Supplementary Information: Anisotropic thermal conductivity tensor of $\beta$-Y$_2$Si$_2$O$_7$ for orientational control of heat flow on micrometer scales

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1. Scanning Electron and Electron-Backscatter Diffraction Micrographs

Scanning electron micrographs of the three regions examined in this work are shown in Fig. S1. Two sets of FIB marks were placed on the sample in order to view the areas under our optical setup prior to TDTR mapping, as well as to allow for SEM, EBSD, and thermal map overlays for identification of grains between the three techniques. Electron backscatter diffraction (EBSD) micrographs were taken to identify the phase of the grains, as Y$_2$Si$_2$O$_7$ exhibits numerous polymorphs. Figure S2 shows phase images for each of the three regions, which are mainly composed of the $\beta$ polymorph of Y$_2$Si$_2$O$_7$. We note that the $\gamma$ phase of the disilicate is present in region I, however we do not include this grain in our analysis of the thermal conductivity tensor of $\beta$-Y$_2$Si$_2$O$_7$.

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2. Time-Domain Thermoreflectance Analysis

We use time-domain thermoreflectance (TDTR) to spatially monitor and determine the thermal conductivity of $\beta$-Y$_2$Si$_2$O$_7$. In our two-tint system, we spectrally separate the output of an 80 MHz Tsunami Ti:Sapphire oscillator centered at 808.5 nm into pump and probe paths. The pump path is amplitude modulated by an electro-optic modulator, and creates a frequency-dependent heating event at the surface of the sample. The probe is mechanically delayed in time, and monitors the thermoreflectance at the sample surface due to the pump heating event. We fix the modulation of the pump to 8.4 MHz, which allows us to maintain one-dimensionality in our analysis at the spot sizes used in this study. We fit the TDTR scan to the radially symmetric heat diffusion equation assuming the parameters shown in Table S1. The thermal conductivity of the Al transducer is determined by applying the Wiedemann-Franz Law to electrical resistivity measurements made via four-point probe measurements on a reference sample placed in the aluminum deposition at the same time as the samples of interest. The room temperature heat capacity values for aluminum are taken from the literature. The thickness is extracted from the picosecond acoustics response at short time scales, shown in Fig. S3(a). Points are chosen assuming an interfacial layer with that of low stiffness, according to Hohensee et al.; the acoustic response is uncharacteristic of what is typically observed at a metal/nonmetal interface. The heat capacity of fully dense $\beta$-Y$_2$Si$_2$O$_7$ is taken to be $2.14 \pm 0.12$ MJ m$^{-3}$ K$^{-1}$ based on values found in the literature. From archimedes density tests we find that our sample is 90% dense,
and adjust the volumetric heat capacity used in our analysis accordingly. A representative TDTR curve can be seen in the inset of Fig. S3(a), where we fit for the thermal conductivity of $\beta$-$Y_2Si_2O_7$ and the conductance at the Al/$\beta$-$Y_2Si_2O_7$ interface.

In order to perform high throughput thermal conductivity mapping, the delay time is fixed depending on the thermal boundary conductance at the Al/$\beta$-$Y_2Si_2O_7$ interface. We choose the pump-probe delay time such that the sensitivity to this conductance is near zero, and correlate the ratio at a single delay time to the thermal conductivity in

<table>
<thead>
<tr>
<th>Layer</th>
<th>Volumetric Heat Capacity (MJ m$^{-3}$ K$^{-1}$)</th>
<th>Thermal Conductivity (W m$^{-1}$ K$^{-1}$)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al Transducer</td>
<td>2.42</td>
<td>111 ± 7</td>
<td>82 ± 2</td>
</tr>
<tr>
<td>$\beta$-$Y_2Si_2O_7$</td>
<td>1.92 ± 0.1</td>
<td></td>
<td>F</td>
</tr>
</tbody>
</table>

Table S1: Parameters for TDTR analysis. The effective pump/probe radii is 1.6 µm with an uncertainty 0.08 µm, while the thermal boundary conductance at the Al/disilicate interface is dependent on the region probed, as described in the text. The fitting parameter of interest is designated by F.
Figure S3: (a) Representative short- and long-time thermoreflectance signals from a region II grain. The arrows denote points which were used to extract the thickness of the Al transducer, while the inset shows the data and best fit used to obtain baseline thermal properties. (b) Sensitivity analysis corresponding to the thermal fitting curve from (a). A delay time is chosen such that sensitivity to the thermal boundary conductance is near zero, occurring at \( \sim 350 \) ps, in order to maximize our sensitivity to the cross-plane thermal conductivity. The remaining variables are known and uncertainty in these values is propagated into the error analysis as shown in the values in Table S2. (c) Thermal conductivity correlation curve, showing the relation between the extracted ratio signal \((-V_{\text{in}}/V_{\text{out}})\) and thermal conductivity in black for \( G_1 = 43 \) MW m\(^{-2}\) K\(^{-1}\). Included in gray are variations in the correlation curve when accounting for a 25% variation in \( G_1 \), order to extract the thermal conductivity. Sensitivity curves are shown in Fig. S3(b) for a spot in Region II. The sensitivity of the ratio is defined as \[ S_\alpha = \frac{\partial \ln(-V_{\text{in}}/V_{\text{out}})}{\partial \ln(\alpha)}, \] (S1) where \( S_\alpha \) is the sensitivity to the parameter \( \alpha \). We compute the sensitivity of our model to the thickness of the aluminum \((d_1)\), the boundary conductance between the aluminum and \( \beta-Y_2Si_2O_7 \) \((G_1)\), the in-plane \((\kappa_{2,//})\) and cross-plane \((\kappa_{2,\perp})\) thermal conductivity of the \( \beta-Y_2Si_2O_7 \) relative to the measurement orientation, the heat capacity of the \( \beta-Y_2Si_2O_7 \) \((C_2)\), and the effective pump/probe radius, \( r_{\text{eff}} \). For regions I, II, and III, the measured conductances are 43 \( \pm \) 2, 56 \( \pm \) 3, and 41 \( \pm \) 3 MW m\(^{-2}\) K\(^{-1}\), respectively. Thus, the sensitivity where \( G_1 \) is near zero for regions I, II, and III correlates to \( \sim 350 \), \( \sim 180 \), and \( \sim 460 \) ps, respectively. This is specifically shown in Fig. S3(b) for region II, where \( G_1 \) crosses zero sensitivity at \( \sim 350 \) ps. These are the pump-probe delay times that we choose for each of the thermal conductivity micrographs associated with those regions such that changes in the measured ratio signal are indicative primarily of changes in thermal conductivity, not the conductance at the
Figure S4: Relative sensitivity of the cross-plane thermal conductivity ($\kappa_\perp$) to the in-plane thermal conductivity ($\kappa_{//}$) of our system for a range of conductivity pairs. The contour line is drawn for $\kappa_\perp/\kappa_{//} = 10$.

Al/$\beta$-Y$_3$Si$_2$O$_7$ interface. This is visually represented in the thermal conductivity correlation curve, shown in Fig. S3(c). The black line correlates the extracted ratio from the experiment to the thermal conductivity of the disilicate. The bounds for varying the thermal conductance by $\pm$ 25% are shown in grey, and indicate that even moderate perturbations of $G_1$ do not significantly impact our extracted thermal conductivity. The relative sensitivity of $\kappa_\perp$ to $\kappa_{//}$ of the substrate are shown in Fig. S4 for thermal conductivities ranging from 1-2000 W m$^{-1}$ K$^{-1}$. In the event that the $\kappa_{//}$ is very high, extraction of $\kappa_\perp$ becomes more difficult as the sensitivity to $\kappa_\perp$ is thwarted by that of $\kappa_{//}$.

All thermal conductivity images used to extract the thermal conductivity of particular grains were taken with a step size of 0.25 $\mu$m, unless otherwise specified. We further selectively analyze regions where the probe auxiliary signal, subtracted from the reference beam in our balanced photodetector scheme, is $\leq 0.03$ V. This is done to identify areas on the sample surface that are specularly reflecting the probe beam which are indicative of areas that do not have small artifacts such as stray dust or debris that would diffusely scatter incoming light. The details of the thermal map analysis are shown in Figs. S5-S7 along side SEM micrographs for reference.
Figure S5: Thermal conductivity analysis of the grain present in region I. The SEM micrograph in (a) shows the region comprising the grain of interest. The subtracted auxiliary signal (b), thermal conductivity map (c), and error in thermal conductivity (d) micrographs are shown for grain A. Grain A is labeled in (b) along with its thermal conductivity distribution in (f). In (b)-(d), the step size is 0.25 µm, and the scale bars in (a)-(d) are 5 µm. 

\[ \kappa = 5.1 \pm 0.7 \text{ W m}^{-1} \text{K}^{-1} \]
Figure S6: Thermal conductivity analysis of grains present in region II. The SEM micrograph of the region comprising grains B-I is shown in (a) along with the coarse thermal conductivity map (b) with step size of 0.5 µm. The scale bar in both is 5 µm. The subtracted auxiliary signal (c), thermal conductivity map (d), and error in thermal conductivity (e) micrographs are shown for grains B-I. Grains B-I are labeled in (c), and their thermal conductivity distributions are shown in (f). In (c)-(e), the step size is 0.25 µm, and the scale bar is 4 µm.
Figure S7: Thermal conductivity analysis of grains present in region III. The SEM micrograph of the region comprising grains J-N is shown in (a). The subtracted auxiliary signal (b), thermal conductivity map (c), and error in thermal conductivity (d) micrographs are shown for grains J-N. Grains J-N are labeled in (b), and their thermal conductivity distributions are shown in (e). In (b)-(d), the step size is 0.25 µm, and the scale bar in (a)-(d) is 5 µm.
Figure S8: Knife edge measurements for the (a) x- and (b) y-dimensions of the probe. Dimensions are labeled as $r_x$ and $r_y$ for the radius in the x- and y-dimensions, respectively.

We use the convention of Wei et al. [7] for the determination of the uncertainty in our measured thermal conductivities. Specifically, we employ this analysis with errors of 5% in the pump/probe radii, 7% in the thermal conductivity of the Al transducer, 2.5% in the thickness of the Al transducer, 5% in the boundary conductance at the Al/disilicate interface, and 5% in the volumetric heat capacity of the disilicate. At this modulation frequency, we take into account an error in the phase of 0.2 mrad. Our most sensitive parameter is that of the pump/probe radii. While we fit for the effective pump/probe radii in our initial analysis, we also perform knife edge measurements in a reflection configuration to extract the radius of the probe. Measurements are shown in Fig. S8 where the measured probe dimensions are 0.96 x 0.92 $\mu$m in radius. An uncertainty of 5% is obtained from multiple measurements along various regions of our photolithographically fabricated knife-edge sample. This yields an effective pump radius of 1.29 $\mu$m. The final uncertainty at each point in the thermal conductivity map is determined via the equation

$$
\left( \frac{\delta_\kappa}{\kappa} \right)^2 = \left( R \frac{\delta_\phi}{S_\kappa} \right)^2 + \sum \left( \frac{S_\alpha}{S_\kappa} \frac{\delta_\alpha}{\alpha} \right)^2.
$$

(S2)
Table S2: Mapping region, grain identifier, thermal conductivity calculated from Eq. S8 and the derived tensor components from the main text ($\kappa_{\text{theory}}$), mean thermal conductivity from measurements ($\kappa_{\text{mean}}$), error in thermal conductivity due to spatial variations ($\delta \kappa_{\text{spatial}}$), error in thermal conductivity calculated via Eq. S2 ($\delta \kappa_{\text{calculated}}$), and total error in thermal conductivity ($\delta \kappa_{\text{total}}$).

In this equation, the final uncertainty in thermal conductivity $\delta \kappa$ is dependent on the sensitivity to thermal conductivity $S_{\kappa}$ and additional parameters described previously as $S_{\alpha}$. We take the error in phase as $R \frac{\delta \phi}{S_{\kappa}}$, where $R$ is the ratio signal in the map. We add this uncertainty with the distribution of thermal conductivities measured for each grain in quadrature to report the final uncertainty. A summary of the mean thermal conductivities, $\kappa_{\text{mean}}$, and standard deviation of the distribution extracted from the selected region of each grain, $\delta \kappa_{\text{spatial}}$, are shown in Table S2. Also shown in the Table are the error in thermal conductivities calculated via Eq. S2 ($\delta \kappa_{\text{calculated}}$). The final uncertainty is calculated via the square root of the sum of the squares of $\delta \kappa_{\text{spatial}}$ and $\delta \kappa_{\text{calculated}}$ (i.e., $\delta \kappa_{\text{total}} = \sqrt{\delta \kappa_{\text{spatial}}^2 + \delta \kappa_{\text{calculated}}^2}$).

Shown in Fig. S9 are numerical calculations to the radially symmetric heat diffusion equation for both the in- and cross-plane thermal penetration depths [8]. At low modulation frequencies, the cross-plane thermal penetration depth approximately follows the $1/e^2$ pump radius, while the in-plane thermal penetration depth is enhanced due to heat spreading in the Al transducer. At high modulation frequencies, the cross-
Figure S9: Numerically calculated in- and cross-plane 1/e thermal penetration depths for Al/β-Y₂Si₂O₇ crystallite. The dashed lines correspond to Eq. S3 when calculated using properties of the Al transducer and β-Y₂Si₂O₇ crystallite.

The in-plane thermal penetration depth approaches the commonly accepted equation for thermal penetration

$$\sqrt{\frac{\kappa}{\pi C f}},$$

(S3)

where \( f \) is the modulation frequency and \( \kappa \) and \( C \) reflect the thermal conductivity and heat capacity of β-Y₂Si₂O₇. The in-plane thermal penetration depth, on the other hand, approximately follows \( f^{-0.1} \), and deviates significantly from Eq. S3 when \( \kappa \) and \( C \) reflect the thermal conductivity and heat capacity of the Al transducer.

3. Derivation of \( \kappa(\theta, \phi) \)

For the derivation of \( \kappa(\theta, \phi) \), we explicitly derive the thermal conductivity magnitude from the direction cosines of the orientation. This derivation is not unlike that of Jaing et al. From Fourier’s law of heat conduction, the heat flux is related to the temperature gradient by the thermal conductivity:

$$q = -\vec{K} \nabla T,$$

(S4)
where $q$ is the heat flux, $T$ is the temperature distribution of the system, and $\tilde{K}$ is the thermal conductivity tensor. The thermal conductivity tensor is a second rank tensor defined as

$$
\tilde{K} = \begin{bmatrix}
\kappa_{xx} & \kappa_{xy} & \kappa_{xz} \\
\kappa_{yx} & \kappa_{yy} & \kappa_{yz} \\
\kappa_{zx} & \kappa_{zy} & \kappa_{zz}
\end{bmatrix}.
$$
\hspace{1cm} (S5)

Onsager’s principle states that each of the components of the heat flux is linearly proportional to each of the components of the temperature gradient [10], implying $\kappa_{ij} = \kappa_{ji}$ must be true to satisfy these relations. The appearance of these off-diagonal terms in this tensor depend on the symmetry of the crystal. Only in triclinic systems are all the off-diagonal terms maintained, while just $\kappa_{xz}$ is maintained in a monoclinic system.

For systems of higher symmetry, only the diagonal elements are present in the system. The thermal conductivity tensor components are aligned with that of the cartesian coordinate system, where $\kappa_{xx}$, $\kappa_{yy}$, and $\kappa_{zz}$ relate the heat flux and temperature gradient in the $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions, respectively. The off-diagonal terms relate the heat flux and temperature gradient in orthogonal directions, i.e., $\kappa_{xz}$ relates the heat flux in the $\hat{x}$ direction to the temperature gradient in the $\hat{z}$ direction, and vice-versa.

In Einstein notation, the magnitude of the thermal conductivity in a given direction is [10]

$$
\kappa(\theta, \phi) = K_{ij} l_i l_j,
$$
\hspace{1cm} (S6)

where $l_1$, $l_2$, and $l_3$ are the direction cosines. For a unit vector in spherical coordinates, with $\theta$ the azimuthal angle and $\phi$ the polar angle, the direction cosines are the following:

$$
l_1 = \sin \phi \cos \theta
\hspace{1cm} l_2 = \sin \phi \sin \theta
\hspace{1cm} l_3 = \cos \phi.
$$
\hspace{1cm} (S7)

Evaluating Eq. (S6) assuming a thermal conductivity tensor in which all terms are non-zero, the angular dependence of thermal conductivity can be expressed as:

$$
\kappa(\theta, \phi) = \kappa_{xx} \sin^2 \phi \cos^2 \theta + \kappa_{yy} \sin^2 \phi \sin^2 \theta + \kappa_{zz} \cos^2 \phi + 2\kappa_{xy} \sin^2 \phi \cos \theta \sin \theta + 2\kappa_{xz} \sin \phi \cos \theta \cos \phi + 2\kappa_{yz} \sin \phi \sin \theta \cos \phi.
$$
\hspace{1cm} (S8)
We note that this result is identical to that of Jiang et al. [9]. An effective thermal conductivity can be defined as \( \kappa_{\text{eff}} = \sqrt[3]{\det(\mathbf{K})} \), where the cube root arises due to the rank of the tensor.

4. Debye Velocity Calculation

To calculate the directional-dependence of the Debye velocity, we solve the Christoffel equation assuming literature values for the elastic constants of \( \beta\text{-Y}_2\text{Si}_2\text{O}_7 \). The elastic tensor is taken from Luo et al. [11], and in Voigt notation, takes the form

\[
C_{ijnm} = \begin{bmatrix}
303 & 119 & 131 & 0 & -24 & 0 \\
119 & 207 & 109 & 0 & 42 & 0 \\
131 & 109 & 203 & 0 & -9 & 0 \\
0 & 0 & 0 & 71 & 0 & 31 \\
-24 & 42 & -9 & 0 & 105 & 0 \\
0 & 0 & 0 & 31 & 0 & 72
\end{bmatrix} \text{ GPa.}
\] (S9)

The Christoffel matrix is further defined by

\[
\Gamma_{ij} = q_n C_{inmj} q_m,
\] (S10)

where \( q \) is a vector with components that are the direction cosines. The product of the density and square of the phase velocity (i.e., \( \rho v^2_p \), where \( \rho \) is the density and \( v_p \) is the phase velocity) for a given \( q \) can be further defined by solving for the eigenvalues of \( \Gamma_{ij} \). We use the code from Jaeken et al. [12] to further extract the directional-dependence of the group velocity, assuming a theoretical density of 4.04 g cm\(^{-3}\). The Debye velocity, \( v_D \), is then calculated via

\[
\frac{3}{v_D^2} = \frac{1}{v_l^2} + \frac{1}{v_{t,1}^2} + \frac{1}{v_{t,2}^2},
\] (S11)

where \( v_l \) is the longitudinal component and \( v_{t,1} \) and \( v_{t,2} \) are the two transverse components of the speed.

5. Orientation Images of \( \beta\text{-Y}_2\text{Si}_2\text{O}_7 \)

Orientational images of the monoclinic crystal structure of \( \beta\text{-Y}_2\text{Si}_2\text{O}_7 \) can be found in Fig. S10. \( \beta\text{-Y}_2\text{Si}_2\text{O}_7 \) consists of \( \text{SiO}_4 \) tetrahedra and \( \text{YO}_6 \) polyhedra arranged into
Figure S10: Plan-view orientation images of the monoclinic crystal of $\beta$-Y$_2$Si$_2$O$_7$ in the (a) (100), (b) (010), and (c) (001) planes. Y, Si, and O are represented by green, blue, and red atoms, respectively, while the YO$_6$ polyhedra and SiO$_4$ tetrahedra are designated as green polyhedra and blue tetrahedra, respectively.

a layered-like structure. The [100] and [010] directions are similar in structure, less for the additional O shared between two SiO$_4$ tetrahedra in the [100] direction, while the structure along the [001] direction departs significantly from those of the [100] and [010] directions.


[5] Z. Tian, L. Zheng, Z. Li, J. Li, J. Wang, Exploration of the low thermal con-
ductivities of $\gamma$-$Y_2Si_2O_7$, $\beta$-$Y_2Si_2O_7$, $\beta$-Yb$^2$Si$_2$O$_7$, and $\beta$-Lu$^2$Si$_2$O$_7$ as novel environmental barrier coating candidates, Journal of the European Ceramic Society 36 (2016) 2813–2823.


