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High Thermal Conductivity in Boron Arsenide Single Crystals

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Abstract
High thermal conductivity is very much desired both for understanding phonon transport and for many applications, including thermal management. Diamond has the highest isotropic thermal conductivity at room temperature among all known materials, ~2,200 W m^{-1} K^{-1}, followed by copper, silver, *etc*. at ~400 W m^{-1} K^{-1}. Discovering new materials with thermal conductivity close to or higher than that of diamond is extremely important. Over the past few years, we have found that cubic boron arsenide (c-BAs) single crystals exhibit isotropic thermal conductivity higher than 1,300 W m^{-1} K^{-1} at room temperature. In addition to its high thermal conductivity, BAs has also many other unique and beneficial properties, *e.g.*, a band gap of ~2.1 eV, wider than that of Si, and a coefficient of thermal expansion better matched with that of other semiconductors than that for diamond or cubic boron nitride.

Key Word and Phrases
Thermal Conductivity, Boron Arsenide, Single Crystal.

1. Single Crystal Growth of Boron Arsenide

In 2013, Lindsay *et al.* predicted cubic boron arsenide (c-BAs) to have thermal conductivity (*k*) of ~2,200 W m^{-1} K^{-1} at room temperature [1], which triggered a rush to synthesize single crystals of c-BAs. However, early efforts achieved only low *k* of ~200-350 W m^{-1} K^{-1}, much less than the predicted value of 2,200 W m^{-1} K^{-1}, due to a high density of defects [2], [3], as shown in Fig. 1. After modifying the growth procedure by limiting the number of nucleation sites, crystal quality was significantly improved, as shown in Fig. 2, and *k* values above 1,300 W m^{-1} K^{-1} were achieved by multiple laboratories [4]-[6]. These crystals were grown using the chemical vapor transport method [2], [3], [7]-[10]. With the introduction of nucleation sites, including a quartz bar, GaAs, *etc*., we found the crystals grow on the nucleation materials with a limited number of nucleation sites, as shown in Fig. 3 [9].

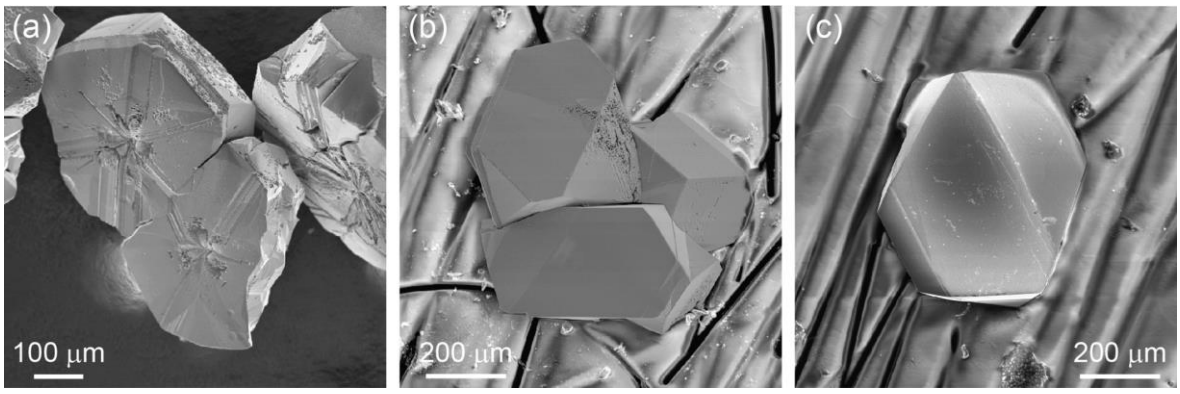

Fig. 1. c-BAs crystals. (a) Multiple crystals grown together with heavy defects, (b) single crystals with defects, and (c) single crystal with fewer defects. From reference [3].

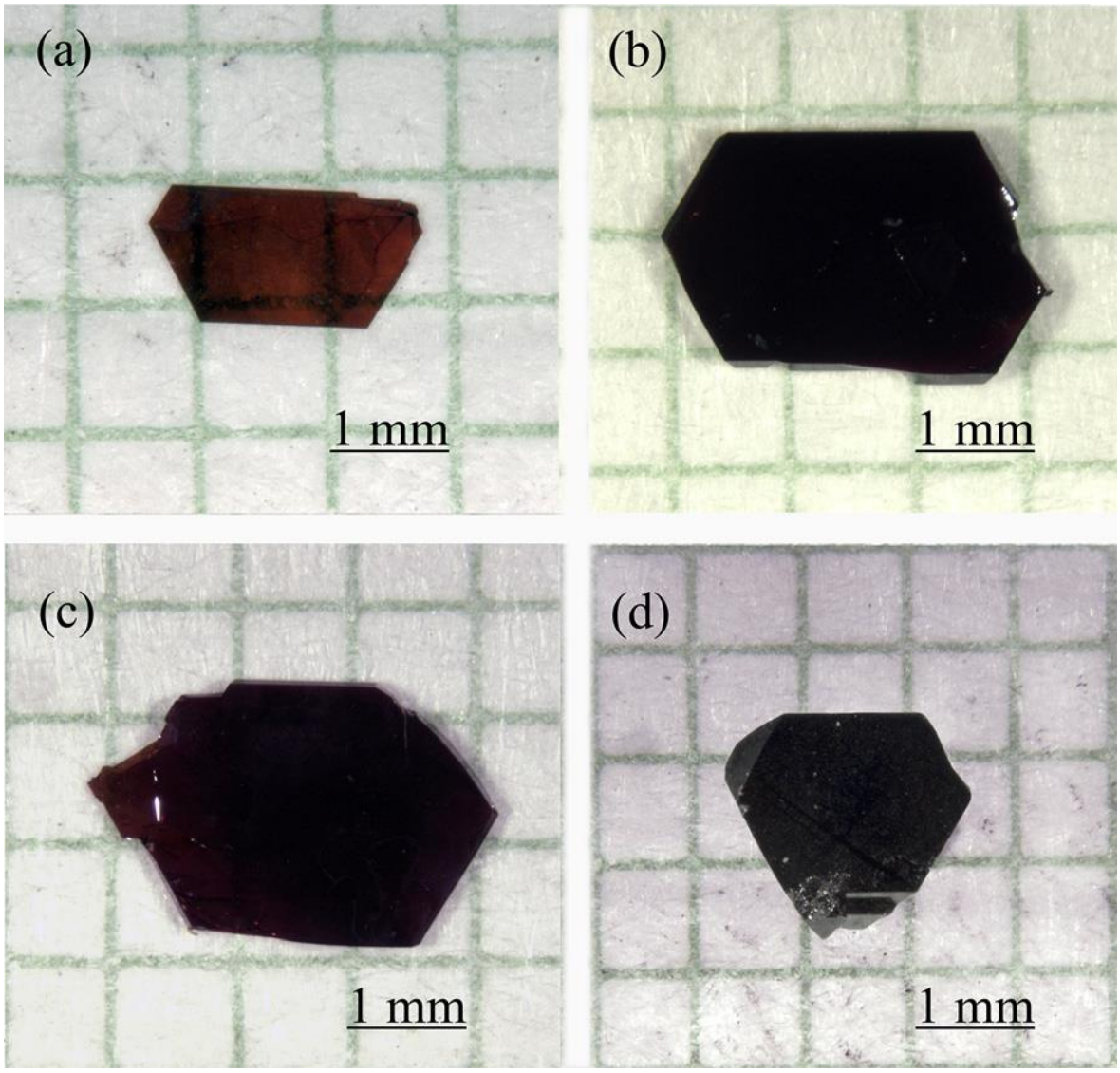

Fig. 2. Optical images of millimeter-sized c-BAs single crystals. (a) Semi-transparent crystal (reddish) and (b-d) single crystals with different shapes and thicknesses. From reference [8].

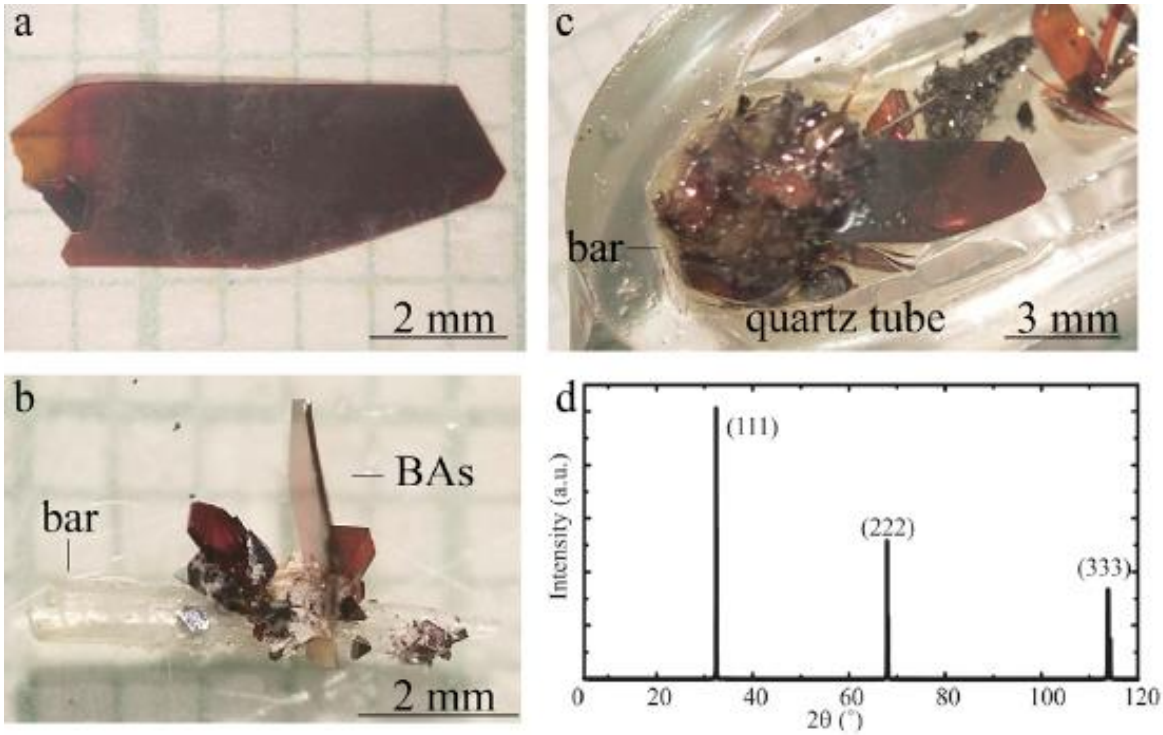

Fig. 3. Growth of BAs single crystals on a quartz bar as the nucleation site. (a) Optical image of a ~7 mm BAs single crystal, (b) optical image of the crystals grown inside the quartz tube, (c) demonstration of BAs crystals grown on a quartz bar acting as the nucleation site, and (d) XRD spectroscopy of a BAs single crystal. From reference [9].

2. Characterizations of Cubic Boron Arsenide Single Crystals

c-BAs single crystals have been extensively characterized by X-ray diffraction (XRD), as shown in Fig. 3d, Raman spectroscopy, pump-probe spectroscopy, and multiple probe transport methods. The highest thermal conductivity reported thus far is ~1,300 W m^{-1} K^{-1}, as shown in Fig. 4, in crystals still full of defects [4]-[6], [9].

Using scanning tunneling microscopy, an intrinsic band gap of about 2.1 eV was found in regions below the surface of the crystals, as shown in Fig. 5, which is likely due to an absence of defects [11].

The lattice parameter *a* of BAs was measured from room temperature to 500 °C, as shown in Fig. 6a, from which its coefficient of thermal expansion was found to be better matched with that of other semiconductors than that for diamond, cubic boron nitride (c-BN), GaAs, *etc.*, as shown in Fig. 6b [12].

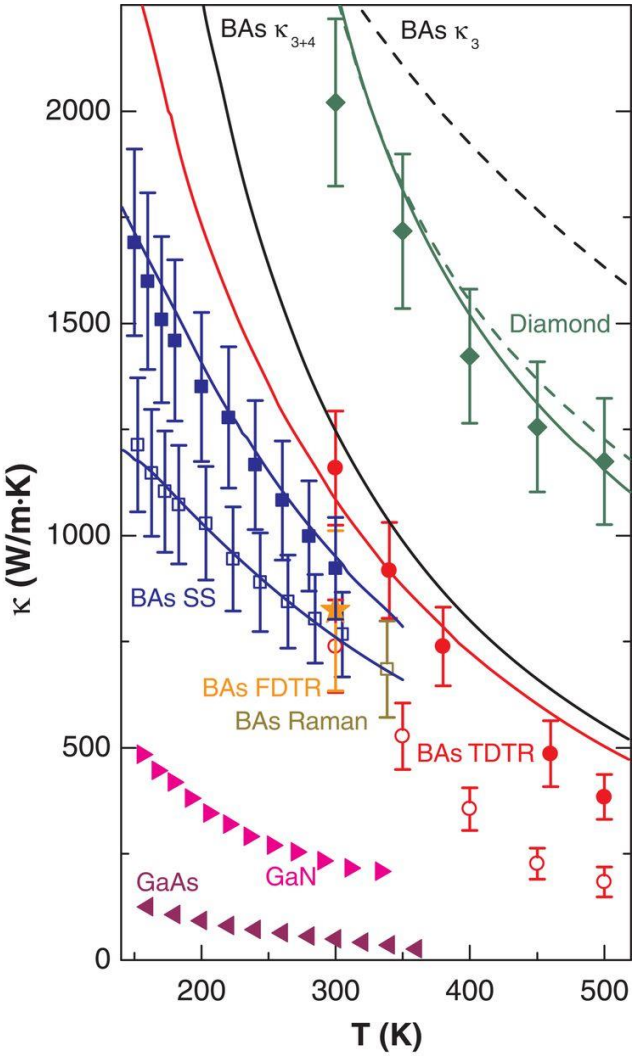

Fig. 4. Measured thermal conductivity of BAs in comparison with values from theoretical calculations and other crystals. Calculated *k vs.* temperature for BAs (black lines) and diamond (green lines) including only three-phonon scattering (dashed lines) and both three- and four-phonon scattering (solid lines); measured *k* for diamond by time-domain thermoreflectance (TDTR; green diamonds); measured *k* for BAs samples 1 (solid red symbols) and 2 (open red symbols) by TDTR; measured *k* for sample 3 by frequency-domain thermoreflectance (FDTR; solid orange star, mean value), steady-state (SS; open blue squares), and lock-in Raman (open brown square) methods; and measured k for sample 5 by the SS method (solid blue squares). Also shown are the fits to measured SS and TDTR *k* for BAs (blue and red solid lines, respectively) and reported measured *k* for GaN and GaAs (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. The error bars for the SS and lock-in Raman measurements were calculated by propagating random errors at 95% confidence and combining them with systematic errors. From reference [6].

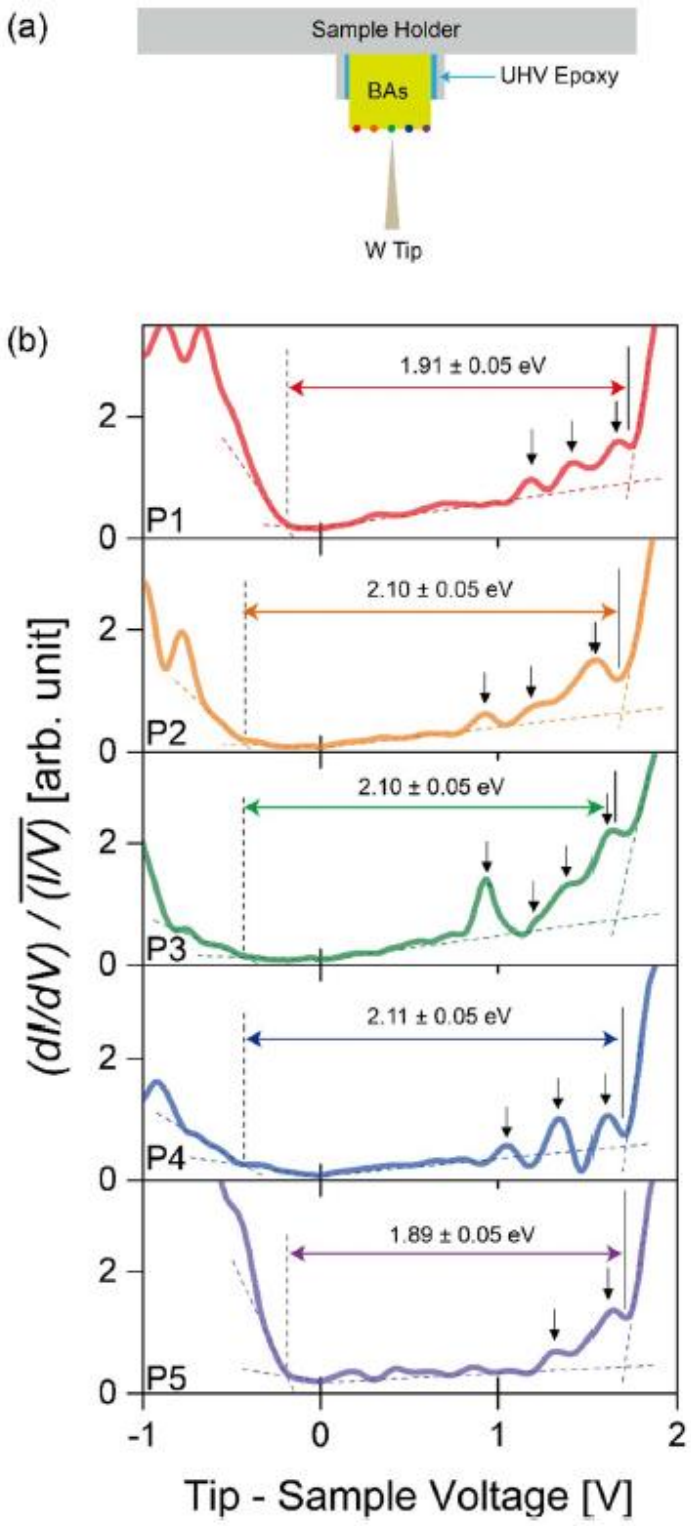

Fig. 5. Band gaps measured by scanning tunneling microscopy at different points in the BAs crystals near the surface and deep into the interior. From reference [11].

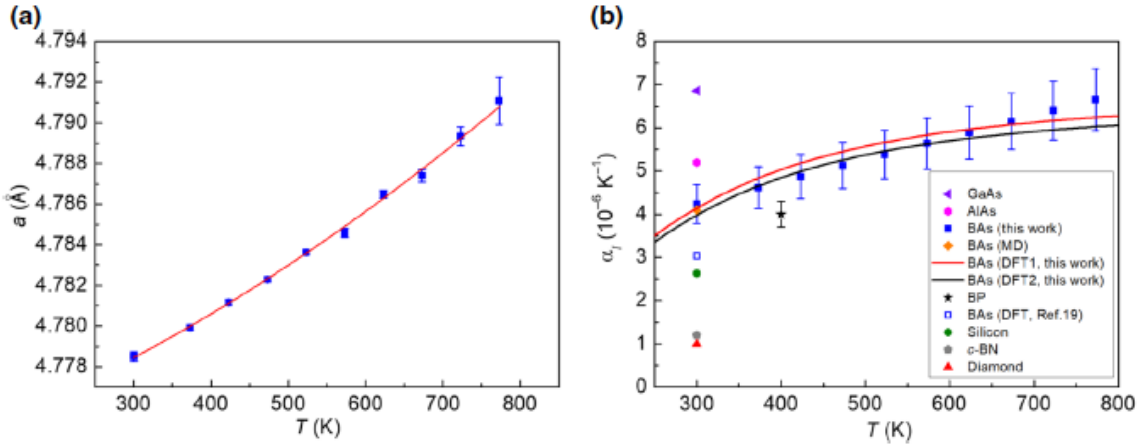

Fig. 6. Temperature dependence of (a) lattice parameter a and (b) coefficient of thermal expansion. From reference [12].

3. The Effect of Four-phonon Scattering on Thermal Conductivity

Further theoretical studies found that four phonons also play a role in phonon scattering, which reduced the predicted *k* value from 2,200 W m^{-1} K^{-1} to ~1,400 W m^{-1} K^{-1} [13].

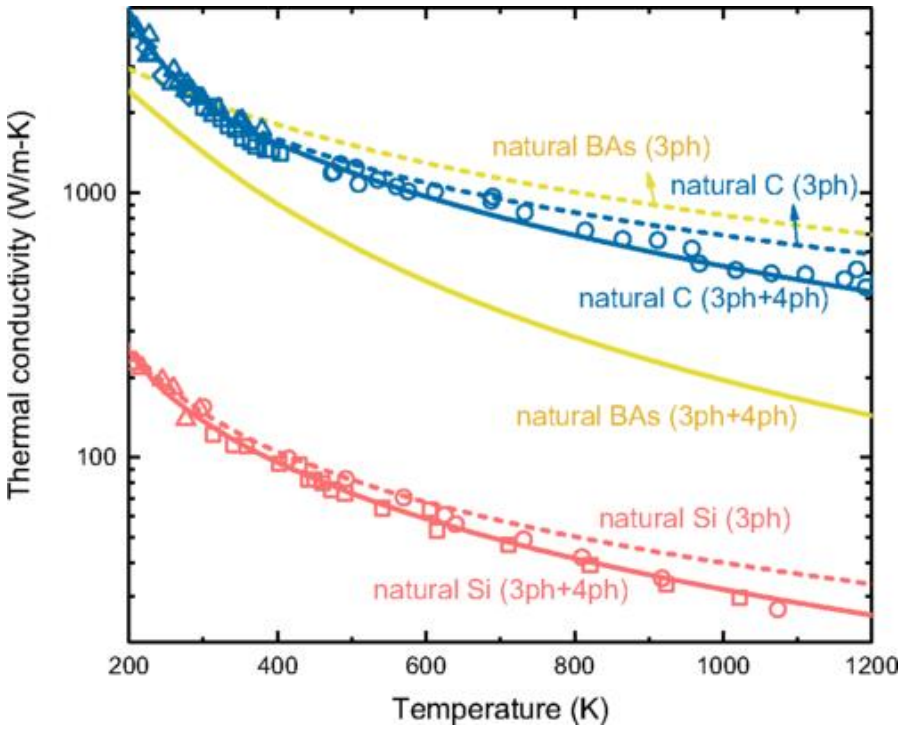

Fig. 7. Theoretically predicted and experimentally measured thermal conductivity of BAs, diamond, and Si with three-phonon and three- and four-phonon effects. From reference [13].

4. Outlook

Clearly the crystal quality of c-BAs is the most important factor for achieving high thermal conductivity in c-BAs. The formation mechanism of defects in the crystals during growth need to be fully understood so that ways can be found to fully control the defects type and concentration to achieve both p- and n-type. Only when the defects are under control at will, uniformity and scale up to industrial required size in the range of many centimeters can be accomplished. With the

uniform high quality c-BAs crystals, all the physical, chemical, mechanical, electrical, *etc*. properties will be fully understood, then full scale of applications in all possible fields will follow.

5. Conclusions

c-BAs single crystals have been successfully grown and thermal conductivity of above 1,300 W m^{-1} K^{-1} at room temperature has been achieved thus far. These crystals are clearly still highly defected. Further improvement of the crystal quality is needed to demonstrate the intrinsic high thermal conductivity. It is still hoped that *k* of ~2,000 W m^{-1} K^{-1} can be achieved in the future in high quality single crystals. BAs is, in principle, better for applications than Si due to its larger band gap and its coefficient of thermal expansion is better matched with that of other semiconductors than that for diamond and c-BN. Clearly c-BAs has great promise for future electronics.

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