

## Ferroelectric KNbO<sub>3</sub> in Orthorhombic Phase

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### 1 Introduction

From the environmental reasons, lead-free piezoelectric ceramics KNbO<sub>3</sub> and associated compounds are attracting attention as alternative candidates for lead zirconate titanate (PZT). KNbO<sub>3</sub> shows a similar phase transition sequence with BaTiO<sub>3</sub> and belongs to several space groups; cubic (*Pm3m*), tetragonal (*P4mm*), orthorhombic (*Bmm2*), and hexagonal (*R3m*) in decreasing order of temperature. Except for paraelectric cubic phase, several types of domain structures are known. Since these domains make diffraction spots split, single crystal X-ray diffraction measurements in ferroelectric phases are quite difficult [1]. However, recently we have noticed that only a few crystals in orthorhombic phase, that we have tested, exhibit no split of the diffraction spots due to domains, even for crystals more than several micrometers in size, although, in orthorhombic phase, 180-degree, 90-degree, and 60-degree domains are typical. Since we are curious about the charge densities in ferroelectric phase of KNbO<sub>3</sub>, we have started the investigation. From the preliminary studies using laboratory X-ray source MoK $\alpha$  and three circle diffractometer installing CCD detector (Bruker Smart APEX2), assumption of *Bmm2* space group does not converged to reasonable structure. To investigate the more details, we performed single-crystal X-ray diffraction measurement using synchrotron radiation.

### 2 Experimental

Single crystals of KNbO<sub>3</sub> were grown by the flux method and mounted on the borosilicate glass capillary by two-component epoxy adhesive. The crystals are

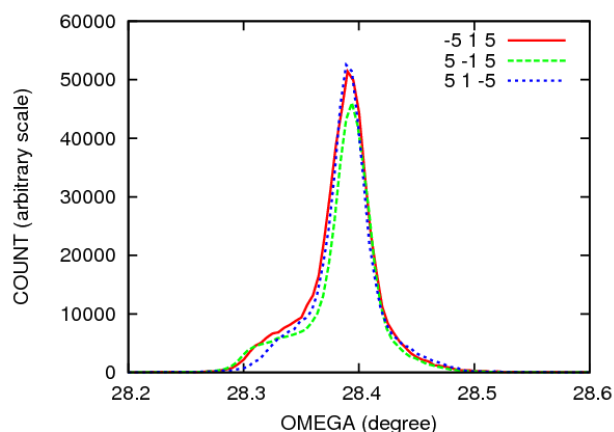


Figure 1: Peak profiles of some equivalent reflections.

tested using four-circle diffractometer (MAC Science MXC18XHF22, MoK $\alpha$ ). Among more than 30 specimens, only one crystal about 10x10x10 micrometer in size was judged to have single diffraction peaks and suitable for single-crystal X-ray diffraction measurement at BL14A. X-ray of 0.7521Å was selected and lead to the four circle diffractometer installing an avalanche photodiode (APD) detector, whose count loss is less than 1% up to 10<sup>7</sup> cps. To minimize the contaminations due to simultaneous reflections, psi-scan simulation software MDC [2] was used and optimum four-circle angle settings were calculated for each reflection and all the diffraction intensities were collected at the calculated angles.

### 3 Results and Discussions

All the peak profiles are asymmetric and have a tail towards lower angles suggesting the existence of slightly larger cells in some extent and this is ascribed to the surface relaxation. Figure 2 shows the intensity statistics of equivalent reflections assuming the space group *Bmm2*. Since intensities vary about 20% among the equivalents, *Bmm2* is not suitable for this crystal macroscopically. More details are under examination.

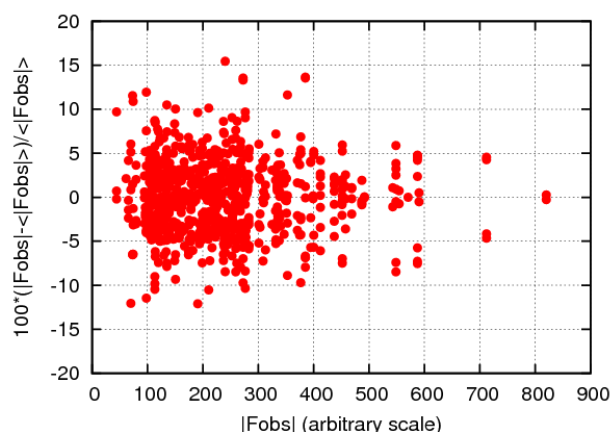


Figure 2: Deviation of intensities among the equivalents; reflections with  $|F_{obs}| > 50 \cdot \sigma(F_{obs})$  are plotted.

#### References

- [1] N. Ishizawa *et al.*, Solid State Chem. **183** (2010) 2731-2738.
- [2] K. Tanaka *et al.*, Acta Cryst. **A50** (1994) 246-252.

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