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Atypical phase-change alloy Ga_2Te_3: atomic structure, incipient nanotectonic nuclei, multilevel writing

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Electronic supplementary information

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Homopolar and heteropolar bond energies in the Ga-Te system

Table S1 shows the homopolar Ga-Ga/Te-Te, and heteropolar Ga-Te bond energies in the Ga-Te binary system.

Table S1 Homopolar and heteropolar bond energies in gallium tellurides

Homopolar bonds	E_{homo} (kJ mol^{-1})	Heteropolar bonds	E_{hetero} (kJ mol^{-1})	$\frac{1}{2}(E_{\mathrm{Ga-Ga}}+E_{\mathrm{Te-Te}})$ (kJ mol^{-1})
Ga – Ga	113	Ga – Te	147	120
Te – Te	126			

The homopolar bond energies were taken from the following sources.[S1,S2] The heteropolar bond energy was calculated according to Pauling:[S3]

$$X_{\mathrm{A}} - X_{\mathrm{B}} = 0.102\sqrt{E_{\mathrm{A-B}} - (E_{\mathrm{A-A}} \times E_{\mathrm{B-B}})^{0.5}}\,. \qquad \text{(S1)}$$

Consequently,

$$E_{\mathrm{A-B}} = \sqrt{E_{\mathrm{A-A}} \times E_{\mathrm{B-B}}} + 96(X_{\mathrm{A}} - X_{\mathrm{B}})^2\,, \qquad \text{(S2)}$$

where X_{Ga} = 1.81 and X_{Te} = 2.10 are the Pauling's electronegativities.

Rough estimation of optical properties of crystallized and amorphous Ga_2Te_3

The expected changes in relative transmittance and reflectivity were estimated without taking into account both the extinction and the absorption since the optical absorption data for crystallized Ga_2Te_3 are not measured yet.

Different densities of amorphous (ρ_g = 5.22 g cm^{-3}) and crystallized (ρ_c = 5.64 g cm^{-3}) Ga_2Te_3 lead to different refractive indices n_g = 3.13 (experimental) and n_c = 3.67, estimated using the Clausius-Mossotti relation:

$$\left(\frac{{n_g}^2-1}{{n_g}^2+2}\right)\left(\frac{{n_c}^2+2}{{n_c}^2-1}\right)=\frac{\rho_g}{\rho_c}.$$

Different refractive indices n_R allow a rough estimation of the reflectivity without taking into account the extinction coefficient:

$$R=\frac{(n_R-1)^2}{(n_R+1)^2},$$

and the estimated reflectivity of amorphous Ga_2Te_3, R_a, appears to be lower than that of crystallized Ga_2Te_3, $R_a/R_c \cong 0.81$. Likewise, the expected transmittivities are also different, $T_c/T_a \cong 0.92$.

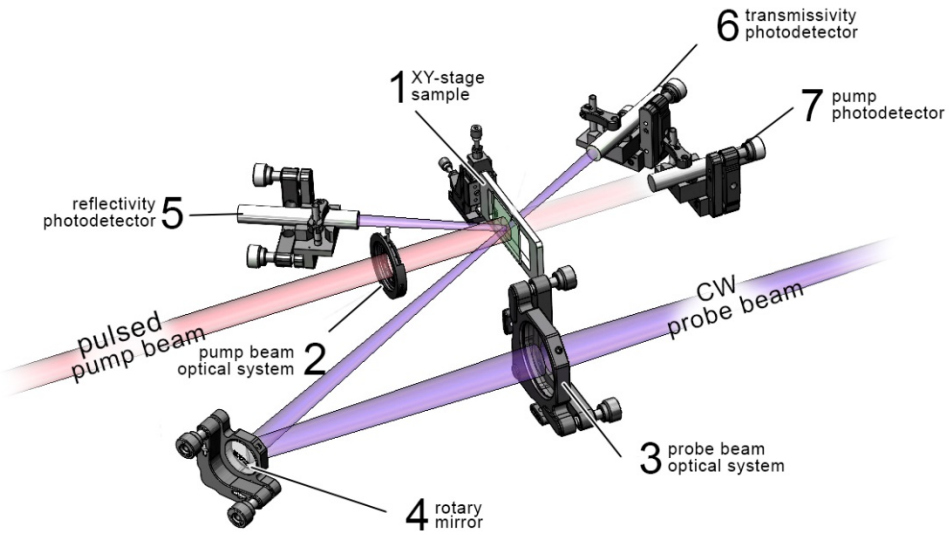

Fig. S1 Schematics of the experimental pump-probe setup used in preliminary optical phase-change experiments.[S4]

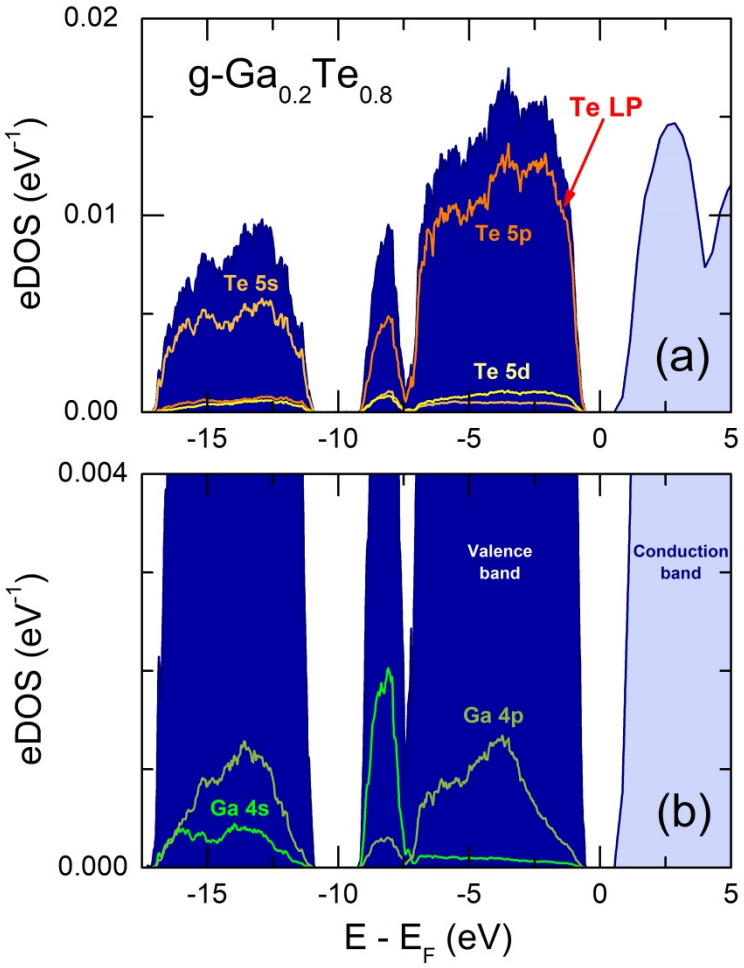

Fig. S2 Electronic density of states (eDOS) in bulk glassy $GaTe_4$ (x = 0.2) at 300 K and the eDOS projections on (a) tellurium and (b) gallium atomic pseudo-wave functions.[S5] The position of Te nonbonding lone-pair states is shown by the red arrow.

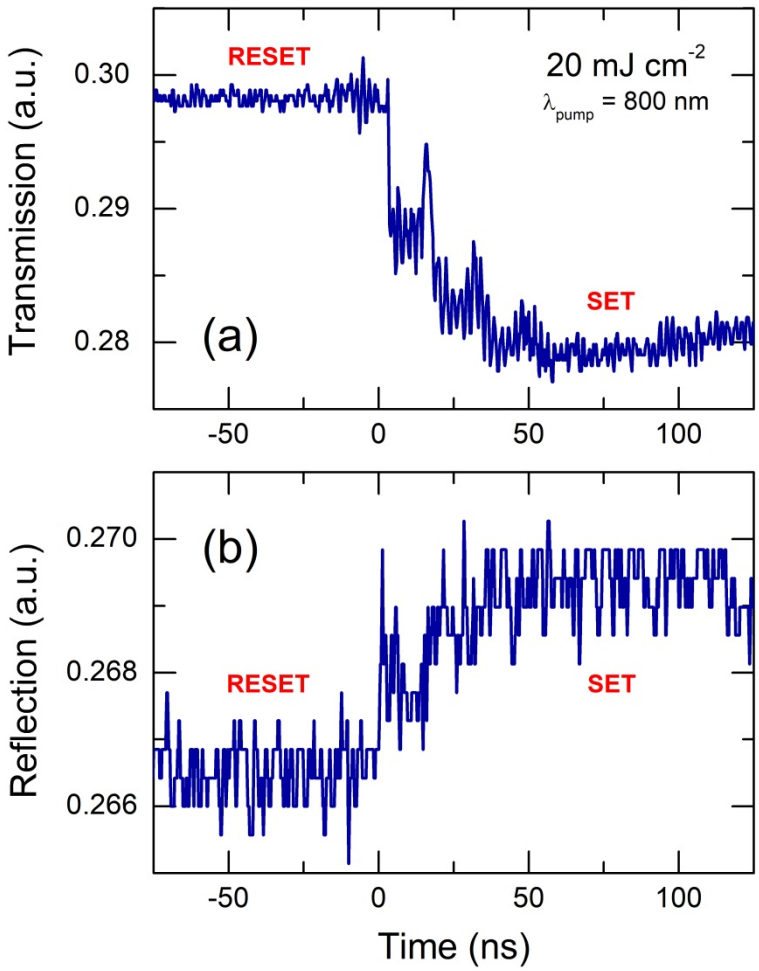

Fig. S3 Optical RESET–SET transition in Ga_2Te_3 PLD film (100 nm) induced by a femtosecond laser with λ_{pump} = 800 nm and the energy density 20 mJ cm^{-2}: (a) transmission mode, (b) reflection mode.

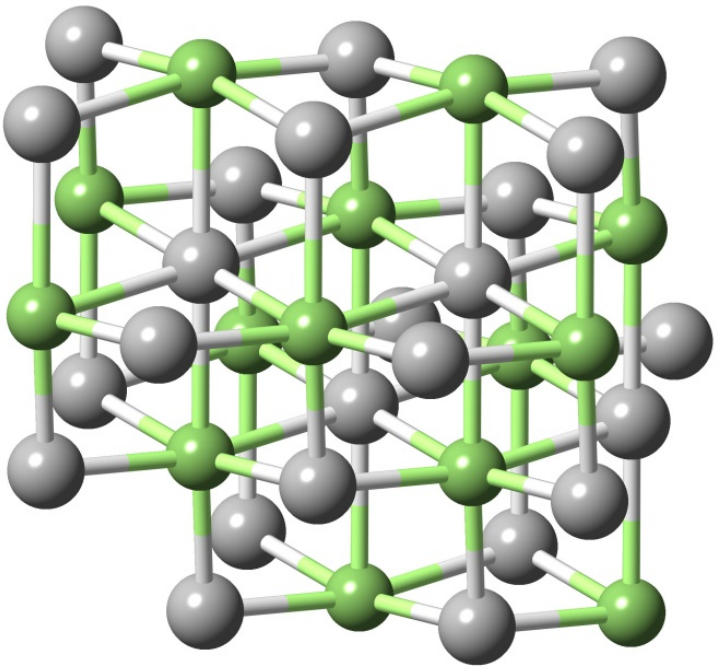

Fig. S4 Crystal structure of rhombohedral high-pressure HP-Ga_2Te_3.[S6].

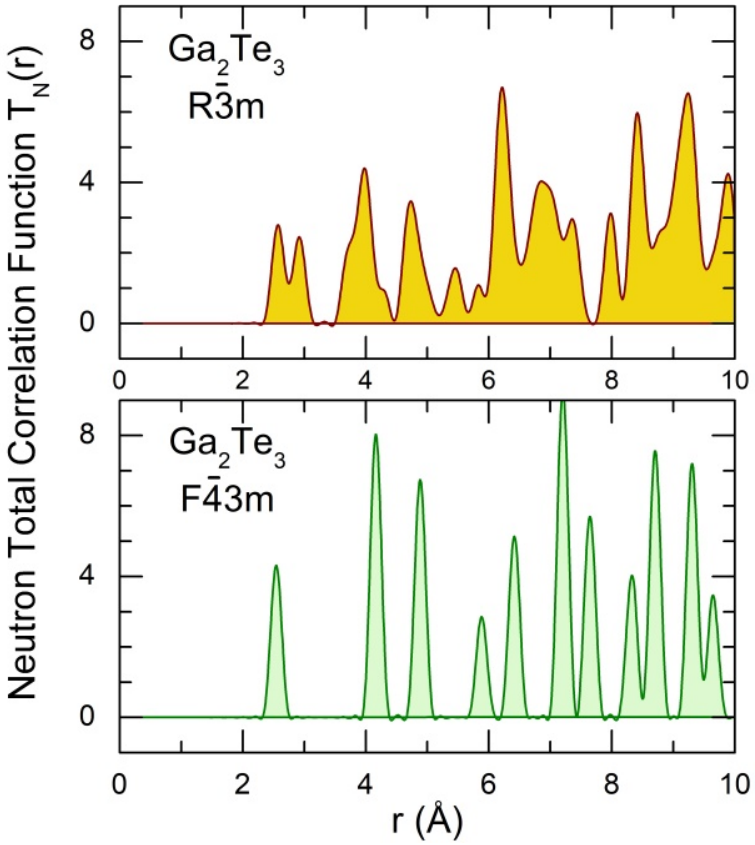

Fig. S5 Neutron total correlation functions of (a) rhombohedral[S6] Ga_2Te_3 and (b) fcc Ga_2Te_3.[S7]

Structural changes during SET-RESET transitions

Diffraction and Raman experiments supported by DFT and FPMD modeling show that amorphous Ga_2Te_3 has essentially the tetrahedral structure with a small population, 2-4%, of incipient nuclei reminiscent of monoclinic HP-Te II and rhombohedral HP-Ga_2Te_3. The fraction of these nuclei increases above the glass transition temperature according to FPMD simulations. Very recently, we have carried out neutron diffraction experiments of liquid Ga_2Te_3 at 1100 K just above melting, which will be reported elsewhere. The experimental neutron total correlation function $T_N(r)$ at 1100 K shows important differences compared to real-space functions of amorphous Ga_2Te_3. The local gallium environment remains four-fold coordinated but the tetrahedral distortion appears to be very strong with two clearly different contributions to the Ga-Te nearest neighbor peak, reminiscent of that in rhombohedral HP-Ga_2Te_3.

The preliminary FPMD simulations enable the orientational order parameter q[S8,S9] to be calculated and determine that the fraction of defect octahedral entities GaX_4 has increased by a factor of 5, from 3% at 300 K to 15% at 1100 K. Similar situation is expected in supercooled Ga_2Te_3 liquid during the SET pulse. Very high viscosity of supercooled liquid and high internal pressure of 4-8 GPa related to nanotectonic compression[S5] will transform the defect octahedral species and under-/over-coordinated species GaX_3, GaX_5, GaX_6 into crystallites of HP-Ga_2Te_3 with octahedral gallium coordination. The fraction of under-/over-coordinated species was also found to be increased from $p_{Ga\neq4} \approx 0.04$ (300 K) to $p_{Ga\neq4} \approx 0.21$ (1100 K).

The short RESET pulse transforms Ga_2Te_3 into normal liquid above melting with low viscosity and hence without substantial nanotectonic compression. Fast cooling of this normal liquid into amorphous material will retain the 4-fold gallium coordination, and structural relaxation will increase the fraction of tetrahedral species.

This hypothesis will be further verified by FPMD simulations reproducing the SET and RESET pulses.

Additional references

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