyridinium cation dynamics reflected in the temperature changes in the proton second moment are very similar to those observed for the tetrafluoroborate [2]. At lower temperatures (phase III) the
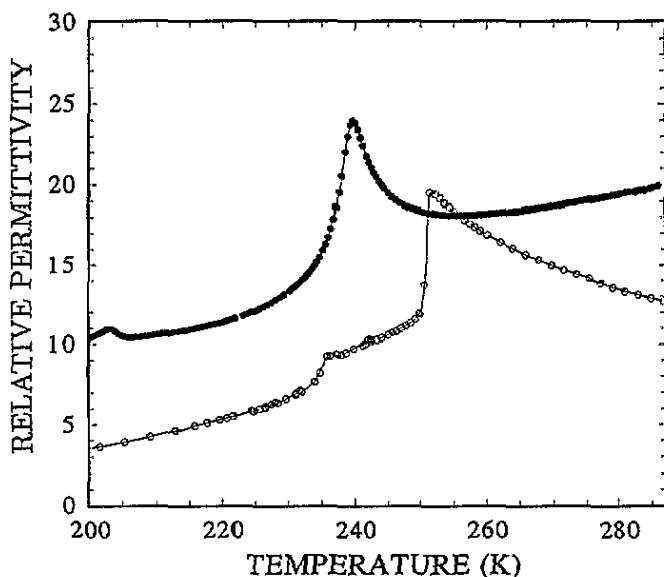
Figure 4. Temperature dependence of the real part ϵ' of the permittivity at 10 kHz on heating for pyridinium perchlorate (O) and pyridinium tetrafluoroborate (●).
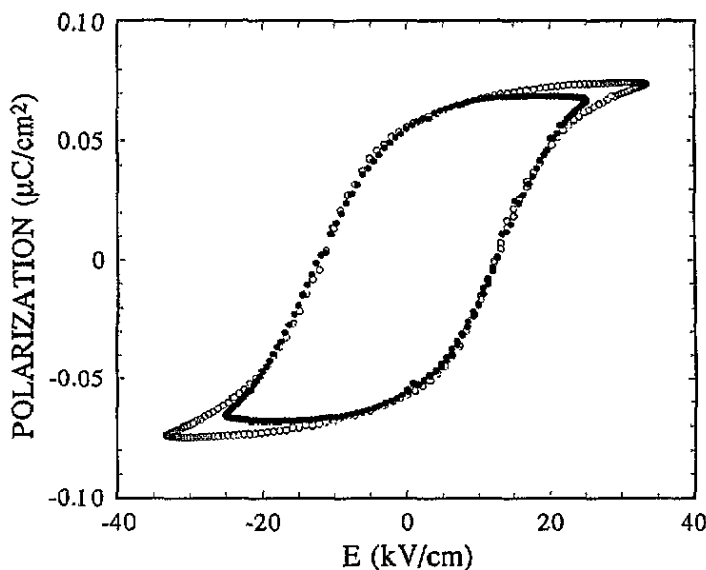

Figure 5. Dielectric hysteresis loops for pyridinium perchlorate (O) and tetrafluoroborate (●) at $T = (T_c - 4)$ K.

second moment of the compound equal to 6.5 G^2 corresponds well to the Van Vleck value for the rigid lattice; the calculated intracation contribution equals 3.5 G^2 while the estimated intercation contribution is 3.0 G^2. However, well below the lower phase transition the second moment starts to diminish to about 2.5 G^2 at 235 K. This means the onset of the cation reorientation with a frequency higher than 10 kHz. Above 252 K (phase I) the experimental

value of the second moment (1.2 G^2) provides clear evidence of dynamic disorder in the pyridinium cation sublattice. It can be interpreted as in-plane $60°$ reorientational jumps of the cation about its pseudohexad axis between equivalent positions, as similarly observed for other pyridinium salts by x-ray and NMR investigations [6–10]. The second moment in the narrow intermediate phase II between 235 and 252 K changes from 2.5 to 1.2 G^2, indicating another type of cation reorientation.

The temperature dependences of the proton spin–lattice relaxation time T_1 are shown in figure 3. A linear plot of log T_1 versus $1/T$ in phase III enables us to determine the Arrhenius activation energy E_a equal to 21.0 kJ mol^{-1} which characterizes the cation reorientation manifested as a diminishing value of the second moment (figure 2). In phase I the respective energy barrier hindering pseudohexad reorientation of the cation between six equivalent sites [6] equals 15.1 kJ mol^{-1}. At both phase transitions, one observes the discontinuities in the log T_1 versus $1/T$ plot. Fortunately, between both transitions in phase II it was possible to find the minima of T_1 equal to 222 ms and 107 ms, at Larmor frequencies of 60 MHz and 25 MHz, respectively. Following the BPP theory [11] from the condition $\omega_0 \tau_c = 0.616$ at the minimum of T_1 the correlation time τ_c characterizing the cation motion responsible for spin–lattice relaxation was found to be of the order of 10^{-9} s. The estimation of the activation energy in the narrow phase II is hazardous; its value seems to be higher than in phase III. The relaxation rate at the minimum equals $T^{-1} = \frac{2}{3} \Delta M_2 \gamma^2 f(\omega, \tau)$; from here a reduction in the second moment due to reorientation of the cation equals $\Delta M_2 = 4\ G^2$ which is the change observed in phase III (6.5–2.5 G^2). It is interesting to note that the ratio of T_1 minima observed (2.14) corresponds nearly to the theoretically expected value (2.4) for both Larmor frequencies. Thus the relaxation data indicate stochastic jumps of the cation between nearly equal potential wells. However, the ratio of 2.3 for the T_1-values in phase III for the Larmor frequencies applied is evidently smaller than the theoretically expected value equal to 5.8. This indicates cation motion between non-equivalent potential wells. It seems reasonable to suggest that the inequivalence of the hindering barriers diminishes with increasing temperature. In phase II it presumably goes to zero at the higher phase transition. A similar effect has been recently reported for pyridinium hexafluorophosphate [10].

The dielectric properties were studied between 190 and 300 K for the pressed polycrystalline sample of pyridinium perchlorate as well as for the pressed polycrystalline sample of pyridinium tetrafluoroborate taken for comparison. The temperature dependence of the real part ϵ' of the dielectric permittivity obtained at 10 kHz is shown in figure 4 for both samples. The very similar behaviours with distinct maxima at both phase transitions are clearly visible for both compounds. Thus it is justified to argue that the ferroelectric properties of pyridinium perchlorate and tetrafluoroborate are very much alike. To prove this statement we have measured the electric field dependence of polarization and for both samples we have observed the typical dielectric hysteresis loops shown in figure 5. They undoubtedly confirm the ferroelectric character of both compounds below the respective Curie points at 248 K and 240 K for perchlorate and tetrafluoroborate, respectively. The roughly estimated spontaneous polarization is about 0.1 $\mu C\ cm^{-2}$ for both compounds. The coercive field, which increases strongly with decreasing temperature, is rather high. The values of ϵ' and ϵ'' for both salts appear frequency dependent below the respective Curie points. The preliminary powder x-ray study performed at room temperature shows that pyridinium perchlorate crystallizes in the trigonal system with similar lattice parameters as measured for pyridinium tetrafluoroborate [2].

Thus we can conclude that a new family of ferroelectric pyridinium compounds has been discovered. The search for other members of this family is now under way.

Acknowledgment

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