

The study of the P-T phase diagram of the pyridinium perchlorate.

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Pyridinium salts belong to the group of molecular-ionic crystals with hydrogen bonds, which exhibit a rich variety of interesting phenomena such as structural phase transitions, ferroelectricity and dynamical orientational disorder of the pyridine cations [1-4]. The existence of ferroelectricity was discovered in pyridinium tetrafluoroborate (PyHBF₄ - C₅H₅NHBF₄) [1], pyridinium perchlorate (PyHClO₄) [2], pyridinium perrhenate PyHReO₄ [3] and pyridinium periodide PyHIO₄ [4]. The para-ferroelectric transition is accompanied by the structural phase transformation, resulting in the change of the disorder degree of pyridinium and perrhenate ions. The precise determination of crystal and molecular structure is essential for explaining the nature of the ferroelectric properties of pyridinium salts.

In order to study the structural P-T phase diagram in the extended pressure range than previously [5] and obtain more detailed information about structural parameters of different phases, we have performed energy dispersive X-rays at pressure up to 3.5 GPa and temperature range 300-400 K.

In situ X-rays diffraction high-pressure experiments were carried out using the multianvil X-ray system MAX80. Diffraction patterns were recorded in an energy dispersive mode using white synchrotron X-rays from the storage ring DORIS III. The ring operated at 4.5 GeV and a positron current of 80-150 mA. The incident X-ray beam was collimated to 100 × 100 μm with a divergence smaller than 0.3 mrad. Spectra were recorded by a Ge solid-state detector with a resolution of 153 eV at 5.9 keV resulting in a resolution of diffraction patterns of $\Delta d / d \approx 1\%$. The Bragg angle 2θ was fixed at 9.093°, counting times for each diffraction pattern was 360 seconds.

The figure 1 shows the X-rays diffraction pattern of the pyridinium perchlorate at ambient and high pressure $P=0.5$ and $P=1.98$ GPa. At ambient condition the rhombohedral phase I with space group R3m was evidenced. At pressures range 0.5-0.9 GPa, slightly changes in the diffraction patterns at ambient temperature were observed. They correspond to the appearance of the monoclinic phase II with space group Cm [6] under high pressure, as evidenced from analysis of the data by profile matching mode. At pressure $P=0.9$ GPa the phase transition to monoclinic phase III with Pm space group was occurred. The structure parameters of three phases of the pyridinium perchlorate are listed in Table 1.

Table 1. The structure parameters of the three phases of pyridinium perchlorate at different pressure.

	<i>Phase I, P=0 GPa</i>	<i>Phase II, P=0.5 GPa</i>	<i>Phase III, P=1.8 GPa</i>
Space group	R3m	Cm	Pm
Lattice parameters	$a=8.675(9) \text{ \AA}$ $c=8.497(4) \text{ \AA}$	$a=8.286(8) \text{ \AA}$ $b=14.758(7) \text{ \AA}$ $c=8.605(8) \text{ \AA}$ $\beta=90.9(6)^\circ$	$a=7.948(7) \text{ \AA}$ $b=14.444(9) \text{ \AA}$ $c=8.526(9) \text{ \AA}$ $\beta=93.2(9)^\circ$

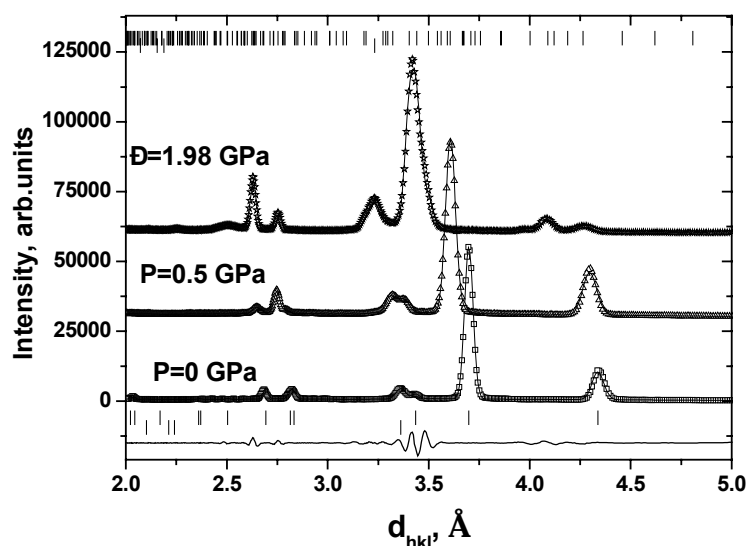


Figure 1: The X-ray patterns of the PyHClO_4 measured at ambient and high pressure $P=0.5$ and $P=1.98$ GPa and processed by the profile matching method. Experimental points, calculated profiles and difference curve (for $P=1.98$ GPa) are shown. The tick rows indicate the calculated position of diffraction peak for rhombohedral (bottom) and monoclinic phase with Pm space group (upper).

The phase diagram of pyridinium perchlorate PyHClO_4 constructed on the basis of the present data and data from ref. [5] are shown at figure 2.

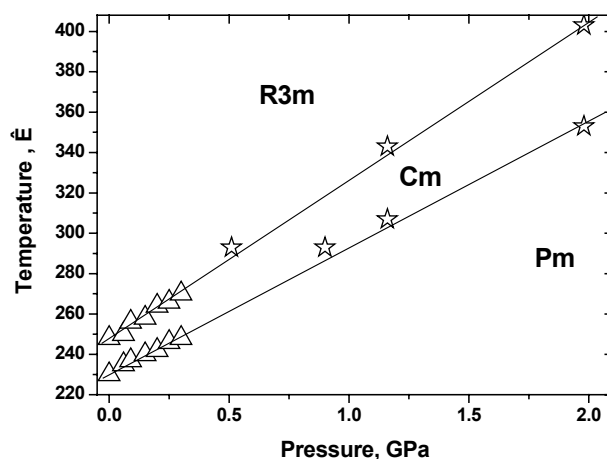


Figure 2. The P-T phase diagram of the PyHClO_4 constructed on the basis of the present data (open stars) and data from ref. [5] (open triangles).

References

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