Application of the Wide-Band Parallel X-ray Beam to Crystallographic Studies

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1. Introduction

In the previous paper, the present authors reported a new X-ray diffraction system at the SR Center at Ritsumeikan University (BL-1: beamline 1), in which a parallel X-ray beam of a band of wavelengths is produced by reflection from a multilayer monochromator of depth-graded thicknesses [1]. The band-width is 600eV and useful photon energy range is from 6000eV to 8000eV. It is provided a sample cooling/heating system and is useful to study on a wavelength modulated diffraction (WMD) in which an energy-dispersive intensity profile of Bragg reflection is measured [2]. The beamline is designed not only for WMD study but also for ordinary structural studies on phase transitions.

A structural phase transition in KH_2PO_4 (KDP) crystal was studied by a fixed single crystal X-ray diffraction method using the wide-band parallel X-ray beam. In the present short note the authors show that an intermediate phase (IP) exists between a paraelectric high temperature and a spontaneously polarized low temperature phases of KDP at 122 K transition. The new phase is stable in a range of about 4 degrees.

2. Experimental and results

It is well known that the ferroelectric crystal KDP undergoes only one phase transition at 122 K (T_C) from a paraelectric into a spontaneously polarized state. The transition does not show a thermal hysteresis; i.e., it occurs at the same temperature whether the temperature is rising or falling. Above T_C, its crystalline structure is tetragonal with the dimensions a=b=0.1048 nm, c=0.690 nm containing 8 KDP molecules in the unit cell. The space group symmetry is D_{2d}-I42d. In view of the spontaneous shear x_y that occur below T_C, the structure becomes an orthorhombic of space group C_{2v}-Fdd2 with the unit cell dimensions a=1.053, b=0.1044 and c=0.690 nm [3].

The diffractometer with the sample cooling/heating system of BL-1 is equipped with a two-dimensional detector of a curved imaging plate, and is used to study on X-ray diffraction structural experiments including structural phase transitions in the temperature range from 90 to 500 K.

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A series of stationary-crystal diffraction patterns were taken using a single KDP crystal at BL-1 as a function of the temperature between 127 and 113 K including T_C. The result is shown in Fig. 1. The bottom pattern in Fig. 1 is taken at room temperature. It is clearly seen that the Bragg spots split below 122 K and the phase transition from the room temperature phase to a low temperature phase was confirmed. The most striking feature observed in the series of the diffraction patterns in Fig. 1 (a) is seen an appearance of an extra spot observed in intermediate between the splitting spots in the temperature range of 122 and 118 K. An enlarged of Fig. 1(a) is shown in Fig. 1(b). The extra spots exist in a temperature range of 4 degrees below 122 K. An existence of the extra spot was never reported up to now. It suggests that an intermediate new temperature phase exists between the paraelectric high temperature and the spontaneously polarized low temperature phases. Figure 2 shows a profile of the position and the intensity of the splitting spot. It is confirmed that an interval between the splitting spots spreads with decreasing temperature. The extra spot vanishes below 118 K. For a more accurate understanding of the phase transition of KDP, the following studies are now in progress: all the observed spots of a hull width at half intensity maximum of the both spots are now measuring.

The wide-band parallel X-ray beam, when applied to crystallographic studies, proves to be a powerful method for the precise measurement of the changes that occur when a crystal undergoes a structural transition. The result presented in this paper for the tetragonal – intermediate – twined orthorhombic transitions in KDP illustrates the power of the method. The result is, though of interest, since this is the first time that such the intermediate temperature phase is observed in KDP.

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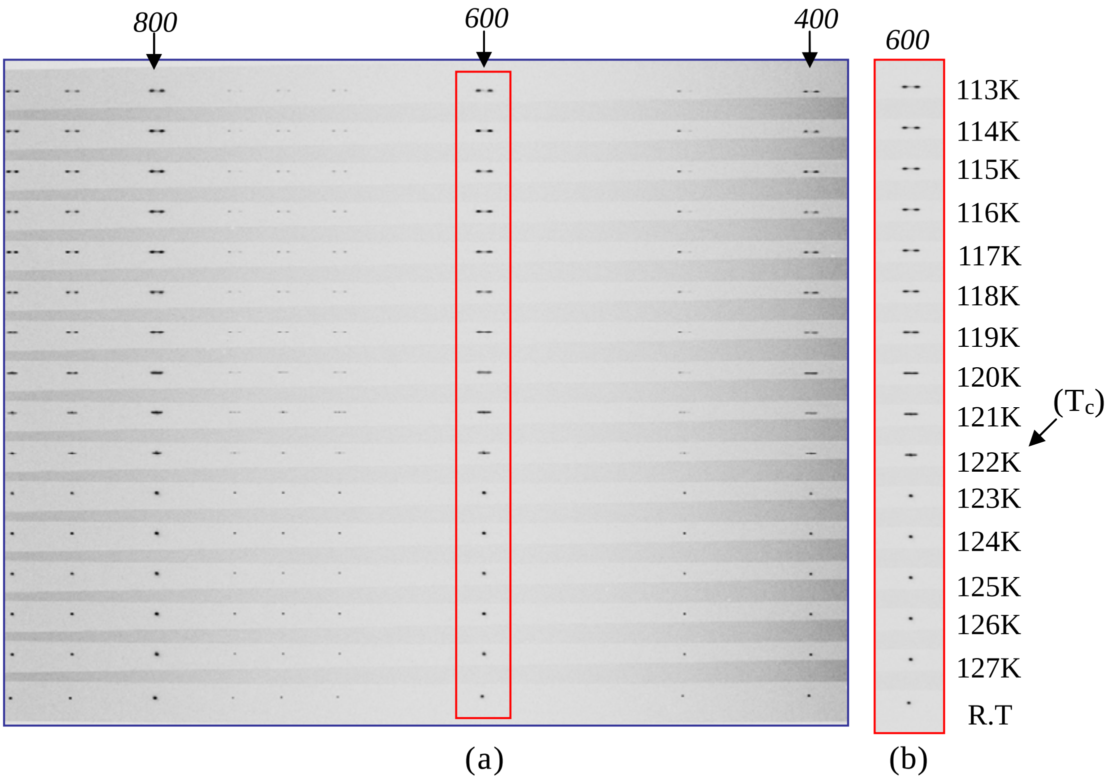

Fig. 1 (a) A series of stationary-crystal diffraction patterns KDP single crystal taken at BL-1 as a function of temperature including T_c. (b) An enlarged photograph of 600 spot in (a).

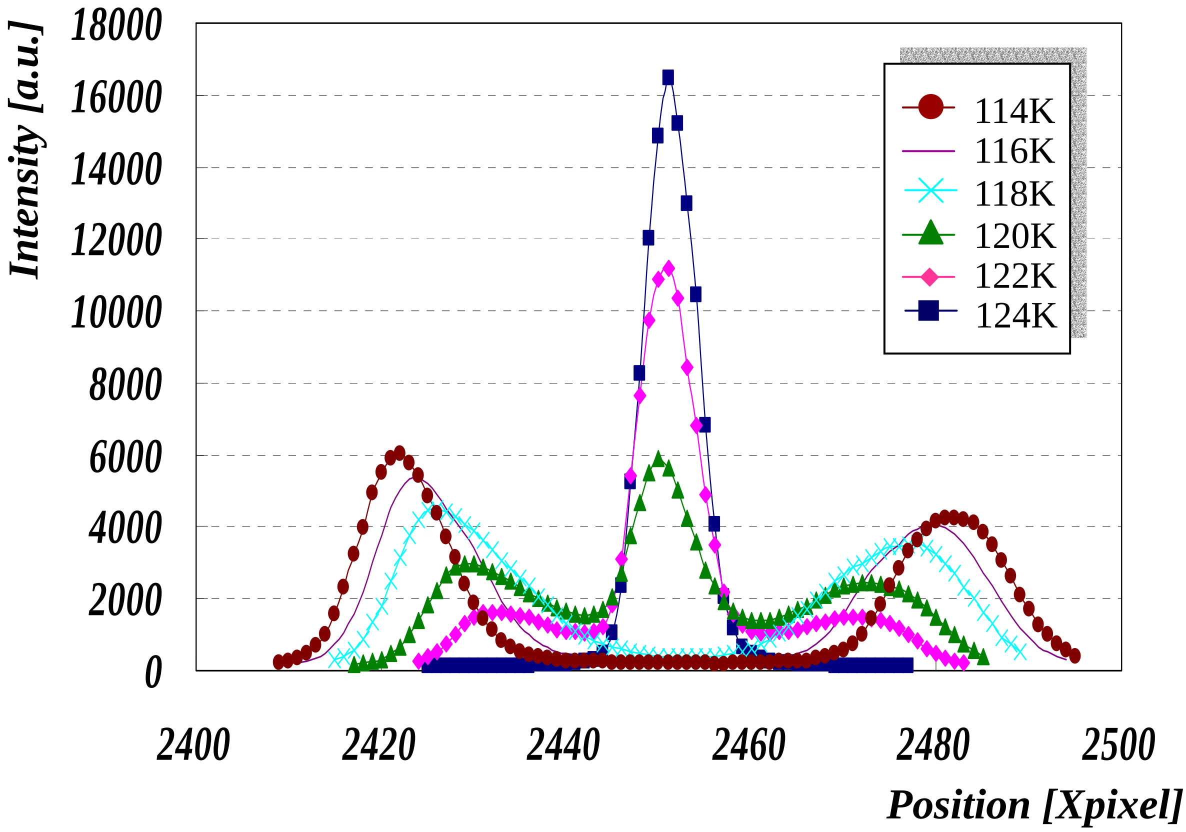

Fig.2 A profile of the position and the intensity of the 600 reflection