

Crystal structure of paraelectric phase and incommensurate nature of intermediate phase of ferroelectric trichloroacetamide

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Introduction

Crystalline trichloroacetamide (TCAA) is an organic ferroelectrics and undergoes two successive phase transitions around 355 K [1], below which the crystal is ferroelectric (FE) [2]. The full crystal structural solution has been reported only for the FE phase due to its high vapor pressure. In a small temperature interval of ca. 2 K between the two successive transitions, the intermediate (IM) phase appears and its structure was suggested to be incommensurate [3]. It was reported that through the successive phase transitions the unit cell remains essentially the same but the space group changes from $P2_1$ (FE phase) to $P2_1/c$ [paraelectric (PE) phase above the higher transition temperature] [4]. In this study, the crystal structure of the PE phase and the incommensurate nature of the IM phase were revealed utilizing synchrotron orbital radiation. Details can be found in [5].

Results and discussion

Crystal structures of FE and PE phases

Collection of sufficient data for full structural solution was performed both for the FE and PE phases. The distribution of diffraction intensity of the PE phase definitely shows its space group is $P2_1/c$ as previously suggested. The result of split atom analysis for chlorine atoms is shown in Figures 1 for the FE and PE phase. In the PE phase, the center of inversion appears at the center of a dimer and the orientation of trichloromethyl group is disordered around the C-C axis at least two-fold.

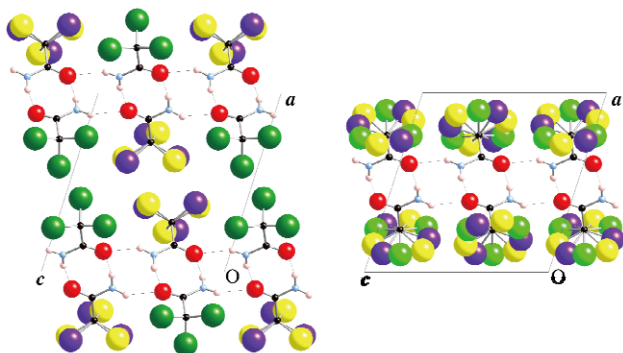


Figure 1. Results of split-atom analyses for the FE (300 K, left) and PE (370 K, right) phases of TCAA.

Independent calorimetric measurements utilizing adiabatic calorimetry yielded the clear evidence that each molecule exhibits orientational disorder independently without notable motional correlation within the dimer.

Incommensurate nature of IM phase

In the course of the structural study at high temperature, the photograph indicating satellite peaks around Bragg peaks was accidentally obtained as shown in Figure 2. Satellite reflections appear only in a small temperature interval. The point of interest is that four satellites are clearly visible around (5 -1 0). Since this is also the case for some Bragg peaks, the number of wavevectors characterizing the incommensurate modulation of the IM phase is 4. Namely, the modulation is two-dimensional. The modulation wavevectors were determined based on satellite reflections around 8 Bragg peaks.

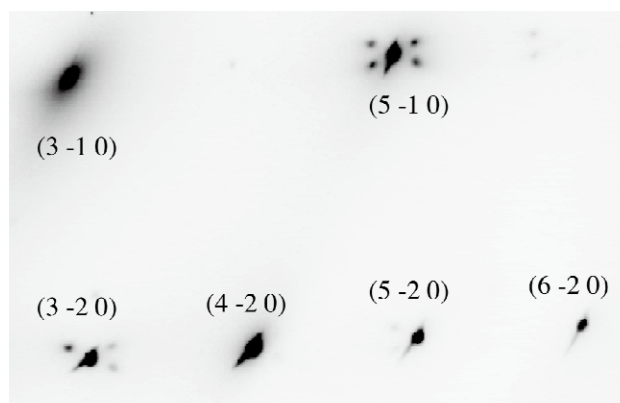


Figure 2. Satellite reflections around (5 -1 0) showing two-dimensional structural modulation of the IM phase of TCAA.

References

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