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doi:10.1017/S1431927622002483
Microsc. Microanal. 28 (Suppl 1), 2022

Towards Spatial Mapping of Atomic Vibration Amplitudes in Thermoelectric Materials: Quantitative Convergent Beam Electron Diffraction (QCBED) Study of BiCuOQ (Q = S, Se, Te)

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Thermoelectric materials can potentially harness waste heat and convert it into usable electricity, their performance is evaluated by the figure of merit, $zT = S^2\sigma T/\kappa$, which can be optimized by improving power factor ($PF = S^2\sigma$) while suppressing the thermal conductivity (κ). The layered bismuth cupper oxychalcogenides BiCuOQ (Q = S, Se, Te) were recently discovered as promising high thermoelectric materials due to their intrinsically low thermal conductivity; the weak bonding of Cu atoms induces large atomic displacement (ADP) and therefore anharmonicity [1]. Here, we utilize convergent beam electron diffraction (CBED) in combination with multi-slice simulation and frozen phonon algorithm to quantitatively measure isotropic ADPs of BiCuOQ (Q = S, Se, Te). This method can be extended for spatial mapping of ADPs and studying their variations near the defects of interest, which is crucial in microstructure engineering of thermoelectric materials.

In transmission electron microscopy (TEM), the interaction of the probe electrons with pre-existing phonons in the sample will cause thermal diffuse scattering (TDS) and contribute to the background noise as atoms deviate from their equilibrium positions [2]. At large scattering angles, the contribution of elastic scattering and TDS dominate; therefore, the signal-to-noise ratio (SNR) of the CBED patterns can be used to extract information about ADPs. Figure 1 shows the simulated higher-order Laue zone (HOLZ) CBED pattern for BiCuOSe along the [001] zone axis with increasing ADP of Cu atoms [3]. Based on the intensity line profile along (-110) and (200) direction in the reciprocal space, the more vibrant Cu atoms leads to significant SNR changes in HOLZ pattern which depends on the Wyckoff positions of atoms. To accurately identify the ADPs for each atomic species, specific zone axes need to be selected for more sensitive detection of changes in SNR.

Figure 2 presents the workflow of the proposed measurement. Position averaged convergent beam electron diffraction (PACBED) patterns with large convergence angle are first taken and fitted with simulated results to extract mistilt condition and sample thickness. The line profiles of HOLZ features along multiple directions in the reciprocal space are then fitted with simulations to extract ADPs with the lowest averaged error. This procedure is repeated for experimental measurements from regions with different thickness (< inelastic mean free paths) and the extracted values along multiple zone axes are used to test for convergence.

This presentation will cover the ADP measurements of BiCuOQ (Q = S, Se, Te) from QCBED and compare them with X-ray/Neutron diffraction results. This method can be potentially extended for spatial mapping of ADPs in the region of interest (e.g., grain boundaries, stacking faults, etc.), which would help develop insights about the design of thermoelectric materials [4].

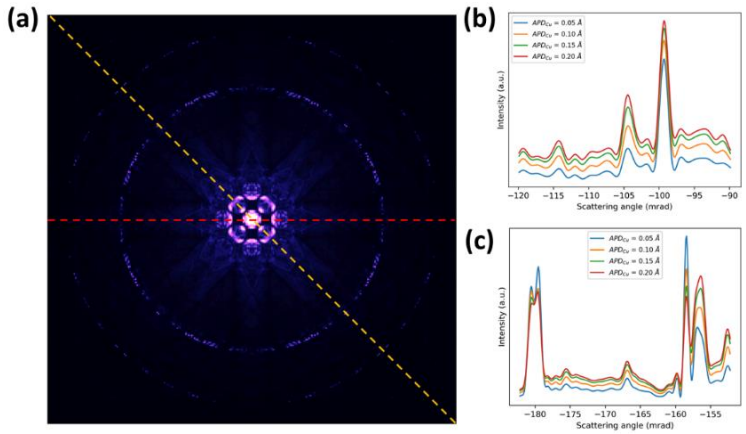

Figure 1. (a) Simulated CBED pattern of BiCuOSe along the [001] zone axis at 80 kV with 8 mrad convergence angle. (b) Intensity line profile along the (-110) direction in the reciprocal space with varying ADPs of Cu (c) Intensity line profile along the (200) direction in the reciprocal space with varying ADPs of Cu.

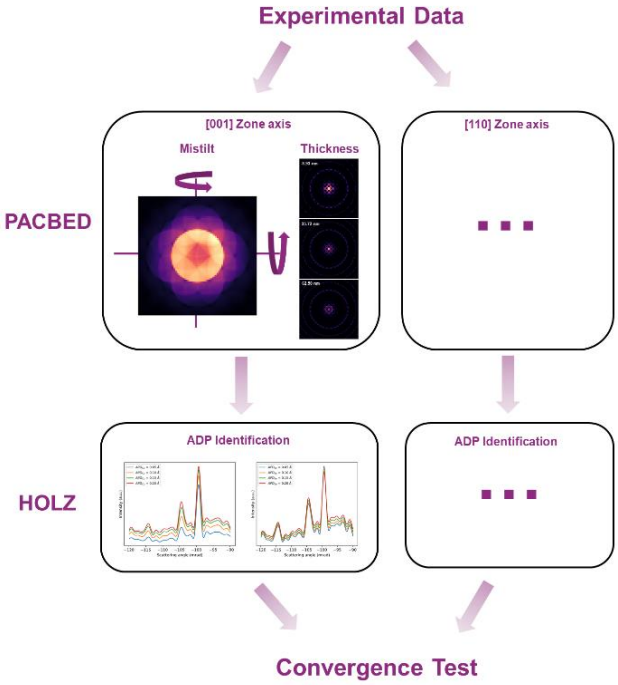

Figure 2. Workflow of the ADP measurement. The mistilt and thickness of the samples are first identified with PACBED with large convergence angle. The HOLZ pattern is then utilized to measure the ADP of each atomic species by fitting the simulation. The results obtained from multiple zone axes.

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https://doi.org/10.1017/S1431927622002483 Published online by Cambridge University Press

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[4] This work was supported by DOE-BES program (DE-SC0014520), made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR-1720139) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN.