Crystal Structure of Polysynthetic Twinned Phase in A_2BX_4-type Ferroelectrics

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1. Introduction

Many of the A_2BX_4-type ferroelectrics, for example, Rb_2ZnCl_4, K_2ZnCl_4 and K_2CoCl_4, undergo successive phase transitions from a paraelectric normal phase (phase I, space group *Pmcn*) to an incommensurate phase (phase II) and to a ferroelectric phase (phase III, $P2_1cn$), which is followed by a monoclinic phase (phase V, $C1c1$). In Rb_2ZnBr_4 and Rb_2CoBr_4, there is another intermediate phase (phase IV with a polysynthetic twined structure), which is characterized by an existence of an extra symmetry rule. The crystal structure for phase IV has not been determined yet because of the disagreement between experimental results and general theoretical considerations.

The purpose of our study is to clarify the structure of phase IV in Rb_2ZnBr_4.

2. Experimental

X-ray diffraction experiments were performed at the Crystal Structure Analysis beamline BL02B1 with monochromatied radiation of 18.0 keV (0.689 Å). A single crystal of Rb_2ZnBr_4 was mounted on a copper sample holder, which was fixed on the cold head of a cryostat for analyzing structure of single crystal with hemispherical Be window.

3. Results and Discussion

In phase IV, the following extra extinction rule for systematic absence was confirmed : reflections $hk0$ are absent with $h+k=4n+2$ and $h, k=2n$. Furthermore, for phases III, IV and V, the observed eight structure factors $|F(\pm h \pm k \pm l)|$ were seen almost equivalent each other within experimental errors. The observed diffraction patterns had the symmetry D_{2h} of the orthorhombic system.

Taking our results, other ones, for instance, dielectric measurements, and results from extended space-group analysis into account, we present four twin-structural models with domain ratio of almost 1:1 in consideration of additional symmetry operations on the basis of the groupoids [1]. It is difficult to determine the superiority and inferiority of the structure models at the moment, because the difference between all eight structure factors $|F(\pm h \pm k \pm l)|$ for four models is not recognized when the domain ratio is equal to 1:1. Therefore, it is necessary to collect scattering intensities very carefully and to perform more detailed structural analysis. The uniaxial stress may be helpful to obtain single domain for scattering experiments.

References

[1] H. Shigematsu, H. Mashiyama, Y. Oohara and K. Ohshima: J. Phys.: Condens. Matter **10** (1998) 5861.