The pyridinium periodate, [C₅H₅NH][IO₄] (abbreviated hereafter PyIO₄), belongs to a large family of molecular-ionic salts in which the organic cation interacts with various inorganic anions. Such pyridinium salts show structural phase transitions derived from a change in reorientation of the cation [1-3]. The PyIO₄ crystal is reported to undergo two phase transitions at 323 and 210K [4]. Below 323K crystal shows a ferroelectricity [5]. The crystal structures of each phase were determined by H. Małuszyńska et al [6, 7]. The space groups are Cmcm (Z=4) for phase I, Cmc₂ (Z=4) for phase II and C112₁ (Z=4) for phase III. According to the result of the dielectric dispersion studies performed by J. Hatori et al, the ferroelectric phase transition from phases I to II is of the order-disorder type and the dielectric relaxation is associated with the reorientation of the Py⁺ cation [8]. It is reported that the temperature variation of the spontaneous polarization of PyIO₄ along the c-axis is almost given by those of the reorientation of Py⁺ cation with permanent dipole moment [7].

We previously reported the temperature variation of the rotation angle of IO₄ tetrahedron about the a-axis in the phase II of PyIO₄ by X-ray structural analysis and pointed out that IO₄ tetrahedron acts as the displacive structural unit on the transition from phases I to II [9]. However the results were not so satisfactory owing to the difficulty of the accurate determination of the site occupancy of N atom in Py⁺ ring and the damage of the specimen by long time irradiation of X-ray.

At this time, we estimate the site occupancy of N atom in Py⁺ ring from 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 (Rigaku MERCURY CCD system) which is able to measure the diffraction intensities more rapidly than a conventional one with scintillation counter.

In order to reinvestigate the temperature variation of the displacement of IO₄ tetrahedron in more detail, we refine the crystal structure of PyIO₄ at 13 temperatures in the phase II. Figure 1 shows the projection of the crystal structure along the b-axis at 213K as a typical example. Figure 2 shows the temperature variation of the rotation angle of IO₄ tetrahedron about the a-axis in the phase II. It is considered that this displacement of IO₄ tetrahedron is related to the reorientation of Py⁺ ring through the N-H-O type hydrogen bonding.

References

Fig. 1 Projection of the crystal structure along the b-axis at 213K.

Fig. 2 Temperature variation of the rotation angle of IO₄ tetrahedron about the a-axis in the phase II.