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Supplemental Material for "Deviatoric stress induced quasireconstructive phase transition in ZnTe"

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Understanding phase evolutions and underlying mechanism under external stimuli is of fundamental importance for novel materials discovery. Here, combining angular dispersive x-ray diffraction and first-principles pathway sampling, we found ZnTe alloy undergoes quasi-reconstructive transition to a metastable rocksalt phase under deviatoric stress. The rocksalt ZnTe has reconstructed chemical bonds and dendrite crystal morphology. It also suffers more severe thermodynamic hysteresis than the same experiments under hydrostatic pressure. However, phase transition towards the rock-salt phase is still described by relatively small atomic displacements and slightly first order, thus is neither fully displacive nor fully reconstructive. The quasi-reconstructive transition in ZnTe narrows its electronic bandgap and may provide insights for the semiconductor-metal transition in II-VI alloys in general.

Hydrostatic condition in a diamond anvil cell



Fig. S1 Pressure gradient measured from the center to the margin of culet in the sample chamber. A few ruby balls were placed on the sample chamber. Pressures were calibrated by measuring the ruby fluorescence line-shift.¹ We use methanol-ethanol mixture as a pseudo-hydrostatic pressure medium which preserves up to ± 3 GPa pressure uncertainty at 30 GPa. Data points of silicon oil and 16:3:1 methanol-ethanol-water are taken from literature.² The phase transition critical points in our pseodu-hydrostatic experiments are consistent with literature³⁻⁵ with only 1-2 GPa difference from ZnTe-I to II and 1.5-2 GPa difference from ZnTe-II to III. Since ZnTe-III appears around 12 GPa, the relatively small pressure gradient below

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20 GPa in our pseudo-hydrostatic experiment has little influence on the phase transition kinetics. Abbreviations: PM, pressure medium.

First-principles simulation

The Stochastic Surface Walking method (SSW) for probing transition pathways was performed under the framework of density functional theory as was implemented by the Vienna ab initio simulation package.⁶ The electron-ion interactions of Zn and Te atoms were approximated by a projector augmented wave scheme.⁷ The exchange-correlation functional was described by the generalized gradient approximation in the Perdew-Burke-Ernzerhof parameterization.⁸ The pathway sampling was carried out in a 24atom simulation lattice cell, which is tripled the size of ZnTe-III and quadruple the size of ZnTe-II. The Brillouin zone of the supercell was sampled by a $3 \times 3 \times 3$ k-point mesh and the enthalpy for each structure was generally relaxed below 0.01 eV/Å in atomic force. The exhaustive SSW sampling include around 2 thousand of initial/final state pairs. The pathways presented in Fig. 3 and below (Fig. S2) were selected to have the lowest kinetic barrier. Therefore, we assumed they are the most kinetically favorable pathways.



Fig. S2. Kinetic barrier between ZnTe-III and rocksalt ZnTe at 10 GPa. The kinetic barrier was estimated by the double-ended surface walking approach by locating the transition state at the saddle point.⁹ The transition kinetic barrier is 4.0×10^{-3} eV, which is at least one order of magnitude smaller than other transition pathways in Fig. 3.

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D0.3 GPa

D4.9 GPa

10.7 GPa

7.6 GP

0.1 GPa

300 350





Fig. S3. The electrical conductivity of ZnTe under non-hydrostatic condition. The error bar is contained in the circles and squares. While literature shows ZnTe is fully recovered from a metal to a semiconductor at 11 GPa during decompression,¹⁰ our nonhydrostatic experiments preserve the metallic ZnTe to ~2 GPa. The large hysteresis is due to the reconstructed high-pressure phase under deviatoric stress.

Raman shift (cm⁻¹) Raman shift (cm⁻¹) Fig. S4. Raman spectra of ZnTe under quasi-hydrostatic conditions with different pressure medium (a) silicone oil and (b) 16:3:1 methanol-ethanol-water. The typical exposure time was 500 second for each spectrum. Intensities were properly scaled for clarity. The peak positions were read by fitting the spectra with a Lorenztian curve after removing a linear baseline. Modes characteristic of the ZnTe-II and ZnTe-III were labelled in the order of increasing

Table S1. Lattice parameters and atomic coordinates from structural refinement. The phase under hydrostatic condition achieved $R_1 = 0.055$ and $R_2 = 0.072$. The coexisted phases of ZnTe-III and rocksalt ZnTe under deviatoric stress has a refinement factor $R_1 = 0.042$ and $R_2 = 0.089$ (Fig. 2c) (Fig. 2d).

frequency.

	Space group	l attic	a paramatara (Å) —		Atomic coordinates			
	Space group	Lattice parameters (A)		ers (A)		x	У	Z
Hydrostatic	Стст	а	b	С	Zn	0.00	0.632(8)	0.25
		5.203(1)	5.703(1)	4.963(9)	Те	0.00	0.203(9)	0.25
Non-Hydrostatic	Стст	а	b	С	Zn	0.00	0.642(4)	0.25
		5.364(3)	5.917(9)	4.990(1)	Те	0.00	0.183(8)	0.25
	Fm3m	а	b	С	Zn	0.00	0.00	0.00
		5.395(6)	5.395(6)	5.395(6)	Те	0.50	0.50	0.50

Table S2, Summary of energy barriers at 5, 10 and 15 GPa. The energy barriers become shallower with increased pressure. Abbreviations: I, ZnTe-I; II, ZnTe-II; III, ZnTe-III; RS, RS-ZnTe.

Pressure (GPa)	I-II (eV/f.u.)	ll-III (eV/f.u.)	II-RS (eV/f.u.)
5	0.27	0.14	0.14
10	0.15	0.032	0.024
15	0.092	0.002*	0.00

*At 15 GPa, the transition from ZnTe-II to RS-ZnTe is almost barrierless and the energy barrier of 0.002 eV/f.u. is actually equivalent to the transition from RS-ZnTe to ZnTe-III.

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