Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Materials

Bandgap Engineering in Mn_3TeO_6: Giant Irreversible Bandgap Reduction Triggered by Pressure

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1. Sample information

Polycrystalline MTO material was prepared by solid-state reactions of a mixture of MnO and TeO3 (molar ratio 3:1). The binary oxides were thoroughly ground, pressed into a pellet and placed in a silica ampoule that was evacuated, sealed, and heated within 3 h to 1103 K and kept at this temperature for 3 days. [1] X-ray powder diffraction of the light-brown product revealed a single phase. Single crystals of MTO were grown by chemical transport reactions. 80 mg of polycrystalline MTO were mixed with 5 mg PtCl2 as the chlorine source (transport agent) and loaded in an evacuated and sealed silica ampoule that was subsequently heated in a temperature gradient from 1103 to 1023 K for five days. Yellow to amber coloured crystals of the title compound with a plate-like form and an edge-length up to 0.8 mm had formed in the colder part of the ampoule.

The chemical compositions of the prepared crystals and ceramic samples were determined by energy-dispersive spectroscopy (EDS) using a JEOL 840A scanning electron microscope and INCA 4.07 (Oxford Instruments) software. The analyses performed on several samples showed that the concentration ratios of Mn:Te were as expected for Mn_3TeO_6 within the instrumental resolution (0.05). [2,3] Structure analysis of MTO single crystals was performed at room temperature on a SMART Bruker three-circle diffractometer.

2. High-pressure Raman experiment

Raman scattering experiments were conducted in the Department of Earth Sciences, Uppsala University using a self-built micro-Raman system with the backscattering geometry. The DPSS laser (Cobolt Samba, 532.42 nm) was used as the excitation source. The laser beam size was

focused down to ~2-4 μm on the sample surface by a 20 X long working distance objective (Nikon). The Rayleigh line was blocked by two holographic notch filters (Semrock). The high-throughput single stage imaging spectrometer (HoloSpec f/1.8i, Kaiser Optical Systems, Inc.) was used to analyse the scattered light. The Raman spectra were collected by the CCD detector (Newton, Andor technology, 1600 × 400 pixels, thermoelectrically cooled to -55 ^{o}C). The system was calibrated with the fluorescence of a neon lamp and the first-order Raman band of single crystal silicon. The spectral resolution of the system is around 4 cm^{-1} and the accuracy estimated from the calibration procedure is around 2 cm^{-1}. Raman spectra were collected in the range 50-2200 cm^{-1} at room temperature. The laser power was set to 10 mW, and the spectral acquisition time varied between 120 and 1800 s. The symmetric DAC with anvils having a culet size of 300 μm was used to generate high pressure. The T301 stainless steel foil with a sample chamber diameter of 110 μm was used as a gasket. One piece of MTO single crystals loaded with two ruby balls in the sample chamber were used for the compression and decompression Raman measurements in the pressure range 0-40 GPa. The silicone oil was used as a pressure medium and the ruby fluorescence was used as a pressure gauge. [4]

3. *In situ* UV-vis absorption experiment

The in situ UV-vis absorption spectroscopy experiment was performed at the Swedish Museum of Natural History. The Spectra were collected from 280-1100 nm using a customized visible microscope system with the transmitting mode. The Merrill-Bassett DAC with a pair of 300 um culet diamonds were used to generate high pressure. A T301 stainless steel foil with an initial thickness of 250 μm was pre-indented to around 30 μm. A hole with a diameter of around 100 μm was drilled in the center using as sample hole. A piece of MTO single crystal with the typical

size around 50 μm was loaded in the sample hole with a ruby ball, which served as a pressure gauge. [4] Silicone oil was also loaded as a pressure medium.

4. *Tauc plot*

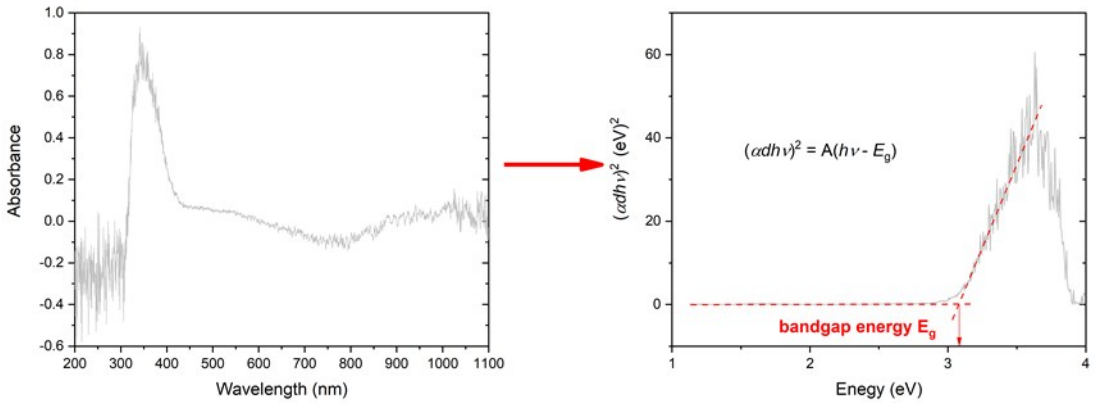

Fig. S1. The absorption spectrum and the converted Tauc plot for measuring the bandgap energy.

Reference

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