Supporting Information

Improvement on the THz response of $Zn_{1-x}Mn_x$ Te bulk crystals grown by

temperature gradient solution method

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S1: Powder X-ray diffraction (XRD)

Fig. S1 Powder XRD patterns of as-grown $Zn_{1-x}Mn_x$ Te and ZnTe crystals grown by TGSM. It is suggested that the $Zn_{1-x}Mn_x$ Te and ZnTe crystals were well-ordered zinc-blende (ZB) structure, which agree with the JCPDS numbers of 15-0746. According to the magnified 2 θ spectra shown by the blue bashed box, diffraction peaks shift lightly, which is dependent on the Mn composition. Furthermore, no extra peak related with other phase was observed.

S2: Identification of Te inclusions



Fig. S2 Typical IR transmission images of as-grown $Zn_{1-x}Mn_xTe$ crystal with triangular and hexagonal Te inclusions. The atomic concentration $C_{Te,S}$ (per unit of volume) of excess Te formed as inclusions in the crystals was estimated using the following equation, with the assumption that the Te inclusions are spheres:

$$C_{\rm Te,S} = \frac{4\pi d_{\rm Te} N_{\rm a}}{3M_{\rm Te}} \sum_{i=1}^{n} r_i^3 \rho_i$$
(1)

where ρ_i and r_i are, respectively, the density and radius of particles of class of diameter *i* in the crystal. M_{Te} and d_{Te} are the atomic mass and mass density of Te respectively. N_a is the Avogadro's number. The atomic concentrations of excessive Te formed as inclusions in the typical ingots are listed in Table 1.

Ingot	Solidified fraction /g	<i>C</i> _{Te, S} /%
ZMT-10	0.2	2.6×10 ¹⁸
	0.65	3.0×10 ¹⁸
	0.9	4.2×10^{18}
ZMT-5	0.2	3.2×10 ¹⁸
	0.4	3.6×10 ¹⁸
	0.8	4.0×10^{18}

Table 1. Atomic concentration of excess Te formed as inclusions

S3: Calculation method summary

The present calculations employ the Vienna Ab-initio Simulation Package (VASP) implementation of DFT, in conjunction with the projector-argumented-wave (PAW) formalism. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was used for the exchange-correction potentials. The related electronic configuration is Zn $3d^{10}4s^2$, Te $5s^25p^4$ and Mn $3p^63d^54s^2$. The energy convergence criterion for the structural relaxation is 1×10^{-6} and the force convergence criterion is set to 0.01 eV/Å. The electronic wave functions are expanded in plane waves using an energy cutoff of 520 eV. The Brillouin zones of the 64-atom orthorhombic supercells are sampled with $2 \times 2 \times 2$ Monkhorst-Pack k-point meshes.

We calculate the defect formation energy for the charge state q dependent on the Fermi level position according to [1, 2]

$$E_{f}[X^{q}] = E^{tot}[X^{q}] - E^{tot}[bulk] - \sum_{i} n_{i}u_{i} + q(E_{F} + E_{v} + \Delta V) + E_{corr}$$
(2)

Where $E^{tot}[X^q]$ is the total energy derived from a supercell with defect X and charge q, and $E^{tot}[bulk]$ is the total energy for the perfect crystal using an equivalent supercell, n_i is the number of atoms of type i that have been added to $(n_i > 0)$ or removed $(n_i < 0)$ from the supercell to form the defect, and u_i are the corresponding chemical potentials of these species. E_F is the Fermi level with respect to the bulk valence-band maximum (VBM) E_v , and ΔV is a correction term to align the reference potential in our defect supercell that in the bulk. E_{corr} is a correction term due to the presence of periodic images that becomes necessary for modeling community, which can correct the finite-size error that arises from the electrostatic interaction between charged defects in neighboring cell images. There are several schemes have been proposed to correct this error [3-5]. In this paper, the correction term suggested by Freysoldt *et al.* [4] is adopted. A planar average of the electrostatic short range potential is used and works well with the small relaxation.

S4: I-V measurements



Fig. S3 Typical I-V curves for as-grown $Zn_{1-x}Mn_xTe$ and ZnTe crystals measured at room temperature.

REFERENCES

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