

Rotational Displacement of IO₄ Tetrahedron in the Phase II of Pyridinium Periodate

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Abstract

In order to investigate the displacement of the IO₄ tetrahedron in the ferroelectric phase II of pyridinium periodate in detail, we performed X-ray structural analysis with the use of the estimated site occupancies of carbon and nitrogen atoms at many temperatures. We confirmed the continuous increase of the rotation angle of the IO₄ tetrahedron about the *a*-axis with decreasing temperature in the phase II. This indicates that the IO₄ tetrahedron acts as the displacive structural unit at the transition from phase I to phase II. It is found that the rotation of the IO₄ tetrahedron is correlated with the reorientation of the pyridinium cation through the N-H···O type hydrogen bond.

Keywords: rotational displacement; ordering of pyridinium; structure analysis; phase transition; hydrogen bond

1. Introduction

The pyridinium periodate, [C₅H₅NH]⁺[IO₄]⁻ (abbreviated hereafter PyIO₄), belongs to a large family of molecular-ionic ferroelectrics in which the organic cation interacts with various inorganic anions. Such pyridinium salts show structural phase transitions driven by a change in reorientation of the cation [1-3]. The PyIO₄ crystal undergoes two structural phase transitions at 320 and 210K [4]. The highest temperature phase (phase I) is paraelectric, and both the intermediate phase (phase II) and the lowest temperature phase (phase III) are ferroelectric [5]. According to X-ray and neutron diffraction studies by H. Małuszyńska *et al.* [6, 7], space groups of PyIO₄ are *Cmcm* (*Z*=4), *Cmc2*₁ (*Z*=4) and *C112*₁ (*Z*=4) with decreasing temperature, respectively. The spontaneous polarization along the *c*-axis is believed to be derived from the ordering of the pyridinium cation because the cation has a permanent dipole moment.

By neutron structural analysis at 352, 300 and 100K, H. Małuszyńska *et al.* reported the site occupancies of carbon and nitrogen atoms at each atomic position of pyridinium cation [7]. In the phase I, each occupancy differs at independent two sites of the pyridinium cation (that is, the pyridinium cation is partially ordered), however, the crystal can not show the ferroelectricity because of the centrosymmetric space group *Cmcm* (*Z*=4). In the phase II,

the site occupancies differ at independent three sites (that is, the pyridinium cation is partially disordered). In conjunction with noncentrosymmetric space group $Cmc2_1$ ($Z=4$), this difference about site occupancies brings a spontaneous polarization along the c -axis.

In the phase III, the pyridinium cation is well ordered. By using the crystal structure analyzed, H. Małuszyńska *et al.* calculated the spontaneous polarization along the c -axis [7]. They compared the calculated value with an experimentally measured value of the spontaneous polarization along the c -axis at 100K, and then concluded that the spontaneous polarization of the PyIO₄ crystal was almost derived from the reorientation of the pyridinium cation and that PyIO₄ was classified as order-disorder type ferroelectrics.

On the investigation of the phase transition in the PyIO₄ crystal, intense interest has been shown towards the order-disorder nature of the pyridinium cation. Recently J. Hatori *et al.* [8] has reported that paraelectric-ferroelectric phase transition at 320K is of order-disorder type, and the dielectric relaxation is associated with reorientation of the pyridinium cation. However, the behavior of the IO₄ anion as the counter ion to the pyridinium cation on the phase transition was not taken into account, so far.

Previously we investigated the temperature variation of the rotation angle of the IO₄ tetrahedron about the a -axis in the phase II of PyIO₄ by X-ray structural analysis, and pointed out that the IO₄ tetrahedron acted as the displacive structural unit at the transition from phase I to phase II [9]. The results were not fully satisfactory owing to the difficulty in determining the nitrogen occupancy accurately and to the damage of the specimen by long time irradiation of X-ray.

In this study, we estimate the site occupancies of carbon and nitrogen atoms in the pyridinium cation by using the results of neutron structural analysis and the measurement of the spontaneous polarization by H. Małuszyńska *et al.* [7]. In order to reduce the damage of the specimen by X-ray irradiation, we use an X-ray diffractometer with the CCD detector which is able to measure the diffraction intensities more rapidly than a conventional one with a scintillation counter. We investigate the temperature variation of the rotational displacement of the IO₄ tetrahedron in the phase II of PyIO₄ in detail.

2. X-ray diffraction experiments

The clear and colorless PyIO₄ crystals were obtained by slow evaporation of aqueous solution with stoichiometric amounts of pyridine and orthoperiodic acid. A number of crystals were polished to spherical shape by wet filter papers, in order to make absorption correction easy. The sizes of spherical specimens ranged from 0.19 to 0.28 mm in diameter. If the sample was suspected to be damaged of X-ray irradiation, then it was exchanged with a new one.

The X-ray experiments were performed by using the MERCURY CCD system (Rigaku) which was able to measure the diffraction intensities more rapidly than a conventional one

with a scintillation counter. As the X-ray source, Mo $K\alpha$ radiation monochromated by PG (0002) reflection was employed. The data collection, the cell refinement and the data reduction were carried out by 'Crystal Clear (Rigaku)', a control software for the MERCURY CCD system. By using the cold and hot nitrogen gas flow system, the temperature of the specimens was controlled within $\pm 1\text{K}$.

Obtained data were applied for the Lorentz, polarization and numerical absorption corrections. The SHELXS-86 ^[10], SHELXL-97 ^[11] and WinGX ^[12] programs were used. The initial atomic positions were obtained by the direct method. The refinement of the crystal structure was performed by the full-matrix least-squares calculations.

3. Analysis

When we try to analyze the PyIO₄ crystal structure in the ferroelectric phase, we note that the rotation angle of the IO₄ tetrahedron correlates strongly with the site occupation probability of the nitrogen atom of the pyridinium cation. Since the resolution of N and C is poor in X-ray measurement, we have to fix the site occupancy in the least-squares calculations. This can be done by the following process.

3.1. Estimation of the site occupancies

It is reported by H. Małuszyńska *et al.* that the displacement component of the spontaneous polarization of the PyIO₄ crystal is negligible, and the contribution of the IO₄ anion to the spontaneous polarization at 100K is about 0.1 times as much as one of the pyridinium cation ^[7]. Hence, the spontaneous polarization of the PyIO₄ crystal would be derived almost from the reorientation of the partially disordered pyridinium cation which has a permanent dipole moment.

Figure 1 shows the pyridinium cation in the phase II schematically. The mirror plane (bc -plane) intersects at the center of the pyridinium ring perpendicularly with dividing the pyridinium ring in half. There are independent three atomic positions in the pyridinium ring; site 1, 2 and 3 in the figure. Site 1', 2' and 3' are corresponding to atomic positions related with the mirror plane. Let us consider $S_i(T)$ as the site occupancy of nitrogen atom at site i . We obtain easily

$$\sum_{i=1}^3 S_i(T) = \sum_{i'=1}^3 S_{i'}(T) = 1/2. \quad (1)$$

Secondly, we have to regard the contribution of the pyridinium cation in the spontaneous polarization along the c -axis (ferroelectric axis). The spontaneous polarization of the phase II, $P(T)$, can be given as $P(T) \propto \sum_{i=1}^3 S_i(T) P_o(T) \cos \theta_i$, where $P_o(T)$ represents the contribution of fully ordered cation with a permanent dipole moment, and θ_i the angle between the site i and the mirror plane. If the temperature variation of $P_o(T)$ and θ_i

are negligible, we are able to assume $P(T) \propto \{S_3(T) - S_1(T)\}$, since $|\cos \theta_1| \cong |\cos \theta_3|$, $\cos \theta_2 \cong 0$. By using the temperature variation of the spontaneous polarization $P(T)$ and the site occupancies $S_1(300)$ and $S_3(300)$ of the nitrogen atom from the neutron structural analysis at 300K by H. Małuszyńska *et al.* ^[7], we obtain the following equation,

$$S_3(T) - S_1(T) = \{S_3(300) - S_1(300)\}P(T)/P(300). \quad (2)$$

Thirdly, let us consider the temperature variation of $S_2(T)$. According to the neutron structural analysis by H. Małuszyńska *et al.* ^[7], $S_2(T)$ at 352K (phase I) and 300K (phase II) are 0.062(4) and 0.069(3), respectively. Therefore, we assume that the temperature variation of $S_2(T)$ in the phase II is tiny, i.e. $S_2(T) \cong S_2 \approx 0.07 = \text{const.}$.

Thus, we can estimate the site occupancy $S_i(T)$ of nitrogen atom in the pyridinium cation at any temperature in the phase II from equations (1) and (2) by using the temperature variation of the spontaneous polarization ^[7]. Figure 2 shows the estimated site occupancies $S_i(T)$ of nitrogen atom at three sites in the pyridinium cation in the phase II.

3.2. Refinement of the crystal structure

The refinement of all atoms except for hydrogen atom was carried out with the anisotropic thermal parameters and the site occupancies $S_i(T)$ in Fig. 2. The hydrogen atom positions of the pyridinium cation were estimated from the site occupancies $S_i(T)$ and the assumption that C-H and N-H distances are 1.090 and 1.034 Å, respectively. And these hydrogen atoms were refined isotropically as a riding model, in which their isotropic displacement parameters U_{iso} were set to 1.2 times U_{eq} of their carrier atoms.

4. Results and discussion

The X-ray experiments using the CCD detector seemed to reduce the damage of specimens because of the speedy data collection and low-powered X-ray. As a typical example, the crystal structure at 213K in the phase II is shown in Fig. 3.

Strictly, in the above estimation of the site occupancies, we have to heed the angle between the pyridinium cation and the ferroelectric c -axis. If this angle changes significantly with temperature, the above estimation should be modified. However, in our analysis, such a significant change of this angle was not confirmed, and the analysis was consistent.

Figure 4 shows the temperature variation of the rotation angle of IO₄ tetrahedron about the a -axis in the phase II. It was found clearly that the IO₄ tetrahedron rotates about the a -axis gradually with decreasing temperature.

Additionally, figure 5 shows the temperature variation of the shortest N-H \cdots O type hydrogen bond length, of which the angle is about 160 degrees in the phase II. It is clear that this bond length shortens with decreasing temperature, in connection with the

increase of the nitrogen occupancy at the donor site 3 (see Fig. 2). That is, the increment of the occupancy of nitrogen atom at the site 3 gives rise to the increase of plus charge at the hydrogen atom position. A hydrogen atom with larger plus charge intensely attracts an oxygen atom of the IO₄ anion. This attraction induces the rotation of the IO₄ tetrahedron about the *a*-axis.

In summary, it is verified that the IO₄ tetrahedron acts as the displacive structural unit on the transition from phase I to phase II. It is considered that the rotational displacement of the IO₄ tetrahedron about the *a*-axis in the phase II is related to the reorientation of the pyridinium cation through the N-H···O type hydrogen bond.

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Figure 1. Schematic illustration of the pyridinium cation in the phase II. The *bc*-plane is the mirror plane.

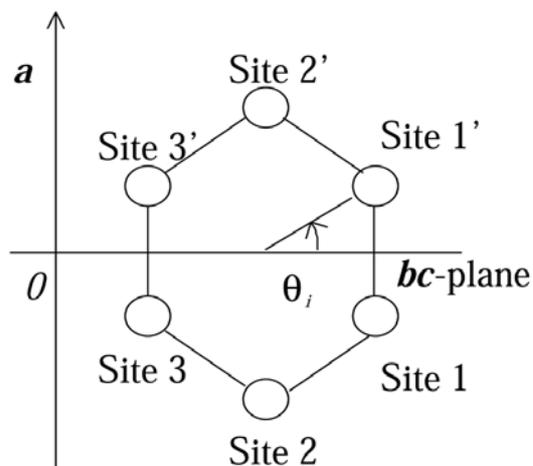


Figure 2. Estimated site occupancies $S_i(T)$ of nitrogen atom at the three sites in the pyridinium cation in the phase II.

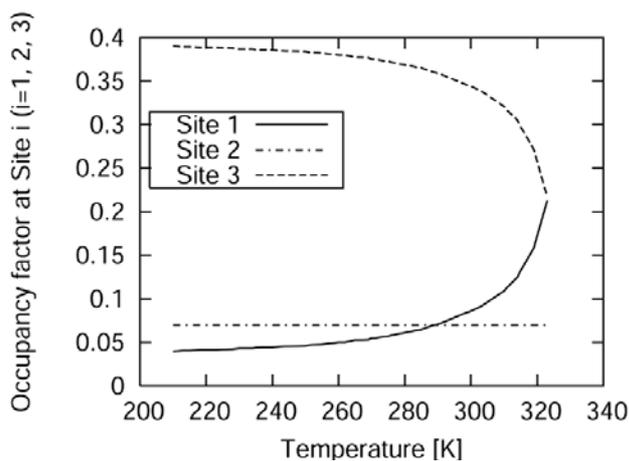


Figure 3. Projection of the crystal structure of PyIO₄ at 213K in the phase II. The thermal parameters are shown by ellipsoids. The broken line indicates the shortest hydrogen bond (3-H3...O1).

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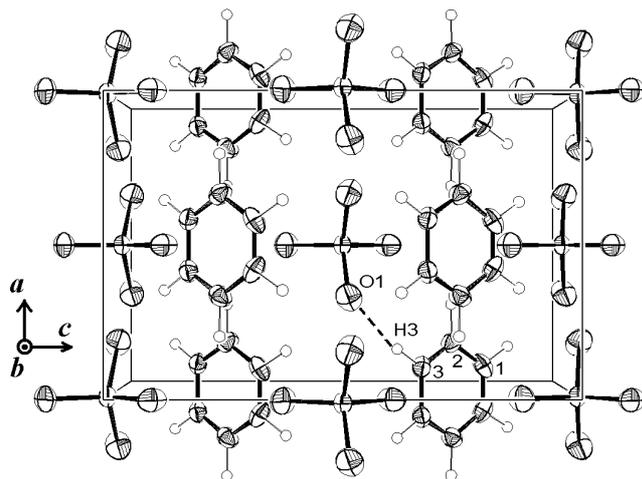


Figure 4. Temperature variation of the rotation angle of the IO₄ tetrahedron about the *a*-axis in the phase II. Symbols 1~5 mean the sample number.

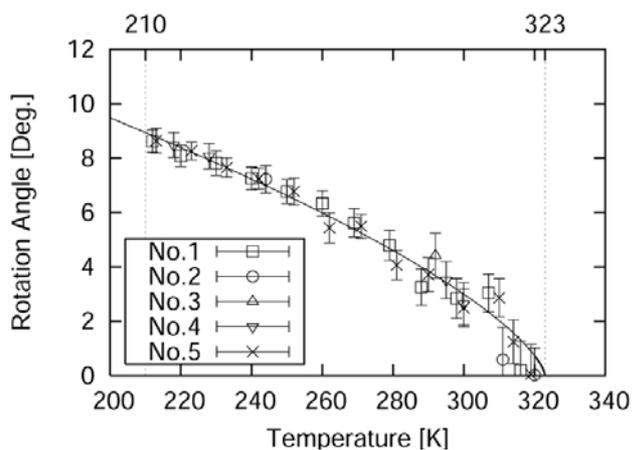


Figure 5. Temperature variation of the shortest hydrogen bond between H3···O1 in the phase II. Symbols 1~5 mean the sample number.

