

Investigations of Order-Disorder Behavior in Perovskite Ferroelectric Crystals

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Introduction

PbTiO₃ is a pure perovskite that has a well-behaved soft mode and a large dielectric coefficient characteristic of an ideal displacive ferroelectric [1]. However, x-ray absorption fine structure (XAFS) measurements have shown that the local atomic distortions in the ferroelectric phase do not vanish above the transition temperature at 763K [2]. Additional evidence, both experimental [3, 4] and theoretical [5], demonstrates an essential element of order-disorder behavior in the structural phase transition in PbTiO₃. In order to characterize the structural disorder in this system, we have begun an investigation of the diffuse x-ray scattering from high-quality single crystals as a function of temperature.

Methods and Materials

The PbTiO₃ crystals were grown from stoichiometric melts; this is described in more detail in Reference 6. All x-ray measurements were made at the PNC-CAT bending magnet beamline sector (beamline 20-BM). Energy selection was achieved by using a water-cooled double-crystal Si(111) monochromator, with the second crystal detuned ~30% for harmonic rejection. The incident and fluorescent signals were monitored by using ionization chambers, and the scattered signal was measured by using an Oxford NaI detector. The x-ray scattering measurements were made by running SPEC, using a Kappa four-circle Huber goniometer.

For temperature control of the samples, we constructed a small furnace that could be mounted onto the goniometer head (Huber 1003). Heating is achieved by a single-cartridge heater inserted into a copper plate on which the sample is placed. The sample is surrounded by an aluminum radiation shield, and this assembly is contained in an evacuated aluminum vacuum shroud (pressure ~10 mTorr). Kapton® window slots allow access to the sample over a large solid angle. Sample temperatures as high as 850K have been reached, with control within a few degrees.

Results

The single-domain properties of the crystals can be seen in the Ti K-edge XANES spectra. Figure 1 shows the XANES for two different orientations: incident E-field parallel (solid line) and perpendicular (dashed line) to the tetragonal c-axis. The absorption peak at 4966 eV is enhanced in the former case because of the broken inversion symmetry of the Ti cations displaced along the c-direction relative to the oxygen octahedra. A quantitative analysis of the pre-edge fine structure of PbTiO₃ crystals has been given [7].

Figure 2 shows a scan through the (200) Bragg peak, taken at room temperature with the incident photon energy equal to 12 keV. This peak is quite sharp, indicating good crystal quality. On the low q side of this peak, we observe a much weaker diffuse scattering peak that increases in intensity with temperature in the ferroelectric phase. The properties of this peak suggest

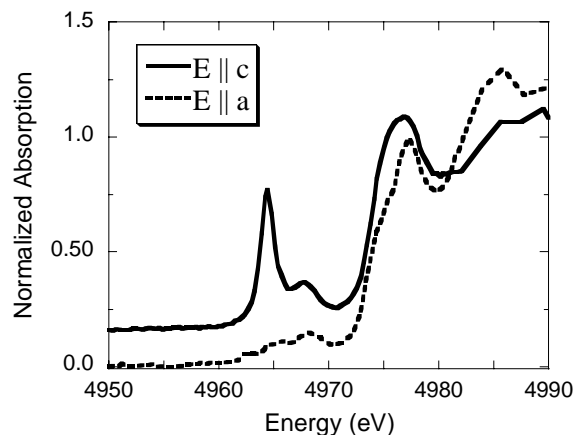


FIG. 1. Room temperature fluorescent XANES spectra of PbTiO₃ for two crystal orientations. The spectra for the case of incident polarization parallel to the tetragonal c-axis, show by the solid line, is shifted vertically for clarity of viewing.

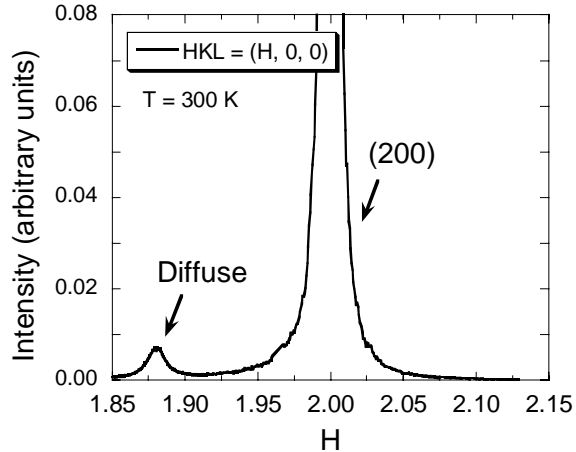


FIG. 2. Room temperature scan of the (200) Bragg peak (peak intensity not shown) showing the low-intensity diffuse peak on the low q side.

that it is caused by a small fraction of disordered tetragonal symmetry clusters oriented along the $\langle 100 \rangle$ direction having a finite correlation length on the order of 200 Å.

More interestingly, the diffuse peak in Fig. 2 is absent in the paraelectric phase, and we observe instead a pronounced increase in the diffuse scattering intensity much closer to the (200) and (400) Bragg peaks. Figure 3 shows a line scan along the H-direction near the (400) Bragg peak observed at a temperature of 800K. This scattering appears to be only weakly temperature-dependent in the paraelectric phase, and the profile of this scattering is highly anisotropic, since it is confined primarily to the (100) plane passing through the Bragg peak.

Discussion

We have presented preliminary measurements of the diffuse x-ray scattering in the ferroelectric and paraelectric phases of PbTiO_3 . The profile of the diffuse scattering in the high-temperature phase indicates a correlation length along the $\langle 001 \rangle$ direction. The anisotropy in the diffuse scattering is qualitatively similar to the planar diffuse scattering sheets that have been observed in the high-temperature phases of the eight-site model systems KNbO_3 and BaTiO_3 [8]. We are currently making a more detailed study of the diffuse x-ray scattering from PbTiO_3 as a function of temperature in the paraelectric phase.

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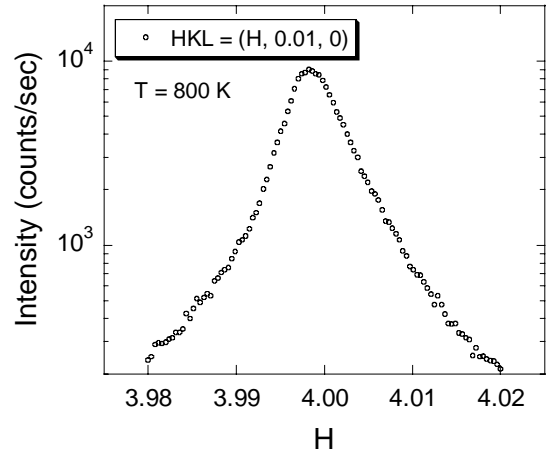


FIG. 3. Logarithmic plot of the diffuse x-ray scattering near the (400) Bragg peak measured in the paraelectric phase at 800K.

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References

- [1] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, England, 1977).
- [2] N. Sicron, B. Ravel, Y. Yacoby, E. A. Stern, F. Dogan, and J. J. Rehr, *Phys. Rev. B* **50**, 13168 (1994).
- [3] M. D. Fontana, K. Wojcik, H. Idrissi, and G. E. Kugel, *Ferroelectrics* **107**, 91 (1990).
- [4] R. J. Nelmes, R. O. Piltz, W. F. Kuhs, Z. Tun, and R. Restori, *Ferroelectrics* **108**, 165 (1990).
- [5] Y. Girshberg and Y. Yacoby, *J. Phys.: Condens. Matter* **11**, 9807 (1999).
- [6] V. Gavrilyatchenko, A. Semenchov, and E. Fesenko, *Ferroelectrics* **158**, 31 (1994).
- [7] R. V. Vedrinskii, V. L. Kraizman, A. A. Novakovich, P. V. Demekhin, and S. V. Urazhdin, *J. Phys.: Condens. Matter* **10**, 9561 (1998).
- [8] R. Comes, M. Lambert, and A. Guinier, *Acta Crystallogr. A* **26**, 244 (1970).