Readme file for: Data for “**Bi4O4Cu1.7Se2.7Cl0.3: an intergrowth of BiOCuSe and Bi2O2Se stabilized by the addition of a third anion**”

Physical Properties Measurements:

Thermopower and thermal conductivity were both measured in a pellet geometry (as well as cube geometry for the directional study) using the TTO option of the Quantum Design Physical Properties Measurement System (PPMS).The TTO option used to measure the thermal conductivity factors in the radiation loss in the full temperature range using the Stefan law. The emissivity of the material is estimated using the guidelines provided by the manufacturer. The correction for radiation loss accounts for a <10% reduction in the derived thermal conductivity at 300K. Errors in estimation of the emissivity (which was assumed to be near 1) would therefore result in a very slight (< 5%, or < 0.02W/mK) underestimation of thermal conductivity at 300K, which is within the reported error of the measurement (+/- 0.1 W/mK). Due to difficulty in estimating the radiation loss near 300K, thermal conductivity values at this temperature should be assumed to have an error of about +/- 1mW/K, which corresponds to about 0.05W/mK in the pellet geometry and about 0.1 W/mK in the cube geometry11. Therefore, we report the room temperature thermal conductivity of the material to be 0.4(1) W/mK and 1.0(1)W/mK in the parallel and perpendicular directions, respectively. An example plot showing the raw and corrected thermal conductivity of one of the samples is shown in Figure S24. Resistivity was measured in a bar geometry using the electronic transport option of the PPMS. Transport properties were reported on a 70% dense pellet as the thermopower measurement on the 90% was exceedingly noisy due to its reduced thermal conductivity. All measurements shown in the main text were on pieces of the same pellet, for consistency. The values of thermopower and resistivity were not significantly different from the 70% dense pellet to the 90% dense pellet.

In order to address the higher thermal conductivity in the 70% dense pellet compared to the 90% dense pellet, the extent of preferred orientation was compared by calculating the ratio of intensity of the (0,0,10) peak to the (1,1,0) peak in the powder patterns of each pellet. The patterns were taken with the X-ray beams incident along the pressing axis (Figure S25). This ratio was 295:1 in the 90% dense pellet, 108:1 in the 70% dense pellet, and calculated to be 2.8:1 for a sample with no preferred orientation. This indicates that, like the 90% dense sample, the 70% dense sample has preferred orientation towards the [0,0,1] axis, although significantly less than the 90% dense sample. Thus, the higher thermal conductivity along the pressing axis for the 70% dense pellet compared to the 90% dense pellet is likely due to the difference in texture, which we have shown to have a quite large effect on the thermal conductivity (Figure S23). This effect outweighs that of the increased porosity in the 70% dense pellet, which is expected to reduce the measured thermal conductivity.

**Files:**

QDG\_cube\_BICUSEOCL\_16\_8.txt: Thermal conductivity measurement of a 90% dense sample of Bi4O4Cu1.7Se2.7Cl0.3 in a cube geometry, along the pressing axis of the pellet

QDG\_cube\_BICUSEOCL\_21\_8\_inplane.txt: Thermal conductivity measurement of a 90% dense sample of Bi4O4Cu1.7Se2.7Cl0.3 in a cube geometry, perpendicular to the pressing axis of the pellet

QDG\_33\_4\_pellet\_ETP\_cooling.txt: Resistivity measurement on a bar of 70% dense Bi4O4Cu1.7Se2.7Cl0.3 on cooling.

QDG\_33\_4\_pellet\_ETP\_warming.txt: Resistivity measurement on a bar of 70% dense Bi4O4Cu1.7Se2.7Cl0.3 on warming.

QDG\_33\_4\_heating.txt: Thermal conductivity and thermopower of the 70% dense pellet of Bi4O4Cu1.7Se2.7Cl0.3 on heating

QDG\_33\_4\_cooling\_run2\_00001.txt: Thermal conductivity and thermopower of the 70% dense pellet of Bi4O4Cu1.7Se2.7Cl0.3 on cooling.

QDG\_33\_1\_2\_densepelletTTO\_try2\_cooling.txt: Thermal conductivity and thermopower of the 89% dense pellet of Bi4O4Cu1.7Se2.7Cl0.3 on cooling.

All of the above files can be read directly as .txt files and opened in any software such as Excel or Origin. **Powder XRD Data:**

Laboratory Powder X-Ray Diffraction data were collected on a Bruker D8 Advance diffractometer in Debye-Scherrer geometry using monochromated Cu Ka1 incident radiation with a scanning position sensitive detector. Samples were prepared as thin foils and were supported on a rotating sample stage during the measurement. Diffraction data on pellets for the investigation of preferred orientation were collected on a PANalytical X’Pert Pro diffractometer in Bragg-Brentano geometry, with monochromated Co Ka1 radiation and an XCelerator 1D detector. The pellets were mounted on a spinning stage and rotated during the measurement.

**Files**

QDG\_31\_1\_redo\_longscan\_2.raw : Powder data taken on a phase pure Bi4O4Cu1.7Se2.7Cl0.3 sample.

QDG\_33\_3\_longscan\_2.raw: Powder data taken on a sample of nominal composition Bi4O4Cu2Se3

QDG\_33\_4\_longscan\_2.raw : Powder data taken on a sample of nominal composition Bi4O4Cu1.65Se2.65Cl0.35

QDG\_23\_1\_longscan\_2.raw: Powder data taken on a sample of nominal composition Bi4O4Cu1.6Se2.6Cl0.4

QDG\_90\_1ton.xrdml: Powder data taken on a pressed pellet of 70% density of Bi4O4Cu1.7Se2.7Cl0.3.

QDG\_90\_5ton.xrdml: Powder data taken on a pressed pellet of 90% density of Bi4O4Cu1.7Se2.7Cl0.3.

The above .raw files are in Bruker Raw format and must be opened using a powder Xray diffraction data analysis software such as Highscore, Topas, etc.
The .xrdml files may also be opened using powder Xray diffraction data analysis software such as Highscore and Topas.

**Reflectance:**

Diffuse reflectance measurements were taken on a Lambda 900 Perkin Elmer spectrometer with 1 scan every 5 nm from 280-2.5 microns

**Files**

Bi2O2Se\_840 change.txt ---- Raw reflectivity Data taken on Bi2O2Se with the lamp change at 840nm.

Bi4O4Cu17Se27Cl03.asc ----Raw reflectivity Data taken on Bi4O4Cu1.7Se2.7Cl0.3 with the lamp change at 840nm.

BiOCuSe\_840 change.asc--- Raw reflectivity Data taken on BiOCuSe with the lamp change at 840nm

The above files are xy files in txt or ascii format and may be imported directly into Excel, Origin, or any other data analysis software.

XPS:

X-ray photoelectron spectroscopy (XPS) was used to probe the core-level electronic structure and the occupied density of states in the valence band of the sample. The SPECS monochromatic Al Kα X-ray source (hν = 1486.6 eV) was operated at a power of 250 W. This was used along with PSP Vacuum Technology electron-energy analyser with a constant pass energy of 10 eV at an angle of incidence of 54.7 o to the sample normal. The workfunction was determined from the secondary electron cut-off (SEC) which was measured at lower kinetic energies by reducing the power of the X-ray source to 9 W and applying a -10 V bias to the sample (Figure S15). For the calibration of this bias voltage, the binding energy of the Bi 4f7/2 core level was remeasured. The calibration of the spectrometer was performed using a polycrystalline silver foil, cleaned in vacuo by sputtering at an energy of 2 kV until all surface contaminants were removed. The Ag 3d5/2 core level had a binding energy of 368.2 eV with full-width at half maximum (FWHM) of 0.6 eV, determining the tolerance of the binding energies of core levels as ± 0.1 eV. The Fermi edge of the silver foil was measured with a spectral width of 0.3 eV, resulting in a tolerance of ± 0.05 eV for the valence band maximum (VBM) and the SEC. To ensure there were no charging effects in the sample, the contaminant carbon 1s core level was measured. The binding energy of the contaminant carbon was 285.0 ± 0.1 eV, which is in good agreement with other studies of this material10. Therefore, it was determined that there were no charging effects in the sample.

To measure the unoccupied states of the conduction band, Inverse Photoelectron Spectroscopy (IPES) was used in this study. The PSP Vacuum Technology BaO cathode dispenser electron source and Isochromat NaCl photon detector were used together at an angle of 45 o to the sample normal. For the calibration of the spectrometer, the same silver foil was used as for the XPS calibration. The silver Fermi edge had a spectral width of 0.9 eV, establishing a tolerance of ± 0.14 eV for the conduction band minimum (CBM) (Fig S15.) The thermal activity of the electrons and the resolution of the instrument also contribute to this tailing off seen in the conduction band.

**Files**

170229\_VBandCBtogether.opj --- Combined Valence band (from UPS) and conduction band (from inverse UPS) data taken on a Bi4O4Cu1.7Se2.7Cl0.3 sample, with a fit to the data

The above file is a .opj file and must be opened using Origin.