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2005 J. Phys.: Condens. Matter 17 S3131

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Pyridinium salt investigations under high pressure: pressure-induced phase transitions in ferroelectric pyridinium perrhenate

P Czarnecki¹, A I Beskrovny², L Bobrowicz-Sarga¹, S Lewicki¹ and J Wasicki¹

¹ Faculty of Physics, A Mickiewicz University, ulica Umultowska 85, PL-61-614 Poznań, Poland

² Frank Laboratory of Neutron Physics, JINR, RU-141980, Dubna, Russia

E-mail: pczarnec@amu.edu.pl

Received 8 July 2005

Published 23 September 2005

Online at stacks.iop.org/JPhysCM/17/S3131

Abstract

The properties of pyridinium perrhenate have been studied by three methods: dielectric spectroscopy, neutron powder diffractometry and NMR spectrometry under high pressure. It has been shown that under high pressure the temperatures of the two phase transitions in the crystal are shifted towards lower ones. Moreover, the results have shown the occurrence of a new high pressure phase with a triple point corresponding to the pressure of 100 MPa and the temperature of 240 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

For many years, the pyridinium salts PyHX, where X is a monovalent anion (I^- , Br^- , Cl^- , PF_6^- , SbF_6^- , BF_4^- , ClO_4^- , ReO_4^- etc) and PyH is the pyridinium cation ($[C_5H_5NH]^+$), have been subjects of intensive study [1–5]. Some of the salts show ferroelectric properties. At low temperatures the salts show both positional and orientational ordering and with increasing temperature they pass to a disordered phase through one or a few solid–solid phase transitions.

Most interesting are the pyridinium salts with tetrahedral [3, 4] or pseudo-tetrahedral [6] anions, as they reveal ferroelectric properties in the low temperature phases. The high temperature disordered crystalline phases of pyridinium tetrafluoroborane (PyHBF₄) and pyridinium perchlorate (PyHClO₄) crystallize in the rhombohedral system, similarly to non-ferroelectric halogen salts (iodide, bromide and chloride). High pressure study of the salts crystallizing in the rhombohedral system [7, 8] has shown that in these compounds the phase transition temperatures increase with increasing pressure. The pressure changes of the continuous phase transition temperatures in PyHBF₄ [7] follow the Ehrenfest equation, while those of the discontinuous phase transitions in PyHClO₄ [8] PyHI [9] and PyHBr follow the

Clausius–Clapeyron equation. Analysis of the high pressure data for PyHI [9] suggests that for this compound, at pressures above 1 GPa, a tricritical point can be expected in the p – T diagram.

This paper reports results of a high pressure study of pyridinium perrhenate PyHReO₄ using dielectric spectroscopy, NMR and neutron diffraction. The structure of this compound [10] differs from those of the other pyridinium salts such as PyHBF₄ [3] and PyHClO₄ [11]. The perrhenate undergoes two phase transitions: a continuous one at 336 K and a discontinuous one at 250 K. In all phases PyHReO₄ has orthorhombic structure and undergoes the following phase transitions: $Cmcm \rightarrow Cmc2_1 \rightarrow Pbca$. The intermediate phase is ferroelectric, while the disordered high temperature phase and ordered low temperature phase are centrosymmetric. The aim of this study is to determine the p – T phase diagram and its comparison with analogous ones obtained for the rhombohedral pyridinium salts.

2. Experimental details

The high pressure dielectric measurements were performed in a high pressure dielectric chamber connected with a gas compressor, GCA-10 (UNIPRESS). The pressure was measured with a manganin sensor to an accuracy of 2 MPa. The dielectric properties were measured with an impedance analyser, Hewlett-Packard 4192A, for frequencies ranging from 10 kHz to 13 MHz, at a few values of the hydrostatic pressure from the range 50 to 800 MPa in the temperature range covering the phase transitions. The measuring ac electric field was about 1 V cm⁻¹. For dielectric measurements we used pressed polycrystalline samples, 0.5 mm in thickness and 10 mm² in area, covered with evaporated gold electrodes. We chose polycrystalline samples instead the monocrystalline ones because the monocrystals of PyHReO₄ kept breaking at the low temperature discontinuous phase transition. The dielectric measurements allowed us to draw a p – T phase diagram.

Neutron powder diffraction (NPD) spectra were measured by the time of flight method using a NERA-PR spectrometer working in the inverted geometry. This spectrometer installed at an IBR-2 pulsed reactor at JINR in Dubna permitted simultaneous recording of NPD spectra and incoherent inelastic neutron scattering spectra for sixteen angles of scattering. Measurements of NPD spectra as a function of hydrostatic pressure were performed using the same spectrometer with the aid of the high pressure set-up. The high pressure gaseous helium set-up consists of a gas compressor, a gas high pressure cell and a cryostat. The U11 gas compressor (UNIPRESS) is a laboratory high pressure arrangement generating pressure up to 1500 MPa in gases. This compressor is designed for use with helium; however, any inert gas can be used as the pressure transmitting medium. The gas neutron cell GNC-400 was developed for investigation of the structure and dynamics of molecular crystals by the neutron scattering method under high pressure up to 400 MPa. It is connected to a gas compressor by a beryllium–copper capillary and arranged inside a shaft-type cryostat with temperature adjustable in the 78–350 K temperature range. A polycrystalline sample to be studied is placed in a thin-walled aluminium container inserted into the high pressure cell. The working volume of the high pressure cell is 22.7 cm³. The use of helium gas as a pressure transmitting medium in general enables achievement of purely hydrostatic conditions inside the cell. The set-up described gives the possibility of carrying out the measurements of neutron scattering spectra under high pressure maintained during exposure within the accuracy of 5 MPa, at a constant temperature within the accuracy of 0.5 K.

The proton spin–lattice relaxation times T_1 for a polycrystalline sample were measured under hydrostatic pressure varied from 0.1 up to 800 MPa in the temperature range 154–300 K. The measuring set-up included a pulsed NMR spectrometer working at 25 MHz, a U-11 helium gas compressor and a beryllium–copper high pressure cell.

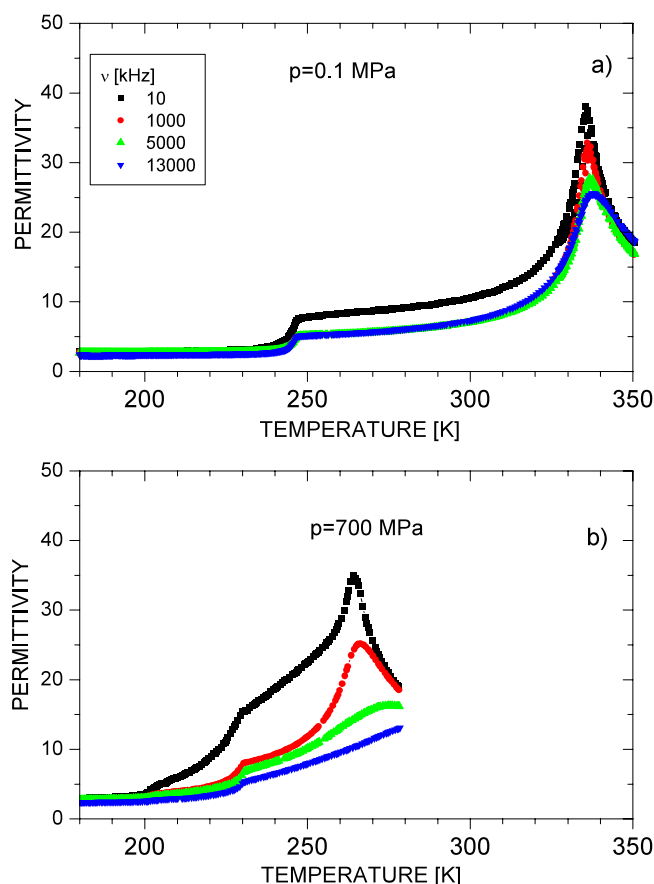


Figure 1. Temperature dependence of the permittivity (a) at 0.1 MPa and (b) at 700 MPa for a few frequencies.

3. Results and discussion

The temperature dependences of the dielectric permittivity obtained for a few frequencies at 0.1 and 700 MPa are presented in figures 1(a) and (b), respectively. The temperature dependences of the loss tangent ($\tan \delta$) at the pressures 0.1 and 700 MPa are presented in figures 2(a) and (b), respectively. The dependences reveal (figure 1) two anomalies at $T_1 = 333$ K and at $T_2 = 250$ K, so indicating that the material occurs in three phases: I—the high temperature one, II—the intermediate one and III—the low temperature one. Under a high pressure the ferroelectric anomaly at T_1 is shifted towards lower temperatures. The low temperature phase transition at T_2 is not only shifted towards lower temperatures but also splits into two, which leads to the appearance of the pressure phase denoted as II'. The two low pressure anomalies are clearly visible, especially in the temperature dependence of the loss tangent (figure 2(b)). Systematic dielectric measurements performed at a few pressures permitted drawing the p - T diagram presented in figure 3. At about 100 MPa and at 240 K there is a triple point joining the two curves of phase equilibrium.

Figure 4 shows the temperature dependences of the spin-lattice relaxation times T_1 measured at hydrostatic pressures: 0.1, 400 and 800 MPa. At 0.1 MPa only the phase transition

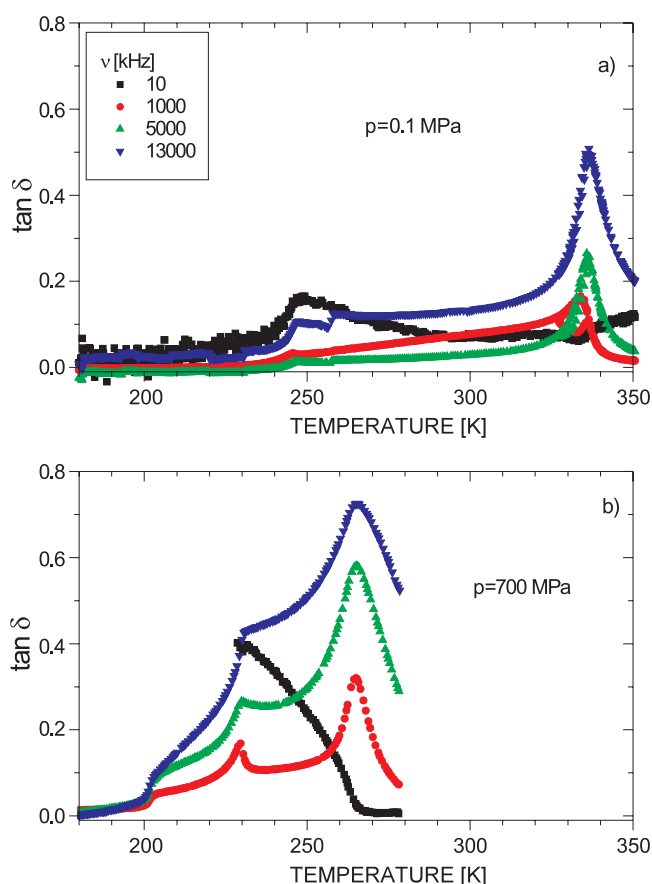


Figure 2. Temperature dependence of the loss tangent (a) at 0.1 MPa and (b) at 700 MPa for a few frequencies.

from phase III to phase II was observed at 250 K in the temperature range of the study. At higher pressures (400 and 800 MPa) three phase transitions were observed. In all phases, except the lowest temperature one, the linear dependence of $\ln(T_1)$ versus $1/T$ was revealed. The value of the relaxation time changes discontinuously at the phase transition between the lowest and intermediate temperature phases. At other phase transitions we observed a change of the slope of the $\ln T_1(1/T)$ dependence.

Figure 5 presents the pressure dependence of the spin–lattice relaxation time T_1 at temperature 222 K. For pressure increasing from 0.1 to 280 MPa, T_1 slowly decreases. At 280 MPa the relaxation time decreases discontinuously by one order of magnitude and then with increasing pressure it slowly decreases. The measurements performed with decreasing pressure revealed a discontinuous change in T_1 at 125 MPa. The phase transition temperature obtained from NMR high pressure measurements (determined with increasing pressure) are shown in the p – T phase diagram (figure 3). It is not clear why we observe the big pressure hysteresis (figure 5) in the NMR experiment. The NMR points in the p – T phase diagram are determined with less good accuracy than the dielectric measurements.

In order to verify the presence of the pressure-induced phase we have performed neutron diffraction measurements under varying pressure. At 230 K neutron diffraction spectra were

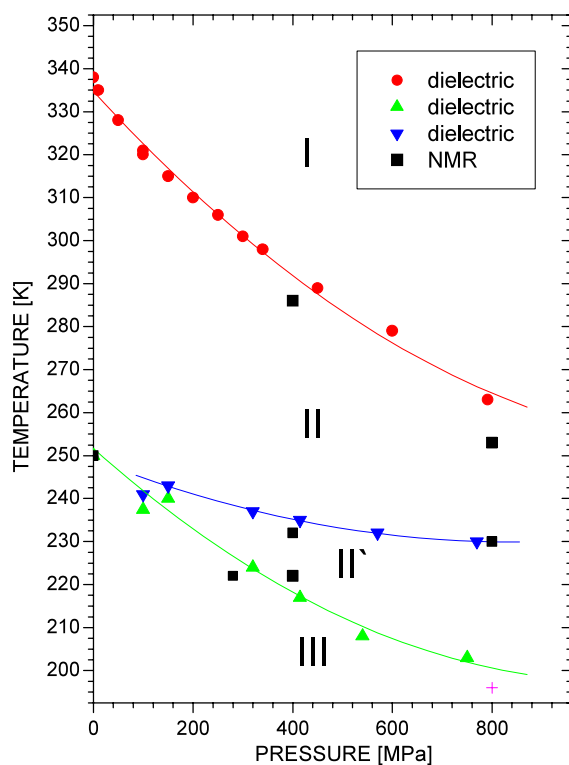


Figure 3. p - T phase diagram of PyHReO₄. The lines dividing the phases are a guide to the eye.

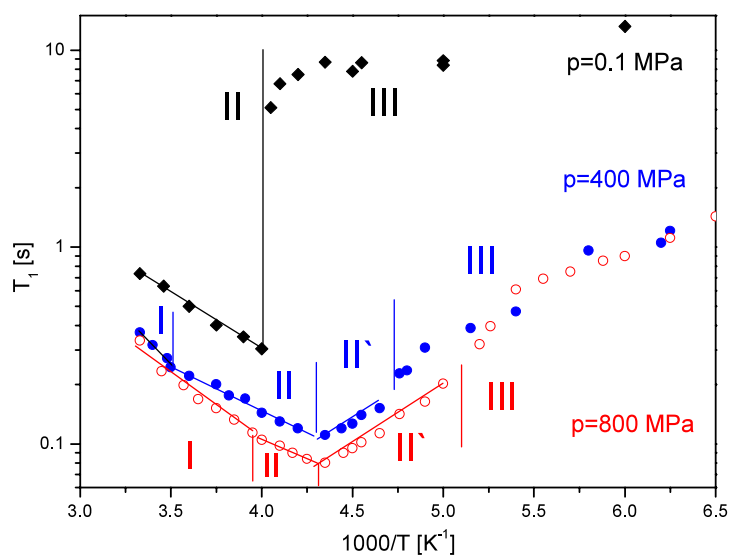


Figure 4. The temperature dependence of the proton spin-lattice relaxation times T_1 for 0.1 MPa (\blacklozenge), 400 MPa (\bullet) and 800 MPa (\circ).

measured at a few pressure values (figure 6): 0.1, 80, 200, 370 MPa and at 260 K at 370 MPa. The neutron diffraction spectra recorded at 230 K and at the pressures 200 and 370 MPa differ

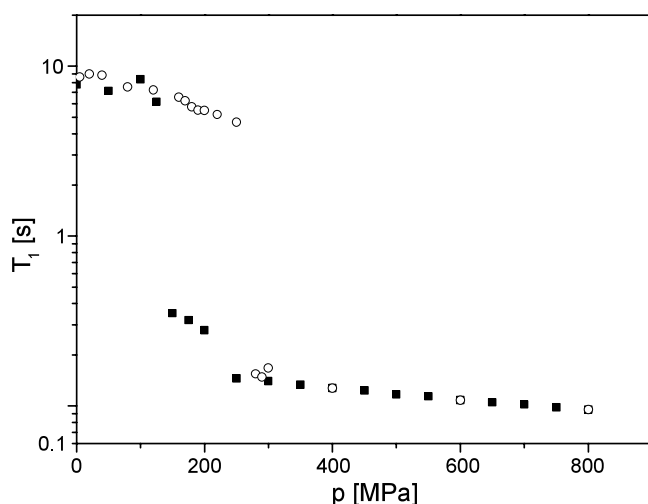


Figure 5. Pressure dependences of T_1 measured at 222 K, with increasing pressure (○) and decreasing pressure (■). Notice the pressure hysteresis (155 MPa) of the phase transition.

Table 1. Thermal expansion coefficients and compressibility obtained from the neutron powder diffraction experiment.

Phase	$\alpha = (1/V)(dV/dT)$ (K^{-1})	$\beta = -(1/V)(dV/dp)$ (Pa^{-1})
I	3.47×10^{-4}	9.03×10^{-11} (at $T = 310$ K)
II	1.76×10^{-4}	7.94×10^{-11} (at $T = 260$ K)
III	1.63×10^{-4}	7.26×10^{-11} (at $T = 90$ K)

from those recorded at 80 and 0.1 MPa, which proves the presence of a new pressure-induced phase. The change in the diffraction spectrum recorded at 370 MPa on changing the temperature of measurement from 230 to 260 K also confirms the presence of a new phase transition between the pressure-induced phase II' and phase II. The volume expansion coefficients α have been determined on the basis of the temperature dependences of the lattice constants at atmospheric pressure by the neutron diffraction method (table 1), while the compressibility β for all phases has been found from lattice constant measurements at a constant temperature and at a few pressures (table 1).

4. Conclusions

The p - T phase diagram obtained for PyHReO₄ differs significantly from those of the other pyridinium ferroelectric salts PyHBF₄ [7], PyHClO₄ [8]. For PyHReO₄ the temperatures of both phase transitions are shifted towards lower values with increasing pressure, whereas for PyHBF₄ and PyHClO₄ they are shifted towards higher values. The pressure dependence of the continuous phase transition temperatures follows the Ehrenfest equation

$$dT/dp = TV\Delta\alpha/\Delta C_p \quad (1)$$

where $\Delta\alpha$ is the jump change in the volume expansion coefficient at the phase transition temperature, ΔC_p is the jump change in the specific heat and V is the molar volume.

As the specific heat jump is practically always positive the sign of dT/dp (equation (1)) depends on the sign of $\Delta\alpha$. The NPD results obtained for PyHReO₄ permitted estimation of

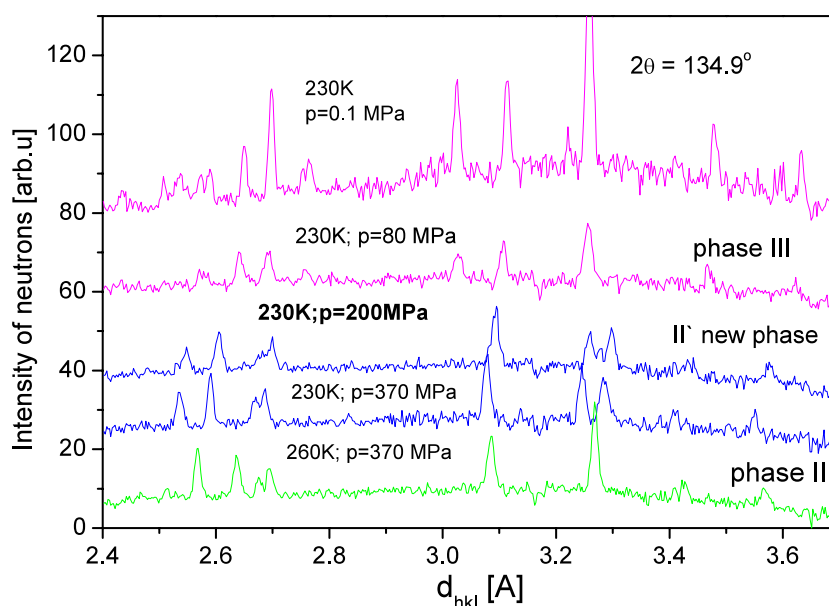


Figure 6. Neutron powder diffraction spectra measured at a few pressures.

the value of $\Delta\alpha$. Because of the negative value of $\Delta\alpha = -1.71 \times 10^{-4} \text{ (K}^{-1}\text{)}$ (table 1), the term dT/dp is negative, so with increasing pressure the temperature of the ferroelectric phase transition is shifted towards lower values, which is qualitatively consistent with equation (1).

The phase transition at T_2 is discontinuous. The pressure dependence of the discontinuous phase transitions is described by the Clausius–Clapeyron equation:

$$dT/dp = \Delta V/\Delta S \quad (2)$$

where ΔS is the change in entropy at the phase transition temperature and ΔV is the jump change in volume.

The shift of T_2 towards lower values under the effect of elevated pressure in PyHReO_4 is caused by a small negative jump change in volume $\Delta V \approx -3 \text{ (\AA}^3\text{)}$ at $T_2 = 250 \text{ K}$.

The compressibility coefficients (table 1) obtained for PyHReO_4 are smaller than the analogous ones for PyHBF_4 [7] undergoing phase transitions of similar character. These differences can be a result of the structural differences between these compounds and the much stronger hydrogen bonds in PyHReO_4 .

The symmetry of the pressure-induced phase II' could not be determined from the NPD measurements; however, the character of the temperature dependences obtained in the NMR experiment suggest that this phase is partly disordered and thus similar to phase III. We will perform a high pressure single-crystal neutron diffraction experiment to obtain the structure of the phase II' .

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