



# MIT Open Access Articles

## *Experimental study of the proposed super-thermal-conductor: BAs*

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

<b>Citation</b>	Lv, Bing et al. "Experimental Study of the Proposed Super-Thermal-Conductor: BAs." Applied Physics Letters 106, 7 (February 2015): 074105 © 2015 AIP Publishing LLC
<b>As Published</b>	<a href="http://dx.doi.org/10.1063/1.4913441">http://dx.doi.org/10.1063/1.4913441</a>
<b>Publisher</b>	AIP Publishing
<b>Version</b>	Final published version
<b>Citable link</b>	<a href="http://hdl.handle.net/1721.1/117852">http://hdl.handle.net/1721.1/117852</a>
<b>Terms of Use</b>	Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.

## Experimental study of the proposed super-thermal-conductor: BAs

Bing Lv,<sup>1</sup> Yucheng Lan,<sup>1</sup> Xiqu Wang,<sup>2</sup> Qian Zhang,<sup>1</sup> Yongjie Hu,<sup>3</sup> Allan J. Jacobson,<sup>2</sup> David Broido,<sup>4</sup> Gang Chen,<sup>3</sup> Zhifeng Ren,<sup>1,a)</sup> and Ching-Wu Chu<sup>1,5,a)</sup>

<sup>1</sup>Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5002, USA

<sup>2</sup>Department of Chemistry and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5003, USA

<sup>3</sup>Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

<sup>4</sup>Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, USA

<sup>5</sup>Lawrence Berkeley National Laboratory, Berkeley California 94720, USA

(Received 21 January 2015; accepted 11 February 2015; published online 20 February 2015)

Recent calculations predict a super-thermal-conductivity of  $\sim 2000 \text{ Wm}^{-1} \text{ K}^{-1}$ , comparable to that of diamond, in cubic boron arsenide (BAs) crystals, which may offer inexpensive insulators with super-thermal-conductivity for microelectronic device applications. We have synthesized and characterized single crystals of BAs with a zinc blende cubic structure and lattice parameters of  $a = 4.7830(7) \text{ \AA}$ . A relatively high thermal conductivity of  $\sim 200 \text{ Wm}^{-1} \text{ K}^{-1}$  is obtained, close to those of best non-carbon crystal insulators, such as SiC, although still an order of magnitude smaller than the value predicted. Based on our XPS, X-ray single crystal diffraction, and Raman scattering results, steps to achieve the predicted super-thermal conductivity in BAs are proposed.

© 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4913441>]

Thermal management has become a major challenge to the modern day microelectronics industry as more and more chips that contain billion of transistors are packed into smaller and smaller devices to achieve their ever increasing functionality. Such device miniaturization, coupled with enhanced device functionality, is resulting in an exponential increase of the heat density generated in the chips that is approaching dangerous levels. Therefore, the heat generated by the electronic devices and the circuitry has to be removed to avoid overheating in order to improve reliability and to prevent premature failure. Over the years, industry has developed sophisticated techniques to remove the unwanted heat according to the three basic principles of heat transfer—namely, conduction, convection, and radiation. Heat transfer through the conduction process is by far the simplest among the three, since it involves only a solid stationary medium that connects the device to a heat sink. The effectiveness of the process depends on the availability of a solid insulator with very high thermal conductivity  $\kappa$ . Diamond is known to have the highest room temperature bulk  $\kappa$  up to  $\sim 4000 \text{ Wm}^{-1} \text{ K}^{-1}$ . Unfortunately, both naturally occurring and artificially synthesized diamonds are too expensive for practical applications. In 2013, Lindsay *et al.* carried out first principle calculations on the class of boron-based cubic III–V compounds and predicted that boron arsenides (BAs) can have an exceptionally high room temperature  $\kappa$  above  $2000 \text{ Wm}^{-1} \text{ K}^{-1}$ , comparable to that of diamond and far higher than other “high  $\kappa$ ” materials such as copper and SiC.<sup>1</sup> If confirmed experimentally, this will remove the cooling dilemma for micro/nano-electronic devices and make possible immense improvement in heat removal efficiency without the use of the prohibitively

expensive diamond. A new chapter will be written for achieving practical inexpensive super-thermal-conductors for defense and civilian device applications. Due to the difficulties in compound formation and in single crystal growth, no experimental results on the  $\kappa$  of BAs single crystals have been available. In this letter, we report the growth and characterization of the BAs single crystals with the cubic zinc blende structure. A relatively large  $\kappa$  of  $\sim 200 \text{ Wm}^{-1} \text{ K}^{-1}$  has been detected. While it is about an order of magnitude smaller than the predicted value and that of diamond, it is comparable to or higher than those of other high  $\kappa$  non-carbon single crystalline insulators. Based on our XPS, XRD, and Raman results, achieving the predicted value of  $\sim 2000 \text{ Wm}^{-1} \text{ K}^{-1}$  in BAs single crystals appears to be possible. Several steps are proposed. Although cubic BAs was first synthesized as early as 1958,<sup>2</sup> very few experimental results, especially in their single crystalline form, have been reported. This is because boron-related materials are known to be difficult to make in dense bulk form, such as single crystals, and the high volatility and toxicity of As further complicates their syntheses. BAs decomposes irreversibly at  $\sim 920^\circ\text{C}$  to  $\text{B}_{12}\text{As}_2$  (Ref. 2) below its melting point ( $2027^\circ\text{C}$ ), which makes single crystal growth much more difficult using conventional techniques such as zone melting or crystallization from the melt. Various approaches have been attempted to synthesize stoichiometric BAs powder, but failed due to the sublimation and high vapor pressure of arsenic.<sup>2–5</sup>

For single crystals, we have used a two-step synthesis procedure: the preparation of the stoichiometric BAs powder using solid state reaction followed by the growth of single crystals of BAs from this powder by chemical vapor transport. Polycrystalline powder precursor of BAs was prepared by reacting pure As (Alfa Aesar, 99.999%) and B (Alfa Aesar,

<sup>a)</sup>Electronic addresses: zren@uh.edu and cwchu@uh.edu

99.99%) with a B:As ratio of 1:1.8 in quartz ampoules (~10 cm long) sealed under vacuum. The quartz ampoules were placed in a horizontal furnace, first heated up slowly to 500 °C for 10 h, and then reacted at 800 °C for 3 days. After reaction, excess As chunks were found well separated from the yellowish gray product in the ampoules. The As chunks were then reground together with the product and heated up again following the same temperature profile. After repeating the procedure several times, a homogenous and close-to-stoichiometric BA<sub>s</sub> powder was obtained as evidenced by the sharp peaks in the X-ray powder pattern without any detectable impurities obtained using a Panalytical X'pert Diffractometer at room temperature equipped with an X'Celerator detector, as shown in Fig. 1, as well as by the XPS results. The sharp peaks and narrow FWHM indicated the good crystallinity of the samples. The small split of the peaks at the high angles is due to K  $\alpha$ 1 and K  $\alpha$ 2 peak doublets from the X-ray source. The refined lattice parameter is  $a = 4.7801(2)$  Å, which agrees with the single crystal diffraction results to be presented later. The BA<sub>s</sub> powder precursor is very homogeneous throughout the whole sample under SEM studies with typical grain size smaller than ~5  $\mu$ m. Single crystals of BA<sub>s</sub> were grown from the powder precursor of BA<sub>s</sub> through chemical vapor transport method using iodine as the transport agent.<sup>6-8</sup> During the experiment, we found that the addition of extra arsenic provides a reasonable transport rate for good crystal growth. Polycrystalline BA<sub>s</sub> powder precursor, arsenic, and iodine were therefore mixed and sealed in a fused silica tube of 25 cm in length and 10.5 mm in inner diameter. The assembly was placed in a two-temperature-zone furnace for 2–3 weeks. The mixture of BA<sub>s</sub> powder with excess As and I<sub>2</sub> was located at one end of the tube in the high temperature zone, and usually held at 900 °C to prevent irreversible decomposition of boron arsenide. The crystals of BA<sub>s</sub> nucleate and grow at the cold end of the tube at ~650 °C together with the As crystals. The aggregated crystals were then cleaned with moderately concentrated HCl acid (with which the excess As crystals react), and later washed with de-ionized water and ethanol to obtain the pure BA<sub>s</sub> crystals for further characterization and measurements.

Single crystal diffraction measurements were performed using a Bruker SMART APEX diffractometer equipped with

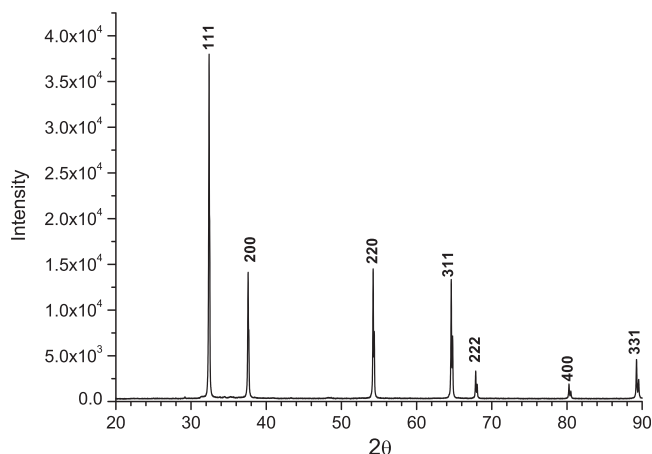


FIG. 1. Representative XRD pattern for powder BA<sub>s</sub> precursor.

a 1 K CCD area detector using the graphite-monochromated Mo K $\alpha$  radiation. An XPS analysis was performed to determine the chemical composition of BA<sub>s</sub> material using a Physical Electronics Model 5700 XPS instrument via a monochromatic Al-K $\alpha$ -ray source (1486.6 eV) operated at 300 W. For the TEM studies, crystals with length of ~100  $\mu$ m were crushed and ultrasonicated in ethanol. The crushed fragments were deposited on a carbon-coated TEM grid. The convergent beam electron diffraction (CBED) was carried out using a JEM 2000FX transmission electron microscope (JEOL, Inc.) operated at 200 kV and equipped with a LaB<sub>6</sub> emitter. The measurements were carried out at room temperature.

The chemical analysis XPS results give a B to As ratio of ~50.7:49.3. The results show a small but non-negligible As-deficiency (~2.8%) in the samples. The As-deficiency should result in a p-type doping, which is in agreement with the positive Seebeck coefficient detected by us in the sample.

Figures 2(a) and 2(b) show the SEM images of two typical as-grown BA<sub>s</sub> crystals of sizes ~300–500  $\mu$ m. The crystal facets shown suggest that the crystals may have multidomains. Crystals with a size of 200  $\mu$ m were selected for X-ray single crystal diffraction studies and were all found to have complex twinned structures, a frequent occurrence during growth of crystals with cubic symmetry.<sup>9</sup>

Small fragments with dimensions of ~60  $\mu$ m cut from the crystals were examined and display a complex twin structure. Reciprocal lattice pictures constructed from measured data of the fragments using the RLATT program of the Bruker Apex2 package are shown in Fig. 3. At least three sets of twin domains were clearly detected. X-ray data used for crystal structure refinements were collected on a twinned crystal and were processed with the programs CELL\_NOW and TWINABS of the Apex2 package. This is consistent with the TEM results, as shown in Fig. 4.

Structure refinements show that our BA<sub>s</sub> samples crystallize in the cubic space group  $F\bar{4}3m$  (#216) with a lattice parameter of  $a = 4.7830(7)$  Å. Both B and As atoms are tetrahedrally coordinated and form interpenetrating face-centered cubic lattices, mimicking the diamond structure, with a B-As bond length of 2.0711(2) Å. The crystal refinement results are consistent with the reported BA<sub>s</sub> zinc blende structure.<sup>2,10</sup>

Crystal fragments with typical size of 500 nm were used for TEM studies. Figures 4(a) and 4(c) show the whole-pattern (WP) and bright-field (BF) symmetry, respectively, of CBED patterns along the [111] zone axis. Both the WP symmetry and BF symmetry are 3m. Figures 4(b) and 4(d)

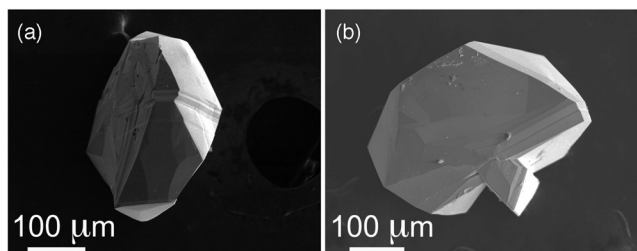


FIG. 2. SEM images of two BA<sub>s</sub> crystals after cleaning with HCl acid.

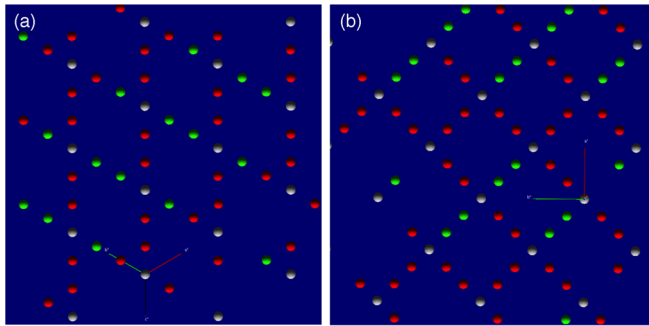


FIG. 3. The reciprocal space pictures synthesized from single crystal diffraction data showing the triple twin of a BAs crystal. White, green, and red are reflections from three twinned domains of the crystal. The green and red domains are related to the white domain by twinning axes of [112] and [121], respectively. (a) Projection view along the [111] direction. (b) Projection view along the [001] direction of the white twinned domain.

show CBED patterns along the [100] zone axis. The WP symmetry is 2mm, and BF symmetry is 4mm. Among all these possible point groups, only  $\bar{4}3m$  is consistent with all the symmetries in the two sets of CBED patterns, which is consistent with the single crystal diffraction results.

The thermal conductivity measurements were carried out on the as-grown crystals using the time-domain thermoreflectance (TDTR) technique.<sup>11,12</sup> TDTR is a simple noncontact optical technique for accurately measuring the thermal conductivity of small size samples for a wide range of materials. A modulated pump laser is used to heat the sample surface, and a probe laser monitors the resultant thermal wave via the temperature dependent reflectance of the surface. The reflectivity is measured with respect to time, and the data received can be matched to a model containing coefficients that correspond to thermal properties including the thermal

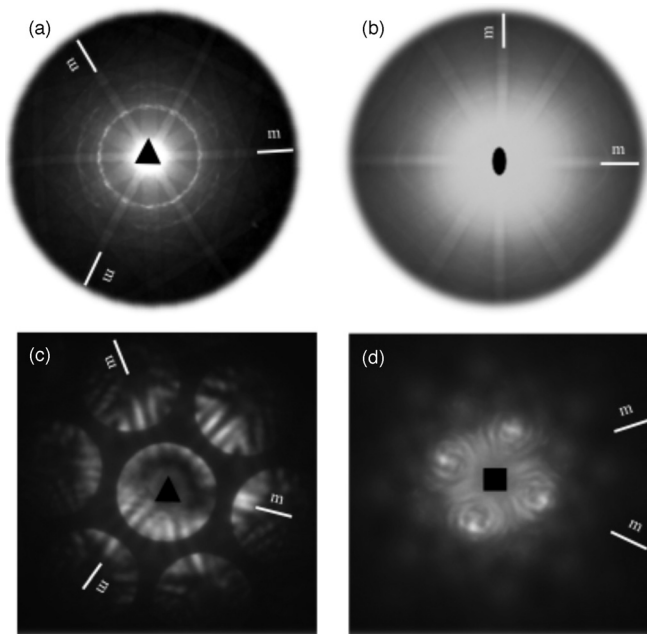


FIG. 4. CBED ((a) and (c)) [111] and ((b) and (d)) [100] zone-axis patterns from BAs crystalline fragments. In ((a) and (b)), the low-L pattern gives the WP symmetry; and in ((c) and (d)), the high-L pattern shows the BF symmetry. The observable symmetry in the patterns is noted by the following symbols:  $\bar{m}$ : mirror symmetry;  $\bullet$ : two-fold rotational symmetry;  $\blacktriangle$ : three-fold rotational symmetry; and  $\blacksquare$ : four-fold rotational symmetry.

conductivity of the materials. As shown in Fig. 5, a  $\kappa$  of  $\sim 196 \text{ Wm}^{-1} \text{ K}^{-1}$  was obtained in our BAs crystal of  $\sim 300 \mu\text{m}$ . Although the measured  $\kappa$  is one order of magnitude lower than the predicted value, it is comparable to that of the best non-carbon crystal insulators. The result is still rather encouraging given the presence of As deficiency, large grain boundaries, crystal twinning in the crystals, and defects associated with the different B-isotopes in the sample.

We have also theoretically examined the effect of defects on  $\kappa$ , where As vacancies were treated as mass defects in the crystal within the Born approximation.<sup>13</sup> The lower thermal conductivity is due to As vacancies, as also confirmed by first principles calculations. The room temperature  $\kappa$  is calculated and shown as a function of defects in Fig. 6. It is evident that a mere presence of 0.1% of As-vacancies would suppress  $\kappa$  by one order of magnitude to  $200 \text{ Wm}^{-1} \text{ K}^{-1}$  from the  $2000 \text{ Wm}^{-1} \text{ K}^{-1}$  for a perfect BAs single crystal. Inclusion of the missing/distorted bonds around the vacancy sites within the Born approximation would have given an additional strong reduction of  $\kappa$ .<sup>14,15</sup> Furthermore, recent *ab initio* Green's function treatment of phonon scattering from vacancies in diamond<sup>16</sup> have found larger phonon scattering rates than those obtained within the perturbative Born approximation, suggesting the BAs  $\kappa$  could be reduced by defects even further.

As Lindsay *et al.* have shown,<sup>1</sup> in BAs there exists an unusual large frequency gap between the acoustic and optic phonons and the bunching of the acoustic branches, depriving the compound of two important thermal scattering channels that involve three acoustic phonons and two acoustic phonons combining with one optical phonon. Our recent Raman experiment<sup>17</sup> did show the theoretically predicted gap between the acoustic and optical phonons and the bunching of the acoustic branches in BAs crystals. Unfortunately, the  $\kappa$  value of the BAs single crystals obtained by us is only  $\sim 200 \text{ Wm}^{-1} \text{ K}^{-1}$ , as shown in Fig. 5, which is only one tenth of the predicted value although relatively high compared

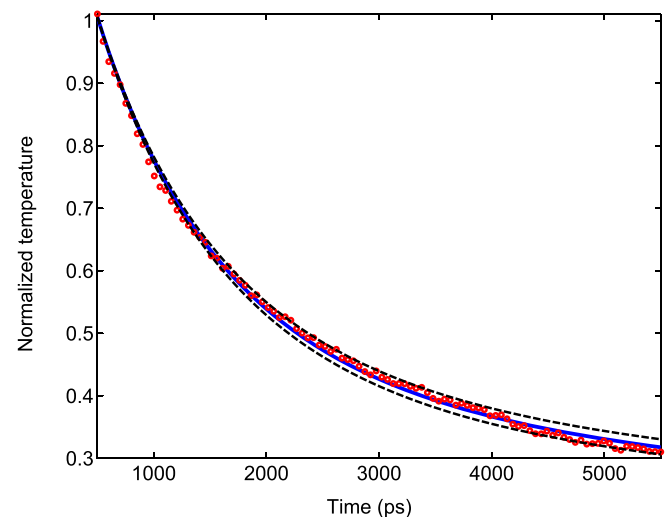


FIG. 5. Thermal conductivity of BAs sample measured by TDTR. Experimental data (red circles) are fit by a diffusive model to obtain the thermal conductivity (blue line). Calculated curves (black dots) using the thermal conductivity changed by  $\pm 10\%$  of best values are plotted to illustrate the measurement sensitivity.



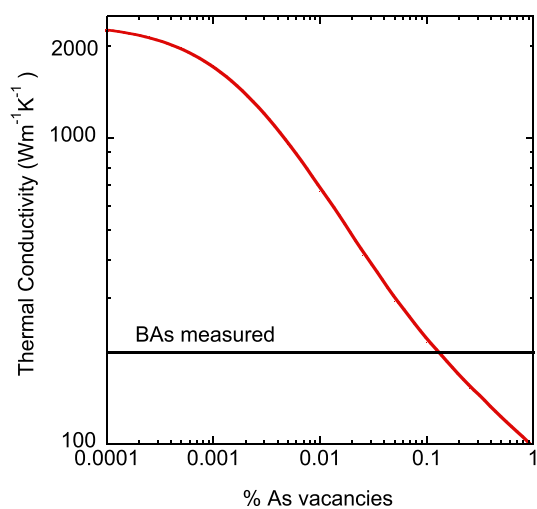


FIG. 6. Calculated thermal conductivity for BAs vs. the percentage of arsenic vacancies (red curve) for  $T = 300$  K. Also shown is the measured value from Fig. 5 (black horizontal line).

with non-carbon crystalline insulators. The XPS chemical analysis of our BAs single crystals do show a small but non-negligible As-deficiency of  $\sim 2.8\%$ , which, according to the above calculations, is more than sufficient to reduce our  $\kappa$  to the  $200 \text{ Wm}^{-1} \text{ K}^{-1}$  observed. However, our detailed analyses on the X-ray diffraction and convergent electron beam diffraction show that our crystals are also loaded with defects besides As-vacancies, such as crystal twins and grain boundaries, not to mention those associated with isotopic mass difference of B. In the face of all the odds noted above, a  $\kappa$  of  $\sim 200 \text{ Wm}^{-1} \text{ K}^{-1}$  in our samples may not be so bad and gives hope that a higher value is possible. It has been demonstrated previously<sup>18–20</sup> that the crystal morphology, size, and quality could be controlled by vapor pressure, supersaturation, substrate, seeds, isotope purity, and growth time during the vapor transport process. We conjecture that the very high thermal conductivity predicted may be achieved by fine-tuning the crystal growth process in the future.

The work in Houston was supported in part by U.S. Air Force Office of Scientific Research Grant No. FA9550-09-1-0656, the T. L. L. Temple Foundation, the John J. and Rebecca Moores Endowment, and the State of Texas through the Texas Center for Superconductivity at the University of Houston. B. Lv also acknowledges the New Faculty Award by University of Houston. X.W. and A.J.J. thank the Robert A Welch Foundation (Grant No. E0024) for support. This work is also partly supported by “Solid State Solar Thermal Energy Conversion Center (S<sup>3</sup>TEC)”, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science under award number DE-SC0001299 (D.B. for simulation and G.C. for pump-probe).

- <sup>1</sup>L. Lindsay, D. A. Broido, and T. L. Reinecke, *Phys. Rev. Lett.* **111**, 025901 (2013).
- <sup>2</sup>J. A. Perri, S. La Placa, and B. Post, *Acta Crystallogr.* **11**, 310 (1958).
- <sup>3</sup>J. Osugi, K. Shimizu, Y. Tanaka, and K. Kadono, *Rev. Phys. Chem. Jpn.* **36**, 54 (1966).
- <sup>4</sup>F. V. Williams and R. A. Ruehrwein, *J. Am. Chem. Soc.* **82**, 1330 (1960).
- <sup>5</sup>S. J. Wang, S. F. Swingle, H. C. Ye, F.-R. F. Fan, A. H. Cowley, and A. J. Bard, *J. Am. Chem. Soc.* **134**(27), 11056 (2012).
- <sup>6</sup>H. Schäfer, *Chemical Transport Reactions* translated by H. Frankfort (Academic Press, New York, 1964).
- <sup>7</sup>A. F. Armington, *J. Cryst. Growth* **1**, 47 (1967).
- <sup>8</sup>T. L. Chu and A. E. Hyslop, *J. Appl. Phys.* **43**, 276 (1972).
- <sup>9</sup>A. Millan, *Cryst. Growth Des.* **8**(2), 407 (2008).
- <sup>10</sup>A. A. Eliseev, A. A. Babitsyna, and Z. S. Medvedeva, *Zh. Neorg. Khim.* **9**(5), 1158 (1964).
- <sup>11</sup>D. G. Cahill, *Rev. Sci. Instrum.* **75**, 5119 (2004).
- <sup>12</sup>A. J. Schmidt, X. Chen, and G. Chen, *Rev. Sci. Instrum.* **79**, 114902 (2008).
- <sup>13</sup>P. G. Klemens, *Proc. R. Soc. London, Ser. A* **208**, 108 (1951).
- <sup>14</sup>V. Gallina and M. Omini, *Phys. Status Solidi B* **7**, 29 (1964).
- <sup>15</sup>C. A. Ratsifaritana and P. G. Klemens, *Int. J. Thermophys.* **8**, 737 (1987).
- <sup>16</sup>N. A. Katcho, J. Carrete, W. Li, and N. Mingo, *Phys. Rev. B* **90**, 094117 (2014).
- <sup>17</sup>V. G. Hadjiev, M. N. Iliev, B. Lv, Z. F. Ren, and C. W. Chu, *Phys. Rev. B* **89**, 024308 (2014).
- <sup>18</sup>P. Prabakaran and R. Dhanasekaran, *Cryst. Growth Des.* **7**(4), 618 (2007).
- <sup>19</sup>C. J. Hawley, B. R. Beatty, G. Chen, and J. E. Spanier, *Cryst. Growth Des.* **12**(6), 2789 (2012).
- <sup>20</sup>N. Roy, Y. Sohn, and D. Pradhan, *ACS Nano* **7**(3), 2532 (2013).