Supplementary Information

Resonant phonon modes induced by molecular rotations in *α*-pentaerythritol crystal

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1. The dominant interactions between layers

To determine the interactions between the layers in the α-PE crystal, a layer of molecules was exfoliated from the crystal in MD simulations. And the single-point energy, that is, the energy as a function of distance was recorded during the peeling process. It is seen from **Figure S1** that the maximum absolute intensity of Van der Waals interactions is five times that of Coulombic interaction. Therefore, the dominant interaction between layers is the Van der Waals interaction.
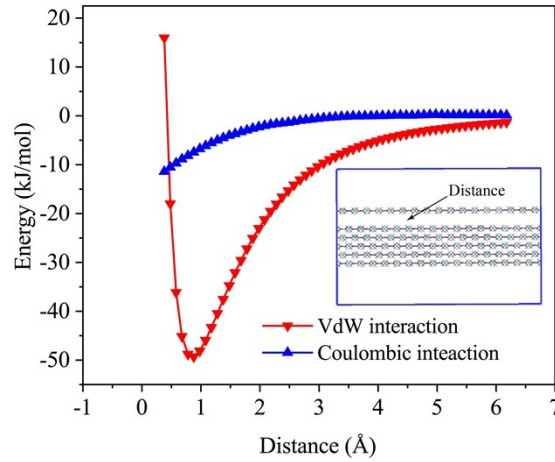

Figure S1. Van der Waals energy and Coulombic energy as a function of the distance between layers. The inset is a setup for a single-point energy calculation with a vacuum large enough to prevent interactions across boundaries along the out-of-plane direction.

2. Validation of the force field

The GROMOS force field was employed to describe the interactions in PE molecules, and the detailed parameters can be found on the *Automated Topology Builder version 3.0* website.[1] To validate the accuracy of the force field, the specific heat capacity of the α-PE crystal was computed as follows:[2]

$$c = 3k_B \int_0^\infty PDOS(\omega) \frac{exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_BT}\right)-1\right)^2}\left(\frac{\hbar\omega}{k_BT}\right)^2 d\omega \qquad (S1)$$

in which $\hbar$ is the reduced Planck constant and ω is the frequency. The PDOS refers to the phonon density

of states, which is obtained by performing the Fourier transform on the velocity autocorrelation function (VACF) as:

$$PDOS(\omega) = \int_{-\infty}^{+\infty} \frac{\langle v(\tau) \cdot v(0) \rangle}{\langle v(0) \cdot v(0) \rangle} e^{-i\omega\tau} d\tau \qquad (S2)$$

in which v is the velocity of the atoms. The theoretical results and the experimental data[3] are compared in **Figure S2**. It can be seen that our MD simulations yielded fairly accurate specific heat capacities for the α-PE crystal, with a maximum error of 16.86 % over the temperature range of 277 to 455 K. In addition, the agreement between the average thermal conductivities calculated by GK-EMD in **Figure 2(a)** in the main text and the experimental data, and the consistency between the phonon dispersions calculated by SED and the finite displacement method, also indicate that the GROMOS force field can accurately describe PE molecules in the MD simulations.
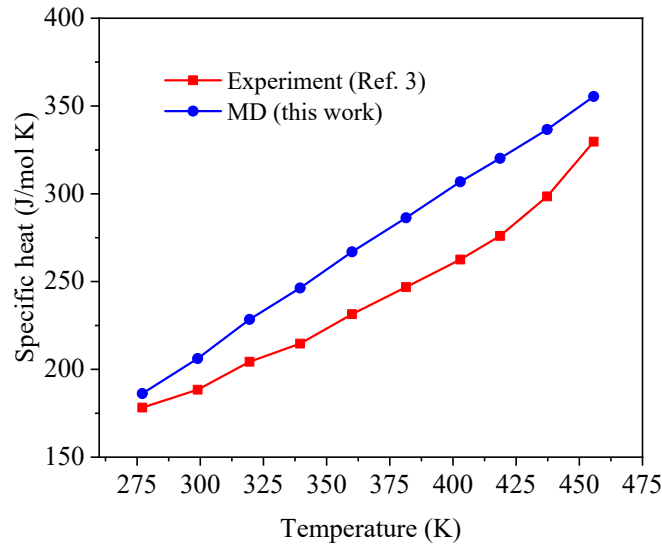

Figure S2. The predicted and measured specific heat capacity of the α-PE crystal as a function of temperature.

3. Convergency of thermal conductivity

We performed 40 independent GK-EMD simulations with the autocorrelation time of 50 ps for every point in **Figure 2** in the main text to obtain the convergent thermal conductivity. It is seen that the numbers

of simulations and autocorrelation time adopted here are large enough and long enough to get a convergent thermal conductivity, as shown in **Figure S3**.
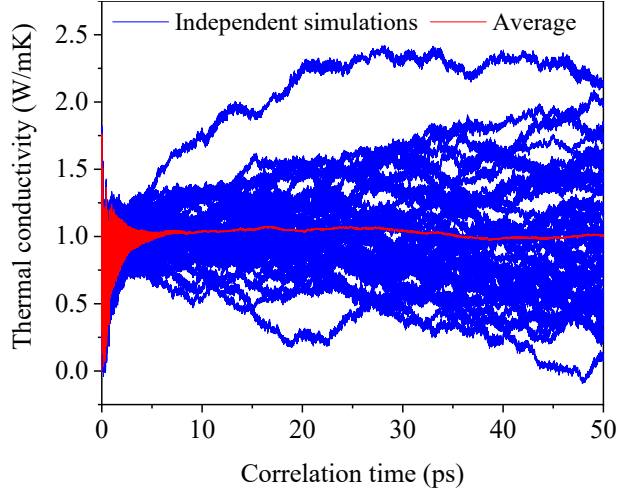

Figure S3. Convergency of the averaged thermal conductivity (red line).

4. Effect of out-of-plane expansion on thermal conductivity

Besides the pressure, out-of-plane expansion can significantly tune the thermal conductivity out of the plane. The out-of-plane thermal conductivity follows an exponential dependence with a four-fold decrease from 0.94 to 1.05 expansion, shown in **Figure S4**. This can be attributed to the weak nature of the out-of-plane van der Waals interaction, which readily varies with the interlayer spacing, resulting in an easy variation in the phonon group velocity (LA branch in **Figure S7**) hence the exponential dependence of thermal conductivity on the out-of-plane expansion.[4] Therefore, a thermal rectifier can be realized by applying the strain or stress to control the heat flow along the *c*-axis.
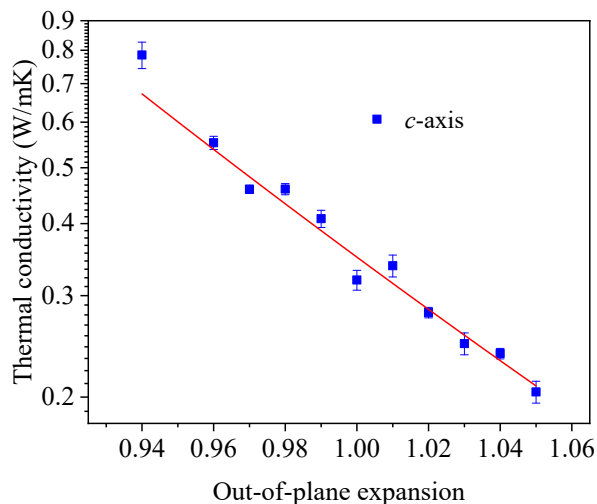
Figure S4. Out-of-plane thermal conductivity as a function of the out-of-plane expansion.

5. DFT calculations

VASP was used to perform the DFT calculations within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof function.[5] To accurately describe the interactions between molecules in the α-PE crystal, the van der Waals correction,[6] which is crucial for the weakly interacted molecular crystals,[7,8] was included in all DFT calculations. A 4×4×3 Γ-centered Monkhorst-Pack mesh was adopted to sample the Brillouin zone, and the energy cutoff for the plane-wave expansion was set as 600 eV. The unit cell was optimized until the energy converged to 10^{-8} eV and the maximum force on each atom was less than 10^{-7} eV/Å. The phonon dispersion was calculated within the harmonic approximation via the finite displacement method with a displacement of 0.01 Å, implemented in Phonopy in combination with VASP, plotted in **Figure S5**.
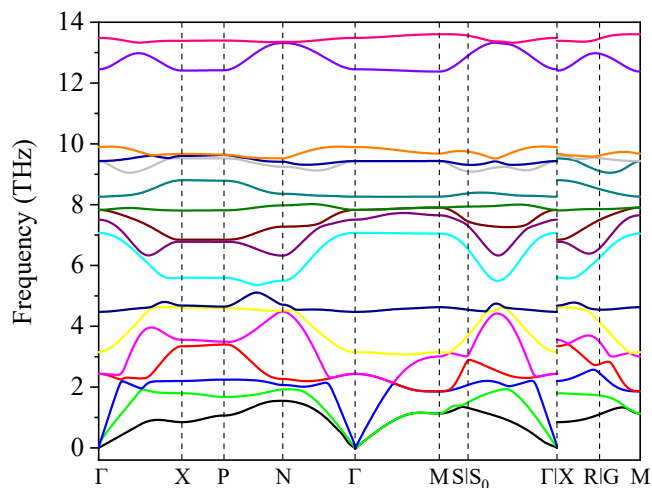
Figure S5. Phonon dispersion calculated by the finite displacement method

6. Raman scattering measurement

The pentaerythritol powders with a purity of 99% were purchased from Sigma-Aldrich. The measured samples were pressed into a 10 mm diameter tablet with a thickness of about 2 mm for the experiment. Raman scattering measurement was performed by a commercial Raman system (LabRAM HR Evolution, HORIBA Jobin Yvon) with incident wavelength $\lambda = 633$ nm at the atmosphere. To collect Raman spectroscopy of samples at low frequencies (5 cm^{-1} - 50 cm^{-2}), the instrument was set to Ultralow-frequency (ULF) Raman mode. The acquired data were analyzed using the built-in LabSpec 6, depicted in **Figure S6**.
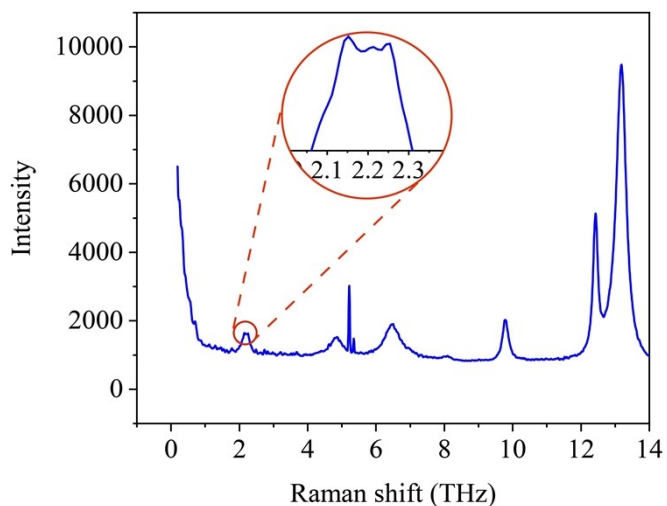

Figure S6. Raman scattering spectrum at 300 K. The inset highlights the peaks at 2.15 and 2.25 THz,

corresponding to flat bands at 2.43THz on the phonon dispersion spectrum.

7. Effect of out-of-plane expansion on phonon dispersion

In addition to the effect on thermal conductivity, pressure plays a vital role in the phase transition of plastic crystals by tuning the molecular rotational dynamics. The pressure increases the energy barriers of orientational disorder and suppresses the rotation of molecular rotations.[7] In the main text, we found that two rotational motions are perpendicular to each other, and they merged when the temperature increased. Thus, the phase stability can be broken by the isotropy of the two rotational motions. To explore the effect of pressure on the phase stability of the α-PE crystal, the pressure-dependent phonon dispersions calculated by SED are plotted in **Figure 4(d)** in the main text. It is seen that when the pressure increases from 0 to 800 MPa, the second-lowest optical branch shifts up. Therefore, high pressure plays an identical role to low temperature. They separate the two lowest optical phonon branches, maintaining the anisotropy of the two rotational motions, thereby stabilizing the α-PE crystal. Meanwhile, high pressure reduces the interactions between acoustic and optical phonon modes, thereby significantly increasing the thermal conductivity. As for out-of-plane expansion, it decreases the inter-layer interactions when increasing from 0.97 to 1.03, resulting in a significant decrease in the phonon group velocity, shown in **Figure S7**, thereby an exponential decrease of the out-of-plane thermal conductivity in **Figure S4**.[4] As out-of-plane expansion increases from 0.97 to 1.03, the crystal becomes unstable. Meanwhile, the two lowest optical phonon branches shift significantly, again indicating the role of rotational dynamics on phase stability.
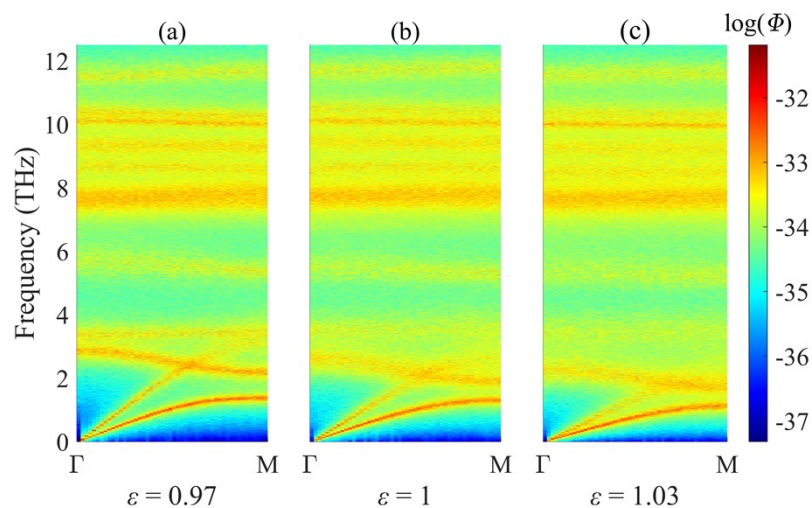
Figure S7. Phonon dispersions computed by the spectral energy density (SED) method as a function of out-of-plane expansion.

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