A combination of accurate, synchrotron X-ray and quantitative electron diffraction for charge density measurement in α-Al_2O_3

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Introduction

Current X-ray diffraction techniques intended for "ideally imperfect" specimens provide structure factors only on a relative scale and ever-present multiple scattering (extinction) in strong low angle Bragg reflections is difficult to correct. Multiple dynamic scattering is implicit in the quantitative convergent beam electron diffraction (QCBED) method, which provides absolutely scaled structure factors. Conventional single crystal X-ray diffraction has proved adequate in softer materials where crystal perfection is limited. In hard materials, the highly perfect nature of the crystals is often a difficulty, due to the inadequacy of the conventional corrections for multiple scattering (extinction corrections). The present study exploits the complementarity of synchrotron X-ray measurements for weak and medium intensities and QCBED measurement of strong low-angle reflections for α-Al_2O_3.

Experimental

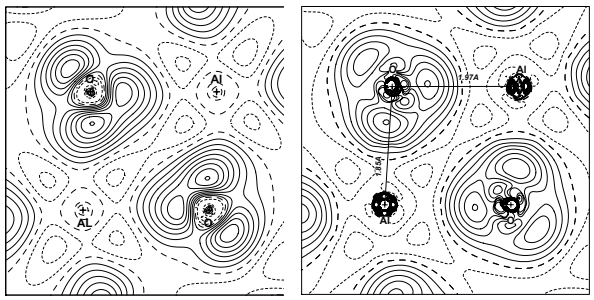
X-ray Diffraction. Synchrotron X-ray diffraction data set for α-Al_2O_3 was used to complement the QCBED data. This data consists of the X-ray diffraction intensities over complete sphere up to $(\sin\theta/\lambda)_{max}$=1.1 Å^{-1} measured at room temperature with λ = 0.7Å radiation using the BL14A beam line four-circle diffractometer. In order to reduce absorption and extinction effects, a tiny, naturally faced specimen with dimensions less than 50 μm was used. Analytical absorption, Lorentz and polarization corrections and anomalous dispersion were applied. Symmetrically equivalent reflections were averaged. Independent structural parameters, including the scale factor, positional and thermal displacement parameters for all atoms were refined by conventional full-matrix least squares including all observed 249 unique structure factors.

Electron Diffraction. Two dimensional, energy filtered zero order Laue zone CBED patterns from a variety of parallel sided and wedged α-Al_2O_3 platelets were recorded using a Philips 430 transmission electron microscope (TEM) with a Gatan Image Filter. A slit width of 10 eV was used to remove inelastically scattered electrons. The accelerating voltage was measured for each data set using deficiency lines due to higher order Laue zone (HOLZ) reflections visible in various zero zone disks. The variation of these measurements made at the same accelerating voltage settings was less than 0.2%. The recorded CBED patterns were firstly corrected for instrumental point spread function (PSF) using a new method developed by the authors. QCBED data have been matched using Bloch-wave and Multislice methods. The reproducibility of QCBED data is better than 0.5%.

Combined X-ray and QCBED data. The low angle strong QCBED structure factors were combined with middle and high-angle extinction-free data from synchrotron X-ray diffraction measurements. The multipole expansion model was refined with VALRAY [1] using the combined data. The refinement converged to R=1.16% with a total number of 249 structure factors and a total of 29 refined parameters.

Results and discussion

Static deformation charge density map ($\Delta\rho$) for α-Al_2O_3 in Fig. 1(*a*) was calculated after multipole refinement of the combined data and compared with density functional theory (DTF) calculation in Fig 1(*b*) based on WIEN2K [1] generalised gradient approximation (GGA) with the full potential linear augmented plane-wave method (FP-LAPW) [3]. The Fig. 1 maps are in excellent agreement. The overall topography of the static $\Delta\rho$ density is similar, and both maps have higher excess density peaks of ~0.28-0.32 e/Å^3 along the shortest Al-O1 bond (1.85Å) directions and a lower density of 0.24 e/Å^3 along the longer Al-O2 bond (1.97Å) directions.



(*a*) (*b*)

Fig. 1. Static $\Delta\rho$ maps from (*a*) combined QCBED/XD data, and (*b*) *ab-initio* DFT calculations. The plane is through the Al and O – O common edge in α-Al_2O_3. Contour intervals are 0.04 e/Å^3 with solid lines positive and short dashed lines, negative.

The necessity for a complementary measurement technique producing absolute extinction free structure factors becomes evident. The reproducibility of QCBED measurements from independent data sets (different crystals, zone axes, beam tilts and accelerating voltages) and the resulting agreement with theoretical calculations inspires confidence in the whole methodology.

References

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