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CRYSTAL STRUCTURE AND LATTICE DYNAMICS

Study of the Structure of $PyHReO_4$ under High Pressure

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Abstract—The structure of deuterated pyridinium perrhenate $(d_5PyH)ReO_4$ ($C_5D_5NHReO_4$) is studied by X-ray diffraction at room temperature and pressures up to 3.5 GPa and by neutron diffraction in the temperature range 10–293 K and at pressures up to 2.0 GPa. Under normal conditions, this compound belongs to the orthorhombic space group $Cmc2_1$ (ferroelectric phase II). At room temperature and pressures above $P > 0.7$ GPa, a transition to an orthorhombic phase (paraelectric phase II) is observed. This paraelectric phase is described by the space group *Cmcm*. At a pressure as high as $P = 2.0$ GPa, phase I remains stable at temperatures down to 10 K. This fact indicates that the high pressure suppresses the ferroelectric state in deuterated pyridinium perrhenate $(d_5PyH)ReO_4$.

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INTRODUCTION

Many pyridinium salts belong to the group of molecular-ionic crystals with interionic hydrogen bonds. Depending on their symmetry and the size of anions, these compounds exhibit a large variety of interesting phenomena: phase transitions, ferroelectricity, dynamic orientational disorder of pyridinium cations, etc., [1–4]. The ferroelectric state was observed in pyridinium tetrafluoroborate $PyHBF_4$ ($C_5H_5NHBF_4$) [1], pyridinium perchlorate $PyHClO_4$ [2], pyridinium perrhenate $PyHReO_4$ [3], and pyridinium periodate $PyHIO_4$ [4]. Interest in studying the latter two compounds listed above is connected with the fact that their Curie temperatures are close to room temperature. The phase transition from a paraelectric to a ferroelectric state is accompanied by structural changes connected with the ordering of pyridinium cations Py^+ and perrhenate anions ReO_4^-. Therefore, the study of structural changes in $C_5H_5NHReO_4$ is of importance for understanding the nature of ferroelectric properties of this compound and for an adequate description of these properties.

The NMR studies of the *P–T* phase diagram of pyridinium perrhenate $PyHReO_4$ at pressures up to 0.8 GPa, along with the studies of the electric properties of this compound [5], showed that, at temperatures $T < 250$ K, there exists a phase transition from ferroelectric phase II to a low-temperature paraelectric phase (phase III). Also, the occurrence of additional phase II' was suggested, whose properties are presently unknown.

Nevertheless, the behavior of the parameters of the unit cell and interatomic bonds of deuterated pyridinium perrhenate $(d_5PyH)ReO_4$ at a high pressure have not been studied yet. The pressure dependence of the unit-cell parameters can be studied by X-ray diffraction. However, it is impossible to determine the positions of hydrogen atoms with this method, especially if hydrogen-containing ions are orientationally disordered. This information can be obtained using the neutron diffraction method. For our investigations, a deuterated compound, $C_5D_5NHReO_4$, was chosen, which is isostructural with $C_5H_5NHReO_4$ and has better characteristics of deuterium atoms for neutron diffraction experiments as compared to hydrogen atoms, whose incoherent neutron scattering cross section is very large.

The crystal structure of deuterated pyridinium perrhenate $(d_5PyH)ReO_4$ was studied by X-ray diffraction at room temperature and pressures up to 3.5 GPa and by neutron diffraction at high pressures up to 2.0 GPa and low temperatures down to 10 K.

EXPERIMENTAL

Experiments on energy dispersive X-ray diffraction at room temperature and high pressures up to 3.5 GPa were performed with an F2.1 channel of a DORIS III source (HASYLAB, DESY, Hamburg, Germany). The pressure on the sample was created by an MAX80 press

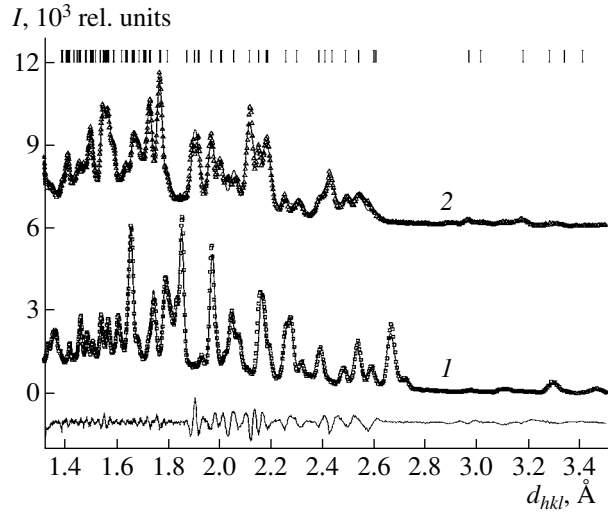

Fig. 1. Energy dispersive X-ray diffraction spectra of $(d_5PyH)ReO_4$ measured at room temperature and at the pressures P = (*1*) 0 and (*2*) 3.5 GPa. The experimental points, the calculated profiles, the difference curve, and the positions of the diffraction peaks calculated for orthorhombic phase I (at P = 3.5 GPa) are shown.

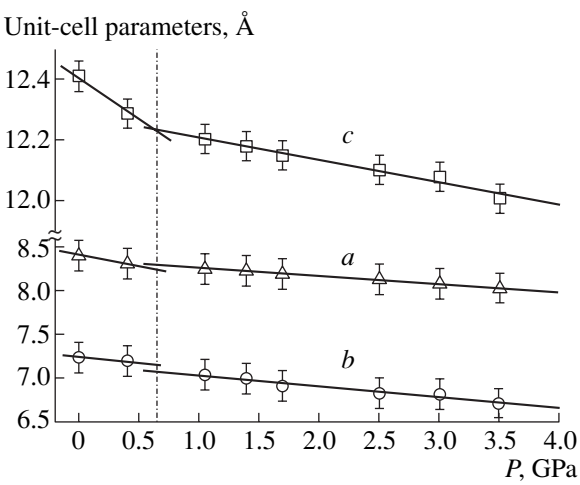

Fig. 2. Behavior of the unit-cell parameters of $(d_5PyH)ReO_4$ subjected to a high pressure. The solid lines are obtained by linear interpolation according to the least squares method.

[6] equipped with tungsten carbide anvils. The diffraction spectrum was measured with the help of a Canberra germanium semiconductor detector at a fixed Bragg angle, $2\theta = 9.09(2)°$. The resolution of the diffractometer for energy $E = 5.9$ keV was $\Delta d/d = 0.010$.

Experiments on neutron diffraction at high pressures up to 2.0 GPa and in the temperature range 10–293 K were performed on a DN-12 spectrometer [7] that was linked with the IBR-2 high-flux reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia) and that used high-pressure cells with sapphire anvils [8]. The low-temperature measurements were performed with a special cryostat based on a close cycle refrigerator. The pressure in the cell was measured (with an error of 0.05 GPa) by measuring the shift of the ruby luminescence line. The volume of the samples under study was $V \sim 2$ mm^3. The diffraction spectra were measured at the scattering angle $2\theta = 90°$. For this scattering angle, the resolution of the diffractometer at the wavelength $\lambda = 2$ Å was $\Delta d/d = 0.015$. The average measurement time of one spectrum was 20 h. The diffraction data obtained were analyzed with the help of the Le Bail and Rietveld method using the programs MRIA [9] and FullProf [10].

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction spectra of deuterated pyridinium perrhenate $(d_5PyH)ReO_4$ measured at room temperature at normal and high pressures (3.5 GPa). Under normal conditions, the structure of $(d_5PyH)ReO_4$ is described by orthorhombic symmetry with the space group $Cmc2_1$. At high pressures above $P > 0.7$ GPa, the diffraction spectra show changes, which correspond to the occurrence of a high-pressure phase, phase I. This phase is likewise described by orthorhombic symmetry but belongs to the space group *Cmcm*. Figure 2 presents the pressure behavior of the unit-cell parameters of these two phases. The linear compressibilities of the unit-cell parameters $k_i = -(1/a_{i0})(da_i/dP)_T$ ($a_i = a, b, c$) are, respectively, equal to $k_a = 0.026(4)$ GPa^{-1}, $k_b = 0.012(7)$ GPa^{-1}, and $k_c = 0.023(3)$ GPa^{-1} for ferroelectric phase II and to $k_a = 0.010(3)$ GPa^{-1}, $k_b = 0.0170(5)$ GPa^{-1}, and $k_c = 0.0060(3)$ GPa^{-1} for high-pressure paraelectric phase I. The behavior of the volume of the unit cell was analyzed with the help of the Birch–Murnaghan third-order equation of state [11],

$$P = \frac{3}{2}B_0(x^{-7/3} - x^{-5/3})\left[1 + \frac{3}{4}(B' - 4)(x^{-2/3} - 1)\right]. \quad (1)$$

Here, $x = (V/V_0)$ is the relative change in the volume of the unit cell; V_0 is the volume of the unit cell at $P = 0$; and B_0 and B' are empirical parameters, which have the meaning of the bulk modulus in the equation of state and of its first derivative with respect to pressure. The calculated values of these parameters are $B_0 = 15(8)$ GPa and $B' = 4(1)$ (phase II) and $B_0 = 16(3)$ GPa and $B' = 4(1)$ (high-pressure phase I). The bulk moduli obtained by us are comparable in value with moduli B of other molecular crystals based on pyridinium salts [12].

The neutron diffraction spectra characteristic of deuterated pyridinium perrhenate $(d_5PyH)ReO_4$ at normal and high pressures are shown in Fig. 3. The high-pressure diffraction spectrum corresponds to the orthorhombic phase with the space group *Cmcm*. Upon cooling to the temperature $T = 10$ K, no changes were observed in this spectrum. This result indicates that the

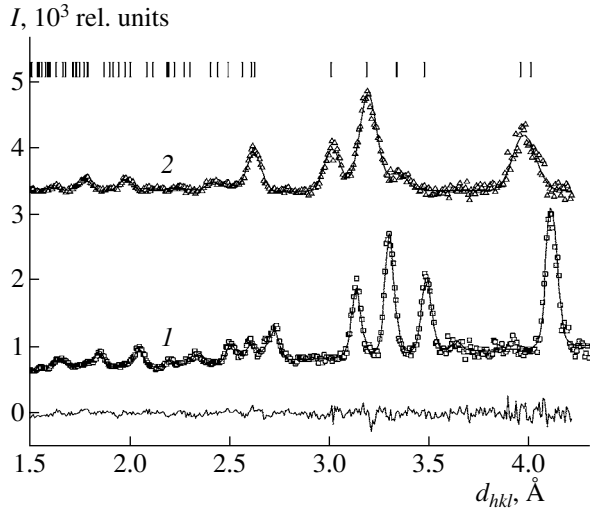

Fig. 3. Parts of the diffraction spectra of $((d_5PyH)ReO_4$ measured at P = (*1*) 0 and (*2*) 2.0 GPa at room temperature (T = 293 K) and processed by the Rietveld method. The experimental points, the calculated profiles, the difference curve, and the positions of the diffraction peaks calculated for P = 2.0 GPa are shown.

high pressure stabilizes paraelectric phase I and suppresses the ferroelectric state in deuterated pyridinium perrhenate.

The refinement of the atomic parameters of normal and high-pressure phases II and I of deuterated pyridinium perrhenate $(d_5PyH)ReO_4$ showed that both the geometry and the bond lengths of the perrhenate tetrahedron and pyridine ring do not vary under the high pressure, a result that is characteristic of other molecular and molecular-ionic crystals [13, 14]. At the same time, the lengths of intermolecular bonds markedly change. Thus, the average length of the deuterium–oxygen D–O bond, which characterizes the hydrogen bond C(N)–D–O, decreased from 2.45(3) Å (at normal pressure) to 2.23(5) Å (at P = 2.0 GPa).

The character of the P–T phase diagram of $(d_5PyH)ReO_4$ points to the occurrence of a triple critical point for phases I, II, and III at the pressure $P \sim$ 1.2 GPa. Stabilization of paraelectric phase I under high pressure is accompanied by suppression of the ferroelectric state in deuterated pyridinium perrhenate.

CONCLUSIONS

The structure of deuterated pyridinium perrhenate $(d_5PyH)ReO_4$ ($C_5D_5NHReO_4$) is studied by X-ray diffraction at pressures up to 3.5 GPa and by neutron diffraction at pressures up to 2.0 GPa. It was found that the high pressure suppresses ferroelectric phase II and stabilizes high-pressure phase I. The character of the phase diagram of $(d_5PyH)ReO_4$ points to the occurrence of a triple critical point for phases I, II, and III at a pressure of about 1.2 GPa.

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