Unusual high thermal conductivity in boron arsenide bulk crystals


†Department of Physics and the Texas Center for Superconductivity, University of Houston, Houston, TX 77204, USA. ‡Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA. §Materials Science and Engineering Program, Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA. ‡Department of Physics, Boston College, Chestnut Hill, MA 02467, USA. ¶Department of Physics, University of Illinois Urbana-Champaign, Urbana, IL 61801, USA. ¶¶Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, USA. ․Department of Mechanical Engineering, University of Houston, Houston, TX 77204, USA. †Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. ††Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, IL 61801, USA.
*These authors contributed equally to this work.
††Corresponding author. Email: david.broido@bc.edu (D.B.); lishi@mail.utexas.edu (L.S.); gchen2@mit.edu (G.C.); zren@uh.edu (Z.R.)

Conventional theory predicts that ultrahigh lattice thermal conductivity can only occur in crystals composed of strongly-bonded light elements, and that it is limited by anharmonic three-phonon processes. We report experimental evidence that is a departure from these long-held criteria. We measured a local room-temperature thermal conductivity exceeding 1000 W m⁻¹ K⁻¹ and an average bulk value reaching 900 W m⁻¹ K⁻¹ in bulk boron arsenide (BAs) crystals, where boron and arsenic are light and heavy elements, respectively. The high values are consistent with a proposal for phonon band engineering and can only be explained with higher order phonon processes. These findings yield new insight into the physics of heat conduction in solids and show BAs to be the first known semiconductor with ultrahigh thermal conductivity.

Materials with high thermal conductivity (κ) can help to address a range of great technological challenges, such as removing the high-density heat generated in nanoelectronic devices to keep them cool. At room temperature (RT), diamond and graphite, the two carbon allotrope bulk crystals, have a record high κ of about 2000 W m⁻¹ K⁻¹ (1–4). However, high quality natural diamond is scarce and expensive. While future technological advance may help to alleviate the cost of high-quality synthetic diamond, the large mismatch in the coefficient of thermal expansion between diamond and common semiconductors can introduce large thermal stresses. Meanwhile, the κ of graphite is highly anisotropic with the cross-plane value being two orders of magnitude smaller than the corresponding in-plane value (1). The thermal anisotropy and the weak interlayer bonding have limited the use of graphite for thermal management. In addition, the electrically insulating property of diamond and semi-metallic behavior of graphite prevent their use as active electronic materials. Common electronic materials such as copper and silicon have a RT κ of about 400 W m⁻¹ K⁻¹ and 150 W m⁻¹ K⁻¹, respectively (1), which are well below the diamond value. The highest measured RT κ values for semiconductors are about 490 W m⁻¹ K⁻¹ in silicon carbide (5) and 460 W m⁻¹ K⁻¹ in boron phosphide (6). Although these values are comparable to the highest electronic contribution to κ in metals, it is desirable to discover semiconductors with κ comparable to the ultrahigh value for diamond.

In semiconductors and non-magnetic insulators, the thermal conductivity is dominated by the phonon contribution. Thermal conductivity is typically limited by the lowest-order process arising from the anharmonicity of the interatomic potential, three-phonon scattering, at and above RT (7). According to the criteria established by Slack about half century ago (2), only crystals composed of strongly-bonded light elements would exhibit ultrahigh κ. However, Lindsay, Broido, and Reinecke recently proposed that ultrahigh κ could be achieved in compounds that combine a light and a heavy atom if (i) the frequency gap between heat-carrying acoustic phonons and optic phonons was sufficiently large, and (ii) some of the acoustic phonons with different polarizations had regions of similar frequencies away from the Brillouin zone center. First principles calculations supported this phonon band engineering concept in predicting that cubic boron arsenide (BAs) should have a RT κ of around 2000 W m⁻¹ K⁻¹.
when only three-phonon interaction is considered \((8, 9)\). Subsequent theoretical calculations found that four-phonon scattering lowered the calculated RT \(\kappa\) in BAs to about 1400 W m\(^{-1}\) K\(^{-1}\) \((10)\), which is still exceptionally high but surprising since three-phonon scattering accurately describes the measured \(\kappa\) data for many semiconductors and insulators, and higher-order processes are expected to be weak at RT.

Synthesis of high-quality BAs bulk crystals has proved challenging, which has prevented experimental verification of the unusual predicted transport properties. Several measurements attained RT \(\kappa\) values of only 200-350 W m\(^{-1}\) K\(^{-1}\) in small BAs particles \((11–13)\). The inability to measure an ultrahigh \(\kappa\) for BAs limited adoption of the phonon band engineering strategy as a viable new route for achieving ultrahigh \(\kappa\), and the possibility of higher order processes suppressing \(\kappa\) remained.

We report experimental evidence that clearly validates the phonon band engineering route. We grew BAs bulk crystals from seed microparticles in a chemical vapor transport (CVT) process. Local measurements of low-defect particles obtained a RT \(\kappa\) that exceeds 1000 W m\(^{-1}\) K\(^{-1}\), while multiple local and bulk transport measurement methods yielded average RT \(\kappa\) values of about 800 and 900 W m\(^{-1}\) K\(^{-1}\) for two bulk crystal samples. The bulk crystal has a high \(\kappa\) despite twin boundaries and other defects known to decrease \(\kappa\). Both the peak and average \(\kappa\) values show a rapid decrease with increasing temperature, which is a clear signature of lattice anharmonicity. This behavior agrees with our detailed first principles theoretical model that included both three- and four-phonon interactions.

Previously reported synthesis efforts of BAs yielded only particles with the maximum dimension less than about 500 \(\mu\)m \((11–13)\). As bulk-size crystals are required for device applications, we investigated a seeded CVT growth mechanism for the synthesis of bulk BAs crystals. In this approach, we used small single BAs crystals with a lateral dimension of a few micrometers as seeds to ensure the nucleation centers were sparse and under control during the growth process \((13, 14)\). We optimized seed crystal quality and distribution to obtain BAs crystals as large as about 4\(\times\)2\(\times\)1 mm\(^3\) within a 14-day seed growth followed by another 14-day crystal growth from the chosen seed crystals \((15)\). This large crystal size allowed us to use transport measurement techniques established for bulk samples. Increasing the growth time will increase the crystal size. To probe the crystal structure of the BAs, we obtained an aberration-corrected, annular dark-field scanning transmission electron microscopy (STEM) image (Fig. 1A) and a low-magnification bright-field TEM image (Fig. 1B) of representative BAs crystals. We found planar defects (Fig. 1B) that are mirror twin boundaries (Fig. 1, C to E).

We discovered unusually high but non-uniformly distributed \(\kappa\) in these BAs crystals using time and frequency domain thermoelectricity (TDTR and FDTR, respectively) techniques with micrometer resolutions \((16–18)\). We used a large 58-\(\mu\)m-diameter pump laser spot and a small 9-\(\mu\)m-diameter probe laser spot in conjunction with a relatively low modulation frequency of 3 MHz to improve the TDTR measurement accuracy \((15)\). The diameter quoted here is the \(1/e^2\) diameter of the Gaussian beam. We used the same TDTR platform and parameters to measure the \(\kappa\) of a synthetic diamond crystal (Figs. 2A and 3). The values we measured for diamond are in good agreement with theoretical calculations and literature values \((1–4)\). Among the single-spot measurements at five locations of BAs Sample #1, the highest and lowest RT \(\kappa\) values were 1160 ± 130 and 640 ± 70 W m\(^{-1}\) K\(^{-1}\), respectively. Among the ten single-spot TDTR measurements on Sample #2, we found the RT \(\kappa\) value ranges from 790 ± 100 to 450 ± 60 W m\(^{-1}\) K\(^{-1}\). We found a sharp decrease in \(\kappa\) as temperature increased to 500 K at the location on Sample #1 where we found our maximum \(\kappa\) for BAs (Fig. 3). We found the same behavior on a location of Sample #2 with a RT \(\kappa = 740 \pm 110\) W m\(^{-1}\) K\(^{-1}\) (Fig. 3). This temperature behavior is consistent with dominant anharmonic phonon-phonon scattering. At the same Sample #1 spot where our TDTR measurements found the highest \(\kappa\), our single-spot FDTR measurements obtained 1310 ± 740 W m\(^{-1}\) K\(^{-1}\), where the large uncertainty is due to the use of a small 3.36-\(\mu\)m-diameter pump beam and 2.60-\(\mu\)m-diameter probe spot to measure the high \(\kappa\) region \((19)\). We observed no spot-size dependence of \(\kappa\) when we increased the pump and probe laser spot sizes to 5.60 \(\mu\)m and 4.80 \(\mu\)m, respectively.

The large size of the bulk BAs crystals allows us to make steady-state comparative measurements of the bulk \(\kappa\) (Fig. 4A) \((15)\). Without accounting for the contact thermal resistance errors between the thermocouples and the sample, we obtained a \(\kappa\) of 770 ± 100 W m\(^{-1}\) K\(^{-1}\) at 305 K on a 0.1x0.2x0.2 mm bar cut from Sample #3. The thermal conductivity increased with deceasing temperature. In comparison, we obtained an average value of 820 ± 140 W m\(^{-1}\) K\(^{-1}\) with FDTR at 14 locations on another piece cut from Sample #3 (Fig. 3). We addressed the uncertainty due to contact resistance using a unique lock-in Raman thermometry approach with sinusoidally-modulated heating current at a low modulation frequency (\(\omega\)) of about 1 mHz \((15)\). A fast Fourier transform (FFT) of the measured Raman peak shift shows clear modulation at the second harmonic frequency corresponding to the Joule heating frequency (Fig. 4B), which we used to measure the temperature drops along the Si and BAs bars (Fig. 4A). The Raman measurements obtain similar temperature gradients in both silicon and BAs as for the thermocouple measurements (Fig. 4C), and a \(\kappa\) of 690 ± 120 W m\(^{-1}\) K\(^{-1}\) at 338 K (Fig. 3). On Sample #4 (15, fig. S19B) and #5 (Fig. 3), we used the steady state method to measure a bulk \(\kappa\) of 920 ± 120 W m\(^{-1}\) K\(^{-1}\) and 570 ± 70 W m\(^{-1}\) K\(^{-1}\) at 300 K, respectively, and similar
temperature dependence as for Sample #1-3.

The measurement results agree with first principles calculations of the κ of BAs including both three- and four-phonon scattering, scattering of phonons by the natural boron isotope mix, and phonon scattering by point defects and grain boundaries. While κ of most high-quality insulating crystals is well described by lowest-order three-phonon scattering, in BAs the phase space for three-phonon scattering is unusually small (8). We show that four-phonon scattering is necessary to accurately capture the intrinsic κ of BAs (10). In comparison to the calculation of Feng et al. (10), we implemented several changes in our calculation to improve the accuracy (15). In addition, we found hole scattering of phonons to be negligible at a hole concentration of $7.6 \times 10^{18}$ cm$^{-3}$ that we measured in the p-type BAs semiconductor sample (15).

Our calculated BAs κ at 300 K including three-phonon, four-phonon and phonon-isotope scattering is 1260 W m$^{-1}$ K$^{-1}$, about half that obtained without four-phonon scattering (2330 W m$^{-1}$ K$^{-1}$), and about 10% smaller than Feng et al. (10) obtained. The BAs κ we calculated including only three-phonon and phonon-isotope scattering, $\kappa_3$ (dashed black curve, Fig. 3) lies well above all measured data. Including also four-phonon scattering, $\kappa_{3+4}$ (solid black curve) suppresses κ and brings the calculation close to the measured local high TDTR values (solid red circles). It also provides a strong T-dependence, as previously found (10). Importantly, the TDTR temperature behavior follows the T-dependence of $\kappa_{3+4}$, which is stronger than that of κ. We fit the steady-state and TDTR data by including additional scattering from assumed point defects and grain boundaries (Fig. 3) (15). Defect scattering mechanisms are typically much less sensitive to temperature change than phonon-phonon scattering, so increasing defect scattering to match the measured room-temperature value weakens the T-dependence of κ. The large defect concentrations needed to match the magnitudes of the measured data when including only three-phonon scattering cannot produce the steep observed T-dependence (15, figs. S30 and S31). In contrast, the best fit of $\kappa_{3+4}$ is excellent for the steady state data (15, fig. S19B) and reasonably good for the TDTR data.

The comparison between the measurements and theoretical calculations provides strong evidence that BAs is unique compared to other known high κ materials in achieving κ through the phonon band engineering concept and in having higher-order phonon-phonon interactions play such a large role. By breaking the conventional theoretical criteria, these findings have firmly established a different route to ultrahigh κ and highlighted the rich physics of phonons. Our strategy for growth of bulk BAs crystal is an important step toward implementation in future applications of BAs, which is now the only known semiconductor with a bandgap (20) comparable to silicon and an ultrahigh room-temperature thermal conductivity.

REFERENCES AND NOTES


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SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S33

References (23–30)

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**Fig. 1. STEM measurements of BAs.**
(A) Annular dark-field STEM image within one grain of BAs, looking down the [110] zone axis. (B) Low-magnification bright-field TEM image near the surface of the BAs crystal. Horizontal lines indicate the locations of mirror twin boundaries. (C) Annular dark-field STEM image showing the atomic structure of the mirror twin boundary from the region highlighted by the red box in (B). (D) Electron diffraction pattern of BAs within a single grain. (E) Electron diffraction pattern of BAs across the grain boundary, showing the presence of the mirror twin.

**Fig. 2. TDTR and FDTR measurements.** (A) Representative TDTR phase signals and the best fitted curves for a diamond crystal acquired from Element Six and a BAs crystal at different temperatures. The diamond sample has the natural carbon abundance (1.1% 13C) and a low level of boron (< 0.05 ppm) and nitrogen (< 1 ppm) impurities. The 300 K data are averaged over 200 and 140 runs at the same location for diamond and BAs, respectively. The data for BAs at higher temperatures are averages of about 10 runs and show slightly increased noise. (B) Representative FDTR signal phase as a function of the pump modulation frequency measured on BAs crystal, diamond, sapphire, and fused silica. The phase lag between the probe and the pump increases with decreasing sample κ.
Fig. 3. Measured thermal conductivity of BAs in comparison with theoretical calculations and other crystals. Calculated $\kappa$ versus temperature for BAs (black) and diamond (green) including only three-phonon scattering (dashed lines) and both three- and four-phonon scattering (solid lines). Measured $\kappa$ for diamond by TDTR (green diamonds). Measured $\kappa$ for BAs Sample #1 (solid red symbols) and #2 (open red symbols) by TDTR. Sample #3 by FDTR (solid orange star for mean value), steady-state (open blue squares) and lock-in Raman (open brown square) methods, and Sample #5 by the steady-state method (solid blue squares). Also shown are the fits to measured steady-state and TDTR $\kappa$ for BAs (blue and red solid lines, respectively), and reported measured $\kappa$ for GaN (21) and GaAs (22) (magenta and purple triangles, respectively). The error bars for the TDTR and FDTR data represent one standard deviation and were obtained via Monte Carlo simulations and derivative matrix-based analysis of uncertainty propagation, respectively (15). The error bars for the steady state and lock-in Raman measurement results were calculated by propagating random errors at 95% confidence and systematic errors (15).

Fig. 4. Steady-state comparative and lock-in Raman thermometry measurements. (A) Temperature modulation amplitudes ($\Delta T$) measured by the Raman thermometry at two locations on the Si and two locations on the BAs bar. The lines are linear fitting to the measurement data. The inset shows the schematic diagram of the experimental set-up for thermocouple (TC) and Raman measurements. (B) Amplitude spectrum of the measured Raman peak modulation for BAs at location $x = 3.38$ mm (1) and $x = 4.39$ mm (2). The curve for $x = 4.39$ mm is shifted manually by +0.2 along the $x$-axis so that it can be distinguished with the other curve. The inset shows the modulation of the Raman peak frequency of BAs at location $x = 3.38$ mm as a function of the cycle number during the first 6 cycles. (C) Temperature gradients on the Si and BAs bars obtained from TC and Raman measurements. The ambient temperature was 308.9 K and the heater power amplitude was 0.081 W.