Supplementary Information

Role of phonon scattering and bonding in resolving lattice thermal conductivity ambiguities of β-Ga_2O_3[†]

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I. LATTICE PARAMETERS AND CRYSTALLOGRAPHIC ANGLES

The DFT-calculated lattice parameters and crystallographic angles in this study are in good agreement with previously reported theoretical and experimental results, as shown in Table S1. [1–5]

	Santia *et. al.**[1]	Yan *et. al.**[2]	Munsi *et. al.**[3]	Guo *et. al.*#[4]	Geller *et. al.*#[5]	This study#
a (Å)	12.28	12.45	12.21	12.21	12.23	12.28
b (Å)	3.05	3.08	3.03	3.03	3.04	3.05
c (Å)	5.64	5.86	5.80	5.80	5.80	5.80
α,β	90°	90°	90°	90°	90°	90°
γ	103.72°	103.76°	103.83°	103.83°	103.70°	103.71°

TABLE I. Reported lattice parameters and crystallographic angles of β-Ga_2O_3. * and # represent the experimental and theoretical values.

II. CONVENTIONAL AND PRIMITIVE SUPERCELLS

The supercells built using conventional and primitive unit cells have been shown in Figs. S1(a-c). The supercell size used in this study is 1×3×2 and has been constructed on a conventional unit cell. The supercell view along [100], [010], and [001] has been shown in the upper section of Figs. S1. The supercell view indicates that all distinct Ga-sites (tetrahedral and octahedral) are surrounded by neighboring atoms in a way such that interactions among all these atoms will be well captured. The

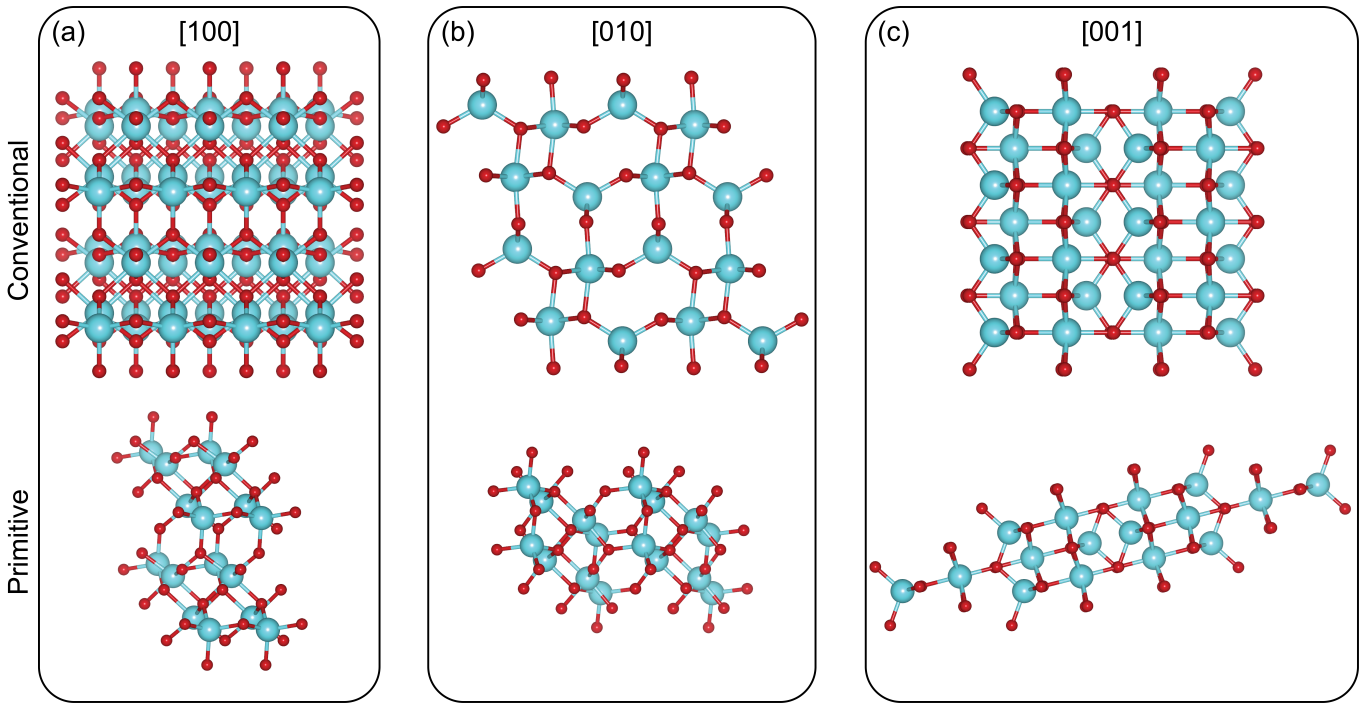

FIG. S1. Supercell view of β-Ga_2O_3 from [100], [010], and [001] directions; (a) conventional unit cell containing 20 atoms (supercell size: 1×3×2), (b) primitive unit cell containing 10 atoms (supercell size: 2×2×2).

isotopic supercell size (2×2×2) used in earlier DFT studies constructed on primitive unit cells has been shown at the bottom of Figs. S1(a-c) along [100], [010], and [001], respectively. It clearly shows nonuniform surroundings around the distinct sites, thereby leading to inaccurate determination of the exact interactions.

III. LATTICE THERMAL CONDUCTIVITY

The calculated lattice thermal conductivity (κ_l) using iterative and direct solution methods considering three phonon interactions have been shown in Figs. S2 by orange and blue color lines, respectively. These results are in great agreement with the experimentally observed values in all three conducting directions, thereby illustrating the significance of the choice of supercell and type of unit cell in the determination of κ_l for β-Ga_2O_3. The κ_l values calculated using three and four phonon interactions are plotted in Fig. S2. The inclusion of four phonon interactions underestimates the κ_l values along all the directions, suggesting the four-phonon interactions as considerably insignificant.

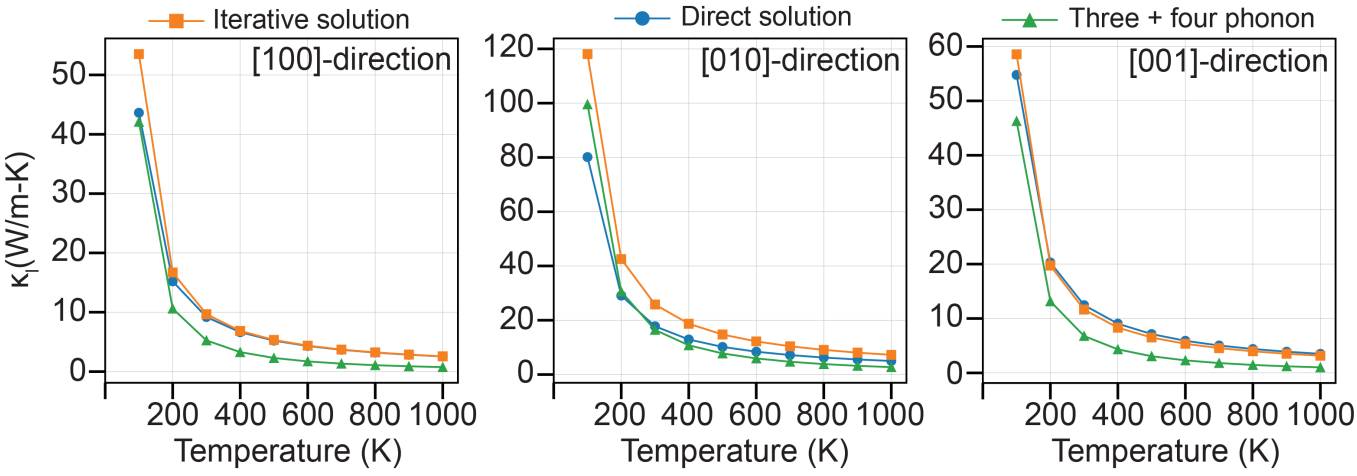

FIG. S2. Lattice thermal conductivity along [100], [010], and [001]-direction considering anharmonic terms up to third order (direct and iterative solution method), and up to fourth order.

A convergence test of κ_l with respect to grid sizes has been performed. The κ_l values along x, y, and z-directions have been plotted in Fig. S3(a), (b), and (c), respectively.

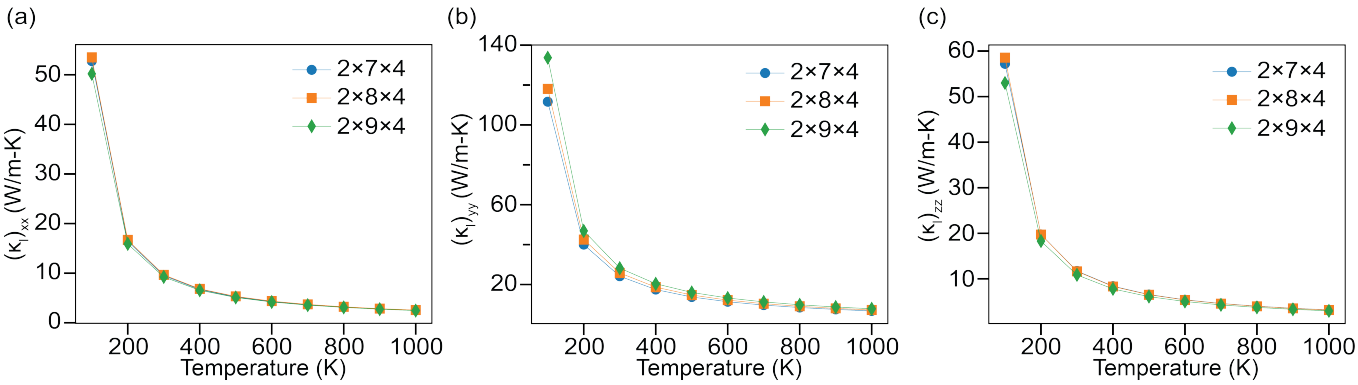

FIG. S3. Lattice thermal conductivity with respect to q-grid at temperature from 100 K to 1000 K along (a) x-, (b) y-, and (c) z-direction.

The parameters used for the lattice thermal conductivity calculations are as follows.

Parameter	Number of displacements	Used parameters
FC2	20	supercell size:1×3×2
FC3 (direct solution)	9983	supercell size:1×3×2 and cutoff-pair=7
FC3 (iterative solution)	420	supercell size:1×3×2 and cutoff up to 3^{rd}-nearest neighbour distance in supercell
FC4 (iterative solution)	3152	supercell size:1×3×2 and cutoff up to 3^{rd}-nearest neighbour distance in supercell

TABLE II. Second-order interatomic forceconstants (FC) have been calculated using phonopy [6]. Direct solution [7] of phonon Boltzmann transport equation has been performed using phono3py. Iterative solutions (*scaleboard*=0.1) of the phonon Boltzmann transport equation, including only three phonon interactions [8] and four phonon interactions [9], have been performed using ShengBTE [8].

IV. LATTICE THERMAL CONDUCTIVITY USING PRIMITIVE UNIT CELL

To compare the obtained κ_l values along the primitive axes with experiments, projections were taken along conventional unit cell directions. Here, we have compared the values obtained along primitive unit cell crystallographic axis directions as obtained by Santia *et al.*[1] with calculated values in the present study. This further confirms the κ_l values calculated by considering the primitive unit cell are correct; However, it fails to predict the experimentally observed κ_l values.

	Santia *et. al.*[1]	This study
Unit cell	10 atoms	10 atoms
Supercell	2×2×2 (80 atoms)	2×2×2 (80 atoms)
k-mesh (for κ_l calculation)	10×10×10	10×10×10
Number of 2^{nd} order displacements	20	20
Number of 3^{rd} order displacements	392	388
$\kappa_{xx} = \kappa_{[100]}$ (W/m-K)	16.06	17.60
$\kappa_{yy} = \kappa_{[010]}$ (W/m-K)	21.54	21.57
κ_{zz} (W/m-K)	∼25	28.37
κ_{xz} (W/m-K)	∼5	5.32

TABLE III. Parameters used and calculated κ_l values along primitive unit cell axes of β-Ga_2O_3.

V. PHONON GROUP VELOCITY

Calculated phonon group velocity along three conducting directions have been shown in Figs. S4 (a-c). Anisotropy of β-Ga_2O_3 structure is reflected in the phonon group velocities along x, y, z-directions.

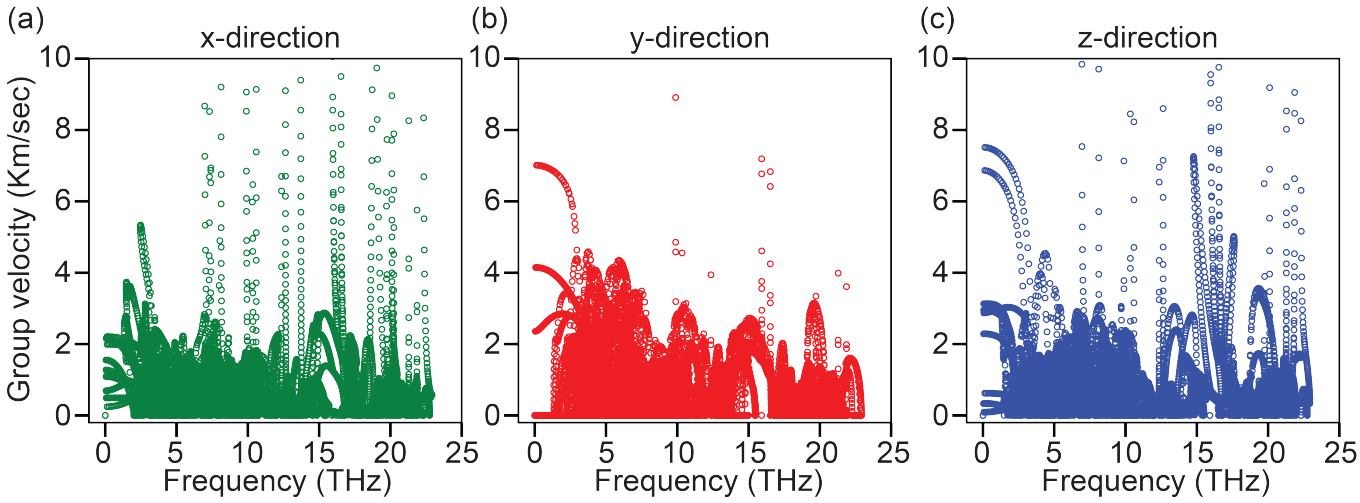

FIG. S4. Varition of phonon group velocity with frequency along (a) x-, (b) y-, and (c) z-direction.

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