Supporting Information for "Room-temperature Electrical Control of the Thermal Conductivity in ZrO_2"

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Monoclinic bulk ground-state

At room-temperature, the thermodynamically ground-state of bulk ZrO_2 is monoclinic (space group $P2_1/c$). We found lattice vectors $a = 5.128$ Å, $b = 5.215$ Å, $c = 5.293$ Å, and an angle $\beta = 99.56°$. The phonon dispersion, whose absence of imaginary modes indicate dynamical stability, is shown on Figure S1. In thin-films, the tetragonal-monoclinic transition temperature is suppressed and thus the most stable phase at room-temperature becomes the tetragonal one.

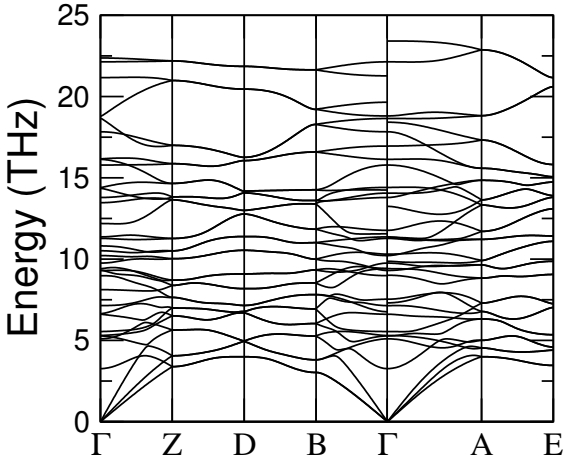

Figure S1: Phonon dispersion of the monoclinic phase.

Selection of the allowed phonon-phonon collision processes

The number of allowed phonon-phonon processes, which is critical to obtain converged values of $\boldsymbol{\kappa}$, is controlled by two parameters: (i) the number of $\mathbf{q}$-points, $N_{\mathbf{q}}$, i.e. the density of the Brillouin zone sampling, and (ii) the width of the Gaussian functions, σ, that are used instead of Dirac deltas to check which phonon-phonon collisions conserve energy and momentum. While carrying out a convergence test with the density of the $\mathbf{q}$-point grid is rather standard, the role of σ is often overlooked, as the default value of ShengBTE/FourPhonon is a rather safe choice and is usually guaranteed to work.[1,2] However, when four-phonon scattering is considered, the number of allowed processes greatly increases, so that reliable calculations,

particularly for systems with a rather larger unit cell, can quickly become unfeasible (see Figure S2).

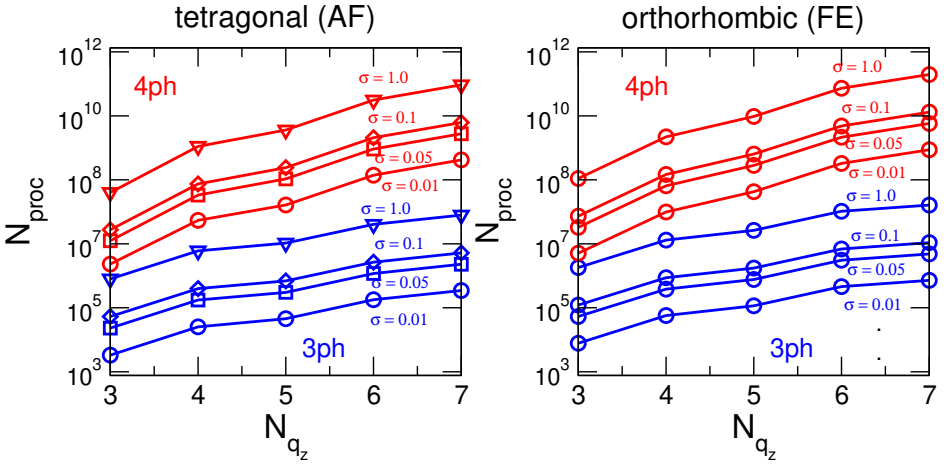

Figure S2: Allowed 3ph (blue symbols) and 4ph phonon-phonon processes (red symbols) as a function of N_{q_z} for different values of γ.

Therefore, besides a meticulous convergence study of $N_{\mathbf{q}}$, we also verified if it is possible to reduce σ. Indeed, while broadly speaking both parameters control the number of phonon-phonon processes, $\boldsymbol{\kappa}$ can depend on them in different ways. Our results for 3ph processes, shown in Figure S3, provide a strong indication that σ can indeed be reduced. There we plot κ_{ii} as a function of the number of $\mathbf{q}$-point (for brevity, we identify the grid with N_{q_z}; we took $N_{q_x} = N_{q_y} \approx 1.5 \times N_{q_z}$ for the $P4_2mc$ phase and $N_{q_x} = N_{q_y} = N_{q_z}$ for the $Pca2_1$ phase) for different values of the scaling parameter, $\gamma = \sigma/\bar{\sigma}$ (where σ is the actual value employed and $\bar{\sigma}$ the default value). As it can be seen, $\gamma = 0.1$ and 0.05 yields essentially the same results of $\gamma = 1.0$ (the unscaled, default value of σ); even $\gamma = 0.01$, corresponding to a σ which is 100 times smaller than the default value, provides a good approximation, as long as the $\mathbf{q}$-point grid is fine enough. This is clearer in the right hand column where, for three selected grids, we plot κ_{ii} as a function of γ. In all the cases $\gamma = 0.05$ yields converged values for the thermal conductivity.

This general behavior is confirmed when also 4ph processes are included, which is the really relevant case for our purposes. Notice that in this case the calculations with $\gamma = 1.0$

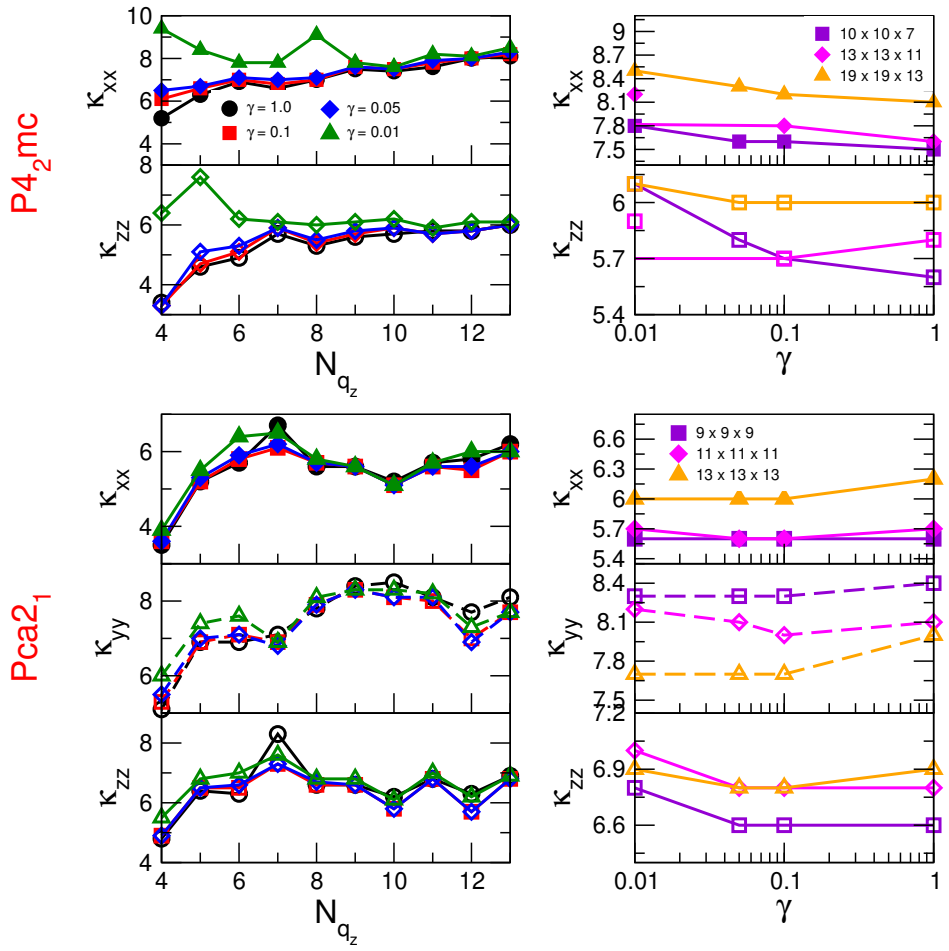

Figure S3: (Left) Thermal conductivity with 3ph scattering as a function of N_q for different values of γ. (Right) Thermal conductivity with 3ph scattering as a function of γ for three selected **q**-point grids. Thermal conductivities are in W m^{-1} K^{-1}.

are simply not feasible, due to the huge number of allowed processes (see Figure S4) and we could get estimate of $\boldsymbol{\kappa}$ only for clearly unconverged values of $N_{\mathbf{q}}$ (not shown), a fact that strengthen the importance of this preliminary study. Similarly to 3ph processes, in the case of 3ph+4ph processes the use of $\gamma = 0.01$ results in some non minor deviations, but $\gamma = 0.05$ give essentially the same value of κ_{ii} obtained with $\gamma = 0.1$. The relative error, shown in the right-hand side column, is at most 4% (marked with an orange dashed line in the insets).

Based on these convergence tests, in the main manuscript we discuss results obtained with $\gamma = 0.1$ and a $7 \times 7 \times 5$ ($5 \times 5 \times 5$) for the $P4_2mc$ ($Pca2_1$) crystal phase.

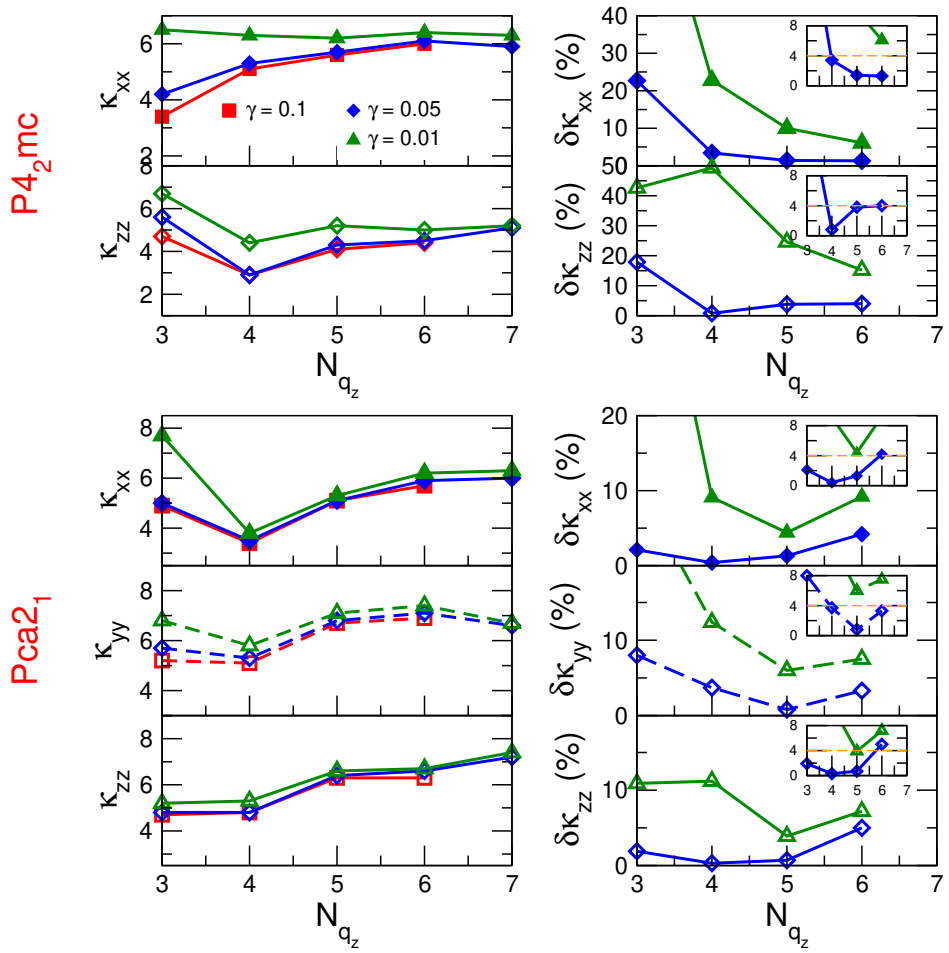

Figure S4: (Left) Thermal conductivity with 3ph+4ph scattering as a function of N_q for different values of γ. (Right) Relative variation of κ_{ij} as a function of N_q for $\gamma = 0.05$ and 0.01 with respect $\gamma = 0.1$. The insets show a zoomed view; the orange dashed line indicate variations of 2%. Thermal conductivities are in W m^{-1} K^{-1}.

Additional considerations about convergence

In Table S1 we report the numerical values, also plotted in Figure S4, of $\boldsymbol{\kappa}$ as a function of the number of **q**-points for both crystal phases and for two different values of γ, the width of the Gaussian functions that are used to check which phonon-phonon collisions conserve energy and momentum; namely, $\gamma = 0.1$ and $\gamma = 0.05$..

These results indicate that, regardless of the value of γ, $\boldsymbol{\kappa}$ is converged for grids of at least $7 \times 7 \times 5$ and $5 \times 5 \times 5$ **q**-points for the tetragonal ($P4_2nmc$) and orthorhombic ($Pca2_1$) phase, respectively.

The analysis carried out in the manuscript is based on a smearing factor $\gamma = 0.1$ and a $7 \times 7 \times 5$ and $5 \times 5 \times 5$ **q**-grid for the tetragonal and orthorhombic phase, respectively. According to our results, the largest variation of $\boldsymbol{\kappa}$ upon further increasing the density of the **q**-grid is 0.6 W m^{-1} K^{-1} for transport along the x-axis in the orthorhombic phase. Noteworthy, κ_{zz}, which is the most interesting component of the thermal conductivity tensor concerning the possible electrophonic effects discussed in the main manuscript, is even better behaved and is converged within 0.2 W m^{-1} K^{-1}.

References

(1) Li, W.; Carrete, J.; Katcho, N. A.; Mingo, N. ShengBTE: a solver of the Boltzmann transport equation for phonons. *Comp. Phys. Commun.* **2014**, *185*, 1747–1758.

(2) Han, Z.; Yang, X.; Li, W.; Feng, T.; Ruan, X. FourPhonon: An extension module to ShengBTE for computing four-phonon scattering rates and thermal conductivity. *Computer Physics Communications* **2022**, *270*, 108179.

Table S1: Dependence of $\boldsymbol{\kappa}$ on the $\mathbf{q}$-point grid and Gaussian width, γ, for the tetragonal ($P4_2nmc$) and orthorhombic ($Pca2_1$) phase of ZrO_2.

$P4_2mc$					
$\mathbf{q}$-grid	κ_{xx}	κ_{zz}		κ_{xx}	κ_{zz}
$4 \times 4 \times 3$	3.4	4.7		4.2	5.6
$6 \times 6 \times 4$	5.1	2.9		5.3	2.9
$7 \times 7 \times 5$	5.6	4.1		5.7	4.3
$9 \times 9 \times 6$	6.0	4.4		6.1	4.5
$10 \times 10 \times 7$				5.9	5.1
$Pca2_1$					
$\mathbf{q}$-grid	κ_{xx}	κ_{yy}	κ_{zz}	κ_{xx}	κ_{yy}	κ_{zz}
$3 \times 3 \times 3$	4.9	5.2	4.7	5.0	5.7	4.8
$4 \times 4 \times 4$	3.4	5.1	4.8	3.5	5.3	4.8
$5 \times 5 \times 5$	5.1	6.7	6.3	5.1	6.8	6.4
$6 \times 6 \times 6$	5.7	6.9	6.3	5.9	7.1	6.6
$7 \times 7 \times 7$				6.0	6.6	7.2