

# Glass-like dielectric relaxation in $C_5NH_6ClO_4$

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Received 23 February 2007; received in revised form 14 May 2007; accepted 29 May 2007 by J.W.P. Hsu  
Available online 5 June 2007

## Abstract

Detailed dielectric measurements have been carried out in polycrystalline pyridinium perchlorate  $C_5NH_6ClO_4$  at temperatures of  $100\text{ K} \leq T \leq 280\text{ K}$  and frequencies of  $10\text{ Hz} \leq \nu \leq 10^5\text{ Hz}$ . Besides the known dielectric anomalies at 248 and 233 K, a glass-like dielectric relaxation is clearly observed at temperatures below 233 K. The frequency dependence of the dielectric constant is interpreted to originate from two different relaxation processes. The relaxation time for the dominant relaxation process is well described by an Arrhenius equation with the activation energy  $E = 3073\text{ K}$  and  $\tau_0 = 6.2 \times 10^{-12}\text{ s}$ . The other weak relaxation process is also analyzed using the same equation with  $E = 1160\text{ K}$  and  $\tau_0 = 1.5 \times 10^{-5}\text{ s}$ . The dominant relaxation process is considered to arise from the coupled reorientation of the pyridinium cation and perchlorate anion, while the weak one seems to be attributed to the ferroelectric domain wall motion. This suggests that the phase below 233 K can be described as a mixed phase comprising the dipolar glass and ferroelectric states.

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PACS: 77.84.-S; 77.22.G

Keywords: A. Ferroelectrics; B. Chemical synthesis; D. Phase transitions

## 1. Introduction

The family of the pyridinium salts derived easily from the reaction of pyridine with inorganic acids is an attractive subject for study because it shows various kinds of phase transitions. The pyridinium salts with tetrahedral anions such as  $BF_4$  [1],  $ClO_4$  [2,3],  $ReO_4$  [4],  $IO_4$  [5,6],  $FSO_3$  [7],  $FCrO_3$  [8] reveal the ferroelectric phase transition. On further cooling from the ferroelectric phase transition temperature,  $PyFSO_3$  (Py denotes the pyridinium cation  $C_5NH_6$ ) undergoes two consecutive non-ferroelectric phase transitions, while the remaining ones exhibit an additional non-ferroelectric phase transition.

The high-temperature phase in these pyridinium salts is characterized by the dynamical disorder of both the pyridinium cations and the corresponding anions. The coupling of both ions through dipolar interaction is believed to play a crucial role in inducing the ferroelectric ordering in the intermediate-temperature phase [3,6–10], although it is not yet confirmed that the anion distortion for the nonzero dipole moment really takes place.

In previous reports, the low-temperature phases in  $PyBF_4$ ,  $PyClO_4$ , and  $PyIO_4$  were proved to remain ferroelectric by the measurements of spontaneous polarization [11–13], while  $PyFCrO_3$  was confirmed to be antiferroelectric in the low-temperature phase [8]. On the other hand, there has been no concrete characterization of the low-temperature phases in  $PyReO_4$  and  $PyFSO_3$  [4,7].

Another interesting feature of the phase transitions in these compounds is the dielectric relaxation observed below the ferroelectric phase transition temperature. Its main origin is considered to be the reorientation of the pyridinium cations or the coupled reorienting motion of both the cation and the anion [6,7].

In this work, detailed investigations on the dielectric properties of  $PyClO_4$  are reported.  $PyClO_4$  shows a ferroelectric phase transition accompanied by a sharp dielectric anomaly at  $T_1 = 248\text{ K}$  and an additional non-ferroelectric phase transition at  $T_2 = 233\text{ K}$ . So far, little has been known about the dielectric relaxation in  $PyClO_4$ . The detailed information of low-temperature dielectric behavior is expected to promote an understanding of cation (anion) dynamics in the low-temperature phase.

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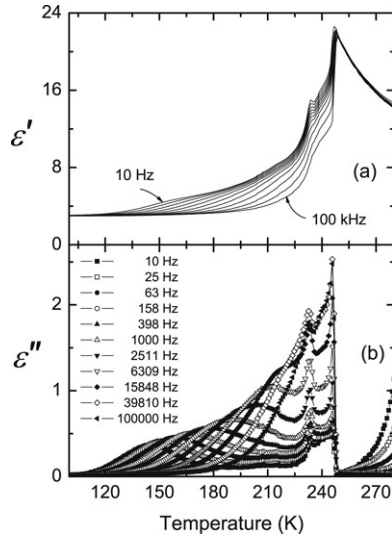


Fig. 1. Temperature dependence of: (a) the real part of the dielectric constant  $\epsilon'$ ; and (b) the imaginary part of the dielectric constant  $\epsilon''$  measured at various frequencies.

## 2. Experiment

PyClO<sub>4</sub> was prepared by the reaction between pyridine and perchloric acid in the solution of 80% ethanol and 20% water. The polycrystalline PyClO<sub>4</sub> was dried and ground to fine powder. Pellets of 10 mm diameter and 0.7 mm thickness were obtained by pressing the powder. Silver was evaporated on both sides of the pellets to be used as electrodes. The dielectric constants were measured by use of a capacitance bridge method employing a two-channel lock-in amplifier (Stanford Research, SR830) and a function generator (Agilent 33220A) as a source. The value of the standard capacitor used in the measurements was 0.1  $\mu$ F. The temperature of the samples was controlled in the closed cycle refrigerator (Janis, CCS250) with a temperature controller (LakeShore 330), where the control stability was  $\pm 0.05$  K. The measurements were made during the cooling process, and the cooling rate was 0.5 K/min.

## 3. Results and discussion

Fig. 1(a) presents the temperature dependence of the real part of the dielectric constant  $\epsilon'$  at various frequencies. The  $\epsilon'$  exhibits a frequency dispersion below the ferroelectric phase transition temperature  $T_1 = 248$  K, and the value of  $\epsilon'$  at a fixed temperature appears to increase with decreasing frequency. The dielectric dispersion in the imaginary part of the dielectric constant  $\epsilon''$  below the non-ferroelectric phase transition temperature  $T_2 = 233$  K is characterized by the presence of frequency dependent maxima as shown apparently in Fig. 1(b). The maximum position shifts upward as the frequency increases. At frequencies higher than about 15 kHz, the maximum is no longer observed due to a significant overlap with the dielectric anomaly related to the phase transition at  $T_2$ .

The Cole–Cole plots of dielectric data in different ranges of temperature below 225 K are displayed in Fig. 2. The solid lines

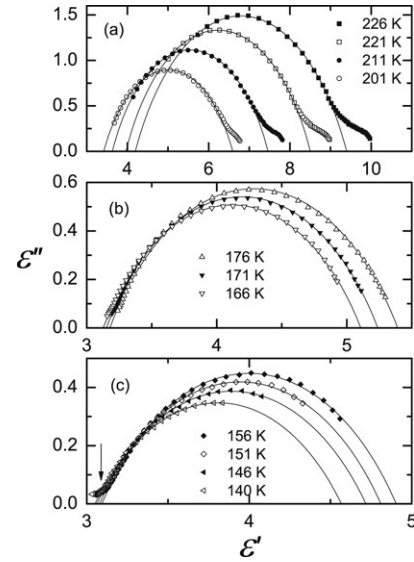


Fig. 2. Cole–Cole plots in three different ranges of temperature. The solid lines represent fits to Eq. (1).

represent the fits to the Cole–Cole formula

$$\epsilon' - i\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} + \epsilon_\infty \quad (1)$$

where  $\epsilon_0$  and  $\epsilon_\infty$  are the static and high-frequency limits of the dielectric constant, respectively,  $\omega = 2\pi\nu$  is the angular frequency,  $\tau$  is the relaxation time, and  $\alpha$  is a parameter for the distribution of the relaxation times. The fit results show that the Cole–Cole plots at temperatures above 180 K deviate from Eq. (1) in the low frequency region as can be seen in Fig. 2(a). The Cole–Cole plots at temperatures between 160 and 180 K show a good fit to the Cole–Cole formula without any prominent deviations (see Fig. 2(b)). At  $T < 160$  K, other deviations start to appear in the high frequency region as indicated by the arrow in Fig. 2(c), although they are not conspicuous compared with those observed in the plots at  $T > 180$  K. This implies that the one-relaxation model such as Eq. (1) is not sufficient for the accurate analysis of the dielectric data at  $T > 180$  K and  $T < 160$  K. As will be shown later, the small difference from the Cole–Cole formula that appears at high frequencies and low temperatures is an artifact. Thus the dielectric constant in these temperature ranges must be described as a contribution from two kinds of relaxation process

$$\epsilon' - i\epsilon'' = \frac{\Delta\epsilon_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\Delta\epsilon_2}{1 + (i\omega\tau_2)^{1-\alpha_2}} + \epsilon_\infty \quad (2)$$

where  $\Delta\epsilon_i = \epsilon_{i0} - \epsilon_{i\infty}$  ( $i = 1, 2$ ) and  $\epsilon_\infty = \epsilon_{1\infty} + \epsilon_{2\infty}$ . The subscripts 1 and 2 denote the dominant and weak relaxation processes, respectively. For the one-relaxation model,  $\omega$  can be represented in terms of parameters such as  $\epsilon'$ ,  $\Delta\epsilon$ ,  $\epsilon_\infty$ ,  $\tau$ , and  $\alpha$  by solving a quadratic equation:  $\sum_{i=0}^2 A_i x^i = 0$  where  $x = \omega^{1-\alpha}$  and  $A_i$  is a multivariable function of those parameters. Substituting this result for  $\omega$  in the imaginary part of Eq. (1),  $\epsilon''(\omega)$  is easily expressed as an explicit function of  $\epsilon'$  which can be used in the fit of the Cole–Cole plot of dielectric data. In the case of the two-relaxation model such as Eq. (2), representing

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