

Isotope Effect of Boron on Boron Arsenide Single Crystal Growth and Thermal Conductivity

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ABSTRACT

With the rapid development of modern microelectronic devices, materials with high thermal conductivities are essential for effectively cooling high-power-density electronic and optoelectronic devices due to the smaller dimensions and compacting units. In principle, heat is transferred via conduction, convection and radiation, of which direct conduction is the easiest and most efficient way. Thus, finding suitable materials with ultrahigh isotropic thermal conductivity for heat dissipation in high-power-density electronic devices is imperative.

Boron arsenide (BAs) with a zinc blende structure has recently been discovered to exhibit unusual and ultrahigh thermal conductivity (κ) of over $2000 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature by first-principles calculations, rendering it a close competitor for the diamond which holds the highest thermal conductivity among bulk materials, providing a new outlook for research on BAs and other high thermal conductivity materials. Technology for BAs crystal growth has been continuously improving, however, the influence of boron isotopes, pure or mixed, on the thermal conductivity in BAs is still not completely clear. Here we report detailed studies on the growth of single crystals of BAs with different isotopic ratios and demonstrate that the κ of isotopically pure BAs is at least 10% higher than that of BAs grown from natural boron. We obtained the highest thermal conductivity of $1260 \text{ W m}^{-1} \text{ K}^{-1}$ for the ^{10}BAs and $1180 \text{ W m}^{-1} \text{ K}^{-1}$ for the ^{11}BAs . Raman spectroscopy characterization shows differences in scattering among various BAs samples and suggests good crystalline quality. The presented results will help to guide further studies on the influence of isotopes on optimizing κ of BAs.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	iii
ABSTRACT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.1.1 Definition of Thermal Conductivity	3
1.1.2 Definition of Electrical Thermal Conductivity	3
1.1.3 Definition of Lattice Thermal Conductivity	4
1.2 Fundamentals of Single Crystal Growth	4
1.2.1 Definition of Semiconductor	5
1.2.2 Flux Method	6
1.2.3 Grown from Vapor	6
1.3 High Thermal Conductivity Materials	11
1.3.1 Metals	12
1.3.2 Traditional High Thermal Conductivity Bulk Materials	12
1.3.3 Diamond	13
1.3.4 Graphite	14
1.4 New Discovery for High Thermal Conductivity Materials	14
1.5 Isotope Effect of BAs	17
1.6 Outlines of This Work	20
CHAPTER 2 CHARACTERIZATION AND MEASUREMENT	22
2.1 Thermal Conductivity Measurement	22
2.2 Phase and Microstructure Characterization	24
2.3 Raman Spectroscopy	25
2.4 Hall Measurement	26
2.5 Heat Capacity Measurement	28
2.6 Optical Measurement	28

2.7 Photoluminescence Mapping and Time-Domain Thermo-Photoluminescence (TDTP) Measurement.....	29
CHAPTER 3 ISOPOTICALLY PURE BORON ARSENIDE SINGLE CRYSTALS GROWTH PROCESS.....	31
3.1 Source Materials Preparation.....	31
3.2 Basic Knowledge of Source Materials.....	31
3.3 Single Crystal Growth Basic Process	33
3.3.1 Source Materials Put at Cold Side	34
3.3.2 Use BAs Precursor.....	34
3.3.3 Use Another Transport Agent (TeI_4)	35
3.3.4 Add Quartz Plate.....	35
3.3.5 Add Quartz Fiber	36
3.3.6 Arc Melting of Boron Source	36
3.3.7 Use BAs Ingot.....	38
3.3.8 Use BAs Small Crystals.....	38
3.3.9 Put Source Materials in Different Sides.....	39
3.3.10 Prevent Direct Contact from Boron and Quartz	39
3.3.11 Change the Amount of Iodine.....	40
3.3.12 Mix Boron Source Manually	40
3.4 Handle the Samples.....	41
3.4.1 Acid Washing.....	41
3.4.2 Vaporize Arsenic	41
CHAPTER 4 RESULTS AND DISCUSSIONS	42
4.1 Chemical Reactions in Chemical Vapor Transport	42
4.2 Adjust Tube Length and Temperature	42
4.3 Optical Images of Crystals.....	44
4.3.1 Source Materials Put at Cold Side	44
4.3.2 Use BAs Precursor.....	45
4.3.3 Use Another Transport Agent Tellurium Tetraiodide (TeI_4)	46
4.3.4 Add Quartz Plate.....	46
4.3.5 Add Quartz Fiber	47
4.3.6 Arc Melting of Boron Source	49
4.3.7 Use BAs Ingot.....	50

4.3.8 Use BAs Small Crystals.....	51
4.3.9 Prevent Direct Contact from Boron and Quartz Tube	52
4.3.10 Change the Amount of Iodine.....	54
4.3.11 Mix Boron Source Manually	55
4.3.12 Two Clean Methods.....	56
4.3.13 Comparison of Crystals with Different Colors and Thickness	58
4.4 SEM and XRD Measurements for Crystals	59
4.5 Raman Spectroscopy.....	61
4.6 TDTR Measurements.....	64
4.7 Heat Capacity.....	67
4.8 Comparison of Isotope Effect of Different High Thermal Conductivity Materials.....	68
CHAPTER 5 SUMMARY.....	72
BIBLIOGRAPHY.....	73
LIST OF PUBLICATIONS	82

LIST OF TABLES

Table 1 Differences of ^{11}B (^{11}B), ^{10}B (^{10}B) and natural boron ($^{\text{nat}}\text{B}$).....	37
Table 2 The influence of different tube lengths during the isotopically pure BAs single crystal growth.	43
Table 3 The influence of different temperature gradients during the isotopically pure BAs single crystal growth.	43
Table 4 Comparison between experimental Raman peak position and calculated Raman peak position.....	62
Table 5 Thermal conductivity of isotopically pure BAs.	64

LIST OF FIGURES

Figure 1 The difference between metal, semimetal, semiconductor and insulator.....	5
Figure 2 The principle of CVD. [19]	7
Figure 3 Scheme of CVT experiments for crystallization of solids in a temperature gradient. [18].....	9
Figure 4 Calculated κ_{nat} vs temperature for cubic BN (orange), BP (purple), BAs (red), BSb (green), and diamond (black). [8]	15
Figure 5 Phonon frequency vs scaled wave vector in the high symmetry $\Gamma \rightarrow K \rightarrow X$ direction for BAs (black) and Si (red) with experimental Raman data for BAs (black circles). [35].....	16
Figure 6 Calculated isotope effect, $P = 100(\kappa_{pure}/\kappa_{nat} - 1)$, as a function of temperature for c-BN (orange), BP (purple), BAs (red), BSb (green), and diamond (black). [9]	18
Figure 7 Computed thermal conductivities κ of ideal (top) cBN and (bottom) BAs and BP crystals, compared with measured values as a function of isotope composition for three $c^{10}\text{BN}$, two $c^{11}\text{BN}$, one $c^{nat}\text{BN}$, and two $c^{eq}\text{BN}$ crystals. [41].....	19
Figure 8 DFPT calculated phonon dispersion and phonon density of states in ^{10}BAs and ^{11}BAs . pDOS is normalized to $3N_{cell} = 6$. [42]	20
Figure 9 (A) Typical sample configurations of thin film and bulk materials measured using the TDTR technique with concentric pump and probe beams. (B) Schematic of a typical transient thermoreflectance setup. [43].....	23
Figure 10 Energy-level diagram showing the states involved in Raman spectra.	25
Figure 11 Illustration of Hall effect.	27
Figure 12 The schematic of pump-probe time-domain thermo-photoluminescence (TDTP). [44].....	29
Figure 13 The three-zone furnace we used for single crystal growth with a proper temperature gradient set.	34
Figure 14 Optical images of isotopically pure boron arsenide. (A) ^{10}BAs ; (B) ^{11}BAs	44
Figure 15 A simple schematic diagram for the precursor and crystal formation.	45
Figure 16 Optical images of isotopically pure BAs crystals grown by BAs precursor on a scale paper with 1 mm per grid. (A) ^{10}BAs ; (B) ^{11}BAs	45
Figure 17 Optical images of Isotopically pure BAs crystals grown by transport agent TeI_4 on a scale paper with 1 mm per grid. (A) ^{10}BAs ; (B) ^{11}BAs	46
Figure 18 Optical images of quartz plate we used on a scale paper with 1 mm per grid.	46
Figure 19 Optical images of isotopically pure BAs crystals grown by a quartz plate on a scale paper with 1 mm per grid: (A) ^{10}BAs ; (B) ^{11}BAs	47

Figure 20 (A) the optical images of quartz fiber; (B) BAs crystals grown along with the fiber; [49] (C) BAs crystals grown from the bottom of the tube.	47
Figure 21 (A) Arc melted ^{10}B ; (B) Arc melted ^{11}B ; (C) Optical image of ^{10}BAs ; (D) Optical image of ^{11}BAs . All crystals are on a scale paper with 1 mm per grid.	49
Figure 22 (A) Source materials we used of ^{10}B powders, which looked like very tiny particles; (B) Source materials we used of ^{11}B powders, which looked like thin sands; (C) ^{10}B ingot we got from previous batches; (D) ^{11}B ingot we got from previous batches.	50
Figure 23 Optical images on a scale paper with 1 mm per grid: (A) ^{10}BAs crystals we got from the ^{10}BAs ingot; (B) ^{11}BAs crystals we got from the ^{11}BAs ingot.	51
Figure 24 Optical images on a scale paper with 1 mm per grid: (A) ^{10}BAs single crystal; (B) ^{11}BAs single crystal.	51
Figure 25 (A) ^{10}BAs crystals grown by BN crucible; (B) ^{10}BAs crystals grown by carbon coating. All crystals are on a scale paper with 1 mm per grid.	53
Figure 26 Optical images of A-F: ^{10}BAs by an increasing amount of I_2 ; G-L: ^{11}BAs by an increasing amount of I_2 . All crystals are on a scale paper with 1 mm per grid.	54
Figure 27 Optical images of (A) $^{10}\text{B}_{0.2}\text{B}_{0.8}\text{As}$; (B) $^{10}\text{B}_{0.5}\text{B}_{0.5}\text{As}$ single crystals. All crystals are on a scale paper with 1 mm per grid.	55
Figure 28 The tube of crystal growth side without acid washing.	56
Figure 29 Optical images of (A) ^{10}BAs crystal with acid washing; (B) ^{10}BAs crystal without acid washing. Both crystals are on a scale paper with 1 mm per grid.	56
Figure 30 Optical images of ^{10}BAs with different colors. All crystals are on a scale paper with 1 mm per grid.	58
Figure 31 SEM images of ^{10}BAs crystals after cleaning with aqua regia. ^{10}BAs crystals with poor quality and central radiative cracks, irregular facets, and plenty of holes.	59
Figure 32 X-ray diffraction pattern taken from a shiny and flat surface on a selected ^{10}BAs single crystal.	60
Figure 33 (A) Raman spectroscopy for ^{10}BAs and ^{11}BAs samples; (B) Expanded view of Raman spectroscopy in $650 - 760 \text{ cm}^{-1}$ for BAs samples with different boron-source ratios (pure ^{10}BAs , $^{10}\text{B}_{0.2}\text{B}_{0.8}\text{As}$, $^{10}\text{B}_{0.5}\text{B}_{0.5}\text{As}$, and pure ^{11}BAs); (C) Raman spectroscopy for ^{10}BAs and ^{11}BAs samples at low frequency; (D) Raman spectroscopy for ^{10}BAs and ^{11}BAs samples at high frequency.	61
Figure 34 Measured thermal conductivity of BAs in comparison with theoretical calculations and other crystals. [38].....	67
Figure 35 (A) C_p measured data and its fitted curve compared with calculated data. The uncertainty of the C_p measurement is 5%; (B) Enthalpy, entropy, and Gibbs free energy of BAs with respect to temperature. [53].....	68
Figure 36 Isotope effect and temperature dependence of heat transport in cubic boron pnictides. [41]	71

CHAPTER 1 INTRODUCTION

1.1 Background

With the rapid advances in technology in modern society, high-power-density electronic devices have become increasingly prevalent in daily life. Avoiding overheating from them has converted one of the most important emerging concerns. Materials exhibiting high thermal conductivity (κ) are becoming increasingly meaningful since they can directly transfer heat out of the devices. In principle, cooling of the devices can be done by heat transfer in mainly three ways: conduction, convection, and radiation [1]. Meanwhile, direct conduction is the most simple and efficient way to transfer the harmful waste heat especially in micro-scale units, which means the most efficient way for heat transferring away from electronic devices is by using materials with high thermal conductivity (κ). Currently, outstanding thermal conductivity has only been sought in simple elemental compounds consisting of light elements with strong interatomic bonding and in electrically conductive metals. Normally, heat is conducted by electrons (κ_e) and phonons (κ_l) [2]. The room-temperature (RT) record for materials with high isotropic κ_e is held by copper (Cu, 483 W m⁻¹ K⁻¹) [3] and the highest RT isotropic κ_l is measured in diamond (2290 W m⁻¹ K⁻¹) [4,5]. However, the cost of diamond is still high due to the difficulties in producing crystals with large enough size in such a rigorous environment with high pressure and temperature. And Cu's thermal conductivity is not high enough for many applications and its high electrical conductivity usually interferes with the circuits in electronic devices. Thus, finding suitable

materials with ultrahigh isotropic κ for heat dissipation in high power density electronic devices is becoming imperative.

After being studied for decades [6,7], since 2013, boron arsenide (BAs) has been predicted to have a remarkable ultrahigh isotropic thermal conductivity at room temperature comparable to that of the diamond by the results of first-principles calculations [8-10]. The high room temperature κ was attributed to three-phonon scattering in c-BAs because of a combination of a big frequency gap between acoustic and optical modes (a-o gap), bunching of acoustic branches, and relatively small optical phonon bandwidth [8]. More recent theoretic studies including the four-phonon scattering in c-BAs predicted thermal conductivity at room temperature to $1400 \text{ W m}^{-1} \text{ K}^{-1}$ [11,12]. Till now, BAs is the only known bulk semiconductor exhibiting isotropic thermal conductivity that exceeds $1000 \text{ W m}^{-1} \text{ K}^{-1}$. At the same time, the mechanical properties of BAs [13] and its coefficient of thermal expansion ($4.1 \times 10^{-6} \text{ K}^{-1}$ at RT) [14] are similar to most of the widely used semiconductors, such as gallium arsenide (GaAs), silicon (Si), and silicon carbide (SiC), indicating the great potential of BAs as a promising future material for the electronics industry. Early experimental efforts showed BAs samples with relatively low but promising κ values [15,16] however, has proved extremely challenging, especially in the preparation of large and high-quality single crystals. BAs crystals have been previously grown by chemical vapor transport (CVT), the growth process relies on spontaneous nucleation and results in small crystals with multiple grains and various defects [11].

1.1.1 Definition of Thermal Conductivity

The thermal conductivity of a material is a measure of its ability to transmit heat, which is mainly carried by electrons and phonons. It is traditionally evaluated by Fourier's Law. The equation of thermal conductivity can be listed as

$$q = -\kappa \Delta T$$

where q is heat flux, κ is the thermal conductivity, and ΔT is the temperature gradient. Generally, heat transfer occurs at a low rate in materials of low thermal conductivity than in materials of high thermal conductivity. Meanwhile, materials with high thermal conductivity can be widely used in heat sinks.

1.1.2 Definition of Electrical Thermal Conductivity

The electronic contribution of the thermal conductivity is proportional to electrical conductivity, and the exact expression was reported by Gustav Wiedemann and Rudolph Franz in 1853, after whom the Wiedemann-Franz law was named, which is [17]

$$\kappa_e = L\sigma T$$

where κ_e is the electrical thermal conductivity, L is the proportional constant Lorenz number ($2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ for most of the metals), σ is the electrical conductivity, and T is the temperature. Wiedemann-Franz law is valid provided that the electrons do not interact with each other and form a degenerate Fermi-Dirac assembly. And the scattering of the electrons is because of impurities or lattice vibrations and is elastic. Qualitatively, this relationship is based upon the fact that heat and electrical transport both involve free electrons in the metal. Currently, we display no interest in identifying new high κ_e materials to obtain high thermal conductivity.

1.1.3 Definition of Lattice Thermal Conductivity

In semiconductors and insulators, heat is carried by the atomic vibration of the lattice by phonons. Therefore, lattice thermal conductivity (κ_L) is given by [2,8]

$$\kappa_L = \frac{1}{V} \sum_{\lambda} C_{\lambda} v_{\lambda\alpha}^2 \tau_{\lambda\alpha},$$

where V is the crystal volume, $C_{\lambda} = k_B n_{\lambda}^0 (n_{\lambda}^0 + 1) \times (\hbar\omega_{\lambda}/k_B T)^2$ is the specific heat per phonon mode, k_B is the Boltzmann constant, and $n_{\lambda}^0 = 1/[\exp(\hbar\omega_{\lambda}/k_B T) - 1]$ is the Bose factor, and ω_{λ} is the phonon frequency. The sum is over all phonon modes, $\lambda = (\mathbf{q}, j)$, with the wave factor $\mathbf{q}$ and the polarization j . We define $\kappa_{\alpha\alpha} = \kappa$, $v_{\lambda\alpha}$ and $\tau_{\lambda\alpha}$ are the velocity component and the phonon transport lifetime along a cubic direction α for the assumed small T gradients. Note that the phonon mean free path can be expressed as $l = v_{\lambda\alpha} \cdot \tau_{\lambda\alpha}$. Since transverse waves have smaller phase velocity than longitude waves, the relaxation length or mean free path of transverse phonons will be much smaller. Thus, thermal conductivity will be mainly determined by the speed of longitude phonons. At the same time, as acoustic phonons have greater energy dispersion and therefore a greater distribution of phonon velocities, scattering of acoustic phonons will much affect κ_L , majorly limited by lattice defects such as dislocations, vacancies, stacking faults, twin boundaries, *etc.*

1.2 Fundamentals of Single Crystal Growth

A single crystal, solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. Basic crystal growth methods can be separated into four categories based on what they are artificially grown from melt, solid, vapor, and solution. For high thermal conductivity researches, as phonon and electron scatterings at grain boundaries and lattice defects play such an important

role in thermal conductivities, single-crystal bulks are wanted to obtain the theoretical maximum. Nowadays various routes are broadly used in both industries and laboratories, and appropriate routes are chosen based on the components, physical and chemical properties, cost, *etc.* Different routes may be related to meet specific requirements on the product, such as the growth speed, crystal size, quality. One of the most used single crystals is that of Silicon in the semiconductor industry. However, there are many other single crystals besides inorganic single crystals capable of semiconducting, including single-crystal organic semiconductors. Single crystal silicon is used in the fabrication of semiconductors and photovoltaics is the greatest use of single-crystal technology today.

1.2.1 Definition of Semiconductor

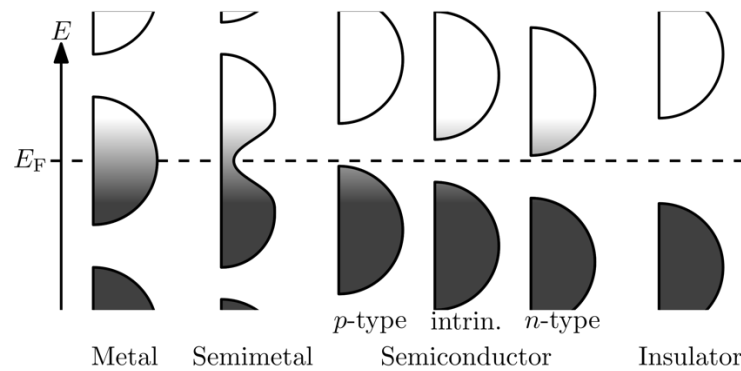


Figure 1 The difference between metal, semimetal, semiconductor and insulator.

Semiconductors are defined by their unique electric conductive behavior, somewhere between that of a conductor and an insulator. To Simplify, in Figure 1, the height is energy while the width is the density of available states for a certain energy in the materials listed. The shade follows the Fermi-Dirac distribution (black= all states filled, white= no state filled). The filling is the electronic states in various types of materials at equilibrium. In metals and semimetals, the Fermi level E_F stays inside at least on band. In insulators and semiconductors, the Fermi level is inside a bandgap. However, in semiconductors the bands are near enough to

the Fermi level to be thermally populated with electrons or holes. The differences between these materials can be understood in terms of the quantum states for electrons, each of which may contain zero or one electron (by the Pauli exclusion principle).

Semiconductors can display a range of useful properties, such as passing current more straightforwardly in one direction than the other, showing variable resistance, and sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by doping, or by the application of electrical fields or light, devices made from semiconductors can be used for amplification, switching, and energy conversion.

1.2.2 Flux Method

The Flux method is a method where all the components of desired substance are dissolved in a solvent. The method is particularly suitable for crystals requiring to be free from thermal strain. It takes place in a crucible made of highly stable, non-reactive material, such as boron nitride, alumina. The crucibles and their contents are often isolated from the air for reaction, either by sealing them in a quartz ampoule or by using a furnace with atmosphere control. A saturated solution is prepared by keeping the parts of the desired crystal and the flux at a temperature slightly above the saturation temperature long enough to form a complete solution. Then the crucible is cooled to allow the desired material to precipitate. Crystal formation can begin with spontaneous nucleation or be encouraged using a seed.

1.2.3 Grown from Vapor

Even though the solution method is the mainstream manufacturing technique in industry, a large amount of single crystal growth proceeds in the gas phase [18], either by the transportation of the precursors (mass transport) with the support of transport agent (chemical

vapor transport, CVT) [18] or by direct reaction and deposition on a substrate (chemical vapor deposition, CVD, Figure 2) [19]. In every CVD process, gaseous reactants are admitted into a reactor. Near or on a heated substrate surface the reactions take place and both solid material and gaseous products are generated. CVD usually forms thin films, we won't discuss too much on it. The following will mainly talk about the CVT method.

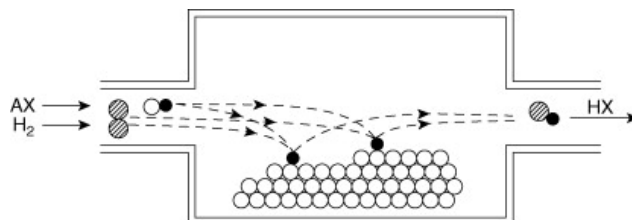


Figure 2 The principle of CVD. [19]

First, there is a sentence here, “If a condensed substance encounters a temperature gradient, it moves from the place of dissolution via the gas phase to the place of deposition, from source to sink”. It concludes with the main idea of the working theory of the CVT method. A lot of processes of crystal growth happen via the gas phase. And CVT method summarizes heterogeneous reactions which show that a condensed phase, typically a solid, has an unsuitable pressure for its evaporation. But the related phase can be vaporized in the presence of a gaseous reactant, which is called the transport agent, an important factor in the CVT method, and deposits elsewhere, usually in the form of crystals at the lowest temperature. The deposition will take place when there are different external conditions for the chemical equilibrium at the position of crystallization than at the position of evaporation (Figure 3). Usually, different temperatures are affected by crystallization [20]. Chemical vapor transport provides the formation process of pure and crystalline solids. Especially, the growth of single-crystalline material is valuable or a novel material, because it allows the determination of the crystal structure by diffraction methods. Beyond the aspect of basic research, chemical vapor

transport reactions have also got practical significance: they form the basis of the operating mode of halogen lamps. Furthermore, an industrial process is based on a chemical transport reaction. Other than transport agents, we should know a concept here, sublimation. Sublimations occur without the decomposition of the initial solid by forming only one dominating gas species. Substances showing sublimation are often solids constituting molecular units, which have only weak interactions. The much stronger bond in the molecular unit persists even under external energy stress, and the molecule can sublime undecomposed. Iodine is a concise example of sublimation. In the CVT, the transport agent helps the solid source to be a gaseous phase. At the same time, sublimations form other gaseous phases which complete the reaction.

In principle, two working methods are applied for the experiments in the laboratory: transport in open or closed systems. An open system is applied with an on both sides opened tube. Inside, a nonstop flow of the transport agent is going through the source materials; the solid, which is kept at a certain temperature, deposits at a different place with another temperature under the release of the transport agent. In a closed system, typically a sealed ampoule, the transport agent remains in the system and constantly participates in the reaction. Thus, in a closed system, a much smaller amount of transport agents is needed. In some cases, only a few milligrams of the transport agent are sufficient to cause a transport effect. In the laboratory working in closed systems is more common to see.

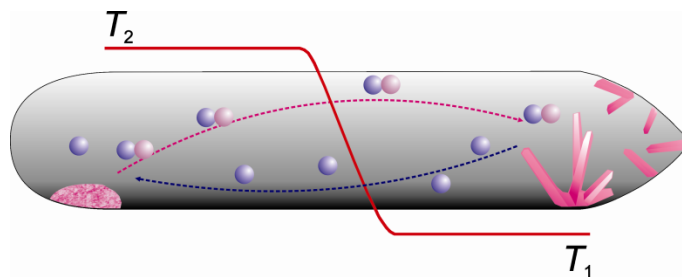


Figure 3 Scheme of CVT experiments for crystallization of solids in a temperature gradient. [18]

Understanding the basic principles and the thermodynamics in the CVT process improves our technique of crystal growth. It is helpful to do a CVT reaction with some prior basic understanding of the methods and the thermodynamic background to avoid unnecessary errors. Conclusions from similar experiments are also worthy of a starting guide. Here list some qualitative considerations: [18,20]

(i) Suitable transport agent. To efficiently undergo the CVT reactions, a suitable transport agent should be taken to transfer all components of the initial solid into the gas phase under the reaction environment. Generally, the halogens such as chlorine, bromine and iodine or halogen compounds are suitable transport agents.

(ii) Basic preconditions. The balanced equilibrium position of the CVT reaction must be reversible and not extreme, so that the transformation into the vapor phase and the re-condensation of solid phase may happen under a slightly changed CVT environment. In principle, possible CVT reactions can be calculated if all the thermodynamic data (*e.g.* respectively Gibbs energy, $\Delta_r G^0$ and equilibrium constant, K_p) is available. In details, for one independent reaction equation, transport can be expected for $10^{-4} < K_p < 10^4$ and $-100 \text{ kJ mol}^{-1} <$

$\Delta_r G^0 < 100 \text{ kJ mol}^{-1}$. A highly endergonic reaction $\Delta_r G^0 > 100 \text{ kJ mol}^{-1}$ ($K_p < 10^{-4}$) results in the solid hardly transferring into the gas phase, while on the contrary, a highly exergonic reaction $\Delta_r G^0 < -100 \text{ kJ mol}^{-1}$ ($K_p > 10^4$) shows a low possibility of the deposition of the solid.

(iii) Suitable temperature. The temperature at which $K_p = 1$ or $\Delta_r G^0_T = 0$ refers to be optimized and suitable. The optimum average temperature [$\tau = (T_2 + T_1)/2$] for chemical vapor transport results from the requirement of $\Delta_r G^0_T = 0$. The result of the calculation from the thermodynamic data $T_{opt} = \Delta_r H^0_T / \Delta_r S^0_T$ is not necessarily to be the exact degree. In fact, a range of $\pm 100 \text{ K}$ is suitable for CVT. A suitable temperature gradient always provides the partial pressure gradient as well, which works as the driving force for the CVT process.

(iv) Transport direction. Different temperatures make the transport happen, and therefore change the equilibrium position. Due to the reaction enthalpy, exothermic transport reactions always transport towards the high temperature zone, while the endothermic transport reactions are towards the low temperature parts. In an exothermic dissolving reaction, the equilibrium constant increases with decreasing temperatures, so deposition takes place at high temperatures. In another word, the transport is directed to the hotter zone. In an endothermic dissolving reaction, the equilibrium constant increases with increasing temperatures, so dissolution takes place at high temperatures. In another word, the transport is directed to the colder zone.

(v) Mass transport rate. For a single transport process, there are three steps, *i.e.*, source material forward reaction, gas motion and the back reaction to

recrystallization, which determine the transportation rate. However, in most cases, reaction rates are much faster, leading to the result that the slowest and therefore the rate-determining step is gas motion, dominated by either diffusion or convection. If we observe the diffusion of gas, the partial pressure gradient can be introduced. Then, the transport amount of material per time is proportional to the partial pressure gradient. If the quartz ampoule is horizontally placed, transportation is affected more by diffusion when the total pressure is between 10^{-3} bar and 3 bar, while convection turns to major at a pressure higher than 3 bar.

The chemical vapor transport method is predictable. Every parameter should be carefully taken into consideration in advance of the transport system.

1.3 High Thermal Conductivity Materials

As electronic devices become smaller, more powerful, and faster, thermal management is becoming a crucial challenge. As a result, the low heat transporting rate, high temperatures not only limit device performance but also greatly reduce reliability and lifetime. To effectively dissipate heat from an electronic chip into the ambient, packaging materials with sufficiently high thermal conductivities are indispensable. In other words, the ability to identify and create materials with high thermal conductivities, especially bulk materials, is becoming increasingly important. Some metals and carbon-based materials, such as diamond and graphite, have been long treated as having the highest thermal conductivity of any bulk materials at room temperature.

1.3.1 Metals

The most widely used material is copper (Cu), with a room temperature thermal conductivity as high as $400 \text{ W m}^{-1} \text{ K}^{-1}$, which is supposed to be the highest in metals. Such high thermal conductivities are all contributed by electrons and are proportional to their high electrical conductivities. Industries of metals make copper and aluminum among the most suitable materials for the heat sink. However, even though the low cost and the full manufacturing techniques of metals cannot be neglected, problems exist. Modern microelectronic devices always require their heat sinks and other supplementary components to be electric insulators or semiconductors while metals are all known as good electric conductors, resulting in applying insulator contact material between the metal heat sink and electronic units, which finally heavily reduces the thermal conductance. Small size and light weight are two keys to the art of designing, while metals are always heavy due to their large densities. Moreover, metals' thermal conductivities are determined by the electrons, therefore proportional to the electrical conductivities but also restricted by the electrical conductivities' limits, which indicates that scientists and engineers are not able to do too many improvements to metals' thermal conductivities.

1.3.2 Traditional High Thermal Conductivity Bulk Materials

To have more availabilities in choosing heat sink materials, and more importantly, more effectively improve the thermal conductance, plenty of efforts on lattice thermal conductivity have been made. A commonly accepted criteria as an instruction to search for high thermal conductivity material is: [21] 1) simple crystal structure, which leads to fewer atoms per unit cell; 2) low average atomic mass M_{ave} , to whom κ is always inversely proportional; 3) strong interatomic bonding, who provides a large Debye temperature θ_D , which gives longer mean

free path and average sound speed in the lattice; and 4) low anharmonicity, which reduces the phonon scattering effect of changing the volume of a crystal lattice, or changing temperature on its dynamics of the lattice and vibrational properties. Based on this rule, Group IV elementary substances (mainly carbon and silicon structures) like diamond, graphite, some carbon nanotubes [22-24] and silicon have very high thermal conductivity [25]. Similarly, Group III-V compounds like boron nitride (BN) and aluminum nitride (AlN), some Group II-VI compounds like beryllium oxide (BeO) also obey this rule and give relatively high thermal conductivity [21]. Here a brief introduction of them is given.

1.3.3 Diamond

Among the several light atoms, carbon (C) is the most representative element whose four electrons are available to form covalent bonding and therefore rich in allotropes. Diamond, the most famous carbon structure, is supposed to be the best thermal conductor in nature, which holds a room temperature thermal conductivity record of more than $2000 \text{ W m}^{-1} \text{ K}^{-1}$. Diamond's cubic structure, very low atomic mass, strong covalent bonding, and good symmetry not only result in the high thermal conductivity, but also provides unforgettable hardness, strength, modulus, and electrical insulation.

However, even though diamond looks like a perfect heat sink material, it is still far away from real applications. As we all know, natural diamond is the most worldwide-famous gemstone and jewelry. Both naturally mined and lab-grown diamonds require high temperature (over 2000°C) high pressure (over 10 GPa) conditions (HTHP) [26], which is difficult to obtain in industry, and further indicates the high cost. Moreover, despite that diamond is available by the graphite HTHP process, the overall size of the obtained diamond is small. They can be used as blades or drills where hardness majorly matters, but boundary

scattering between different grains heavily affects the total thermal conductance. Considering all these advantages and disadvantages, so far diamond has not been widely used as a thermal conductor yet.

1.3.4 Graphite

Another carbon allotrope, graphite, has attracted more and more attention these days. The layered structure with honeycomb lattice strong covalent bonding within a plane and weak van der Waals bonding between planes make graphite's physical properties anisotropic: along with in-plane directions, the phonons propagate quickly which makes the thermal conductivity as high as $400 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, and the out-of-plane weak bonds allow layers of graphite easy to separate and make graphite electrically conductive. Compared to metals to which graphite is quite similar in physical properties, graphite is supposed to be a perfect black body that can transport heat via radiation and further increase the heat sink efficiency. Considering the relatively small density ($\sim 2.1 \text{ g cm}^{-3}$), graphite is widely used as a radiation heat sink in micro-devices like cellphones.

1.4 New Discovery for High Thermal Conductivity Materials

Note that only a few elements and their compounds fit the traditional rule and obstruct the way to explore more heat sink materials. Of course, the development of new routes towards high thermal conductivity is impending. Recently the search for high thermal conductivity materials has been boosted by Lindsay *et al.*'s incredible theoretical calculations and simulations [8-10,27]. High thermal conductivities are predicted from boron-based cubic Group III-V compounds, boron nitride (BN), boron phosphide (BP), boron arsenide (BAs) and boron antimonide (BSb), referred to collectively as BX compounds. Among them, it is

exciting that BAs has an exceptionally high room temperature (RT) above $2000 \text{ W m}^{-1} \text{ K}^{-1}$ shown in Figure 4, which is comparable to that of the bulk carbon crystals. In Figure 4, Measured values for diamond (open black squares [28], triangles [29], circles [4], and crosses [30] and BP (open purple circles [21] and squares [31]) are given. Also shown are RT ($T = 300 \text{ K}$) values (solid black circles) for common high materials [32-34]: gallium nitride ($230 \text{ W m}^{-1} \text{ K}^{-1}$), aluminum ($240 \text{ W m}^{-1} \text{ K}^{-1}$), aluminum nitride ($285 \text{ W m}^{-1} \text{ K}^{-1}$), copper ($400 \text{ W m}^{-1} \text{ K}^{-1}$), and silicon carbide ($490 \text{ W m}^{-1} \text{ K}^{-1}$). This result is surprising given that a prediction based on the commonly accepted criteria above gives RT for BAs of only around $200 \text{ W m}^{-1} \text{ K}^{-1}$, comparable to that of silicon.

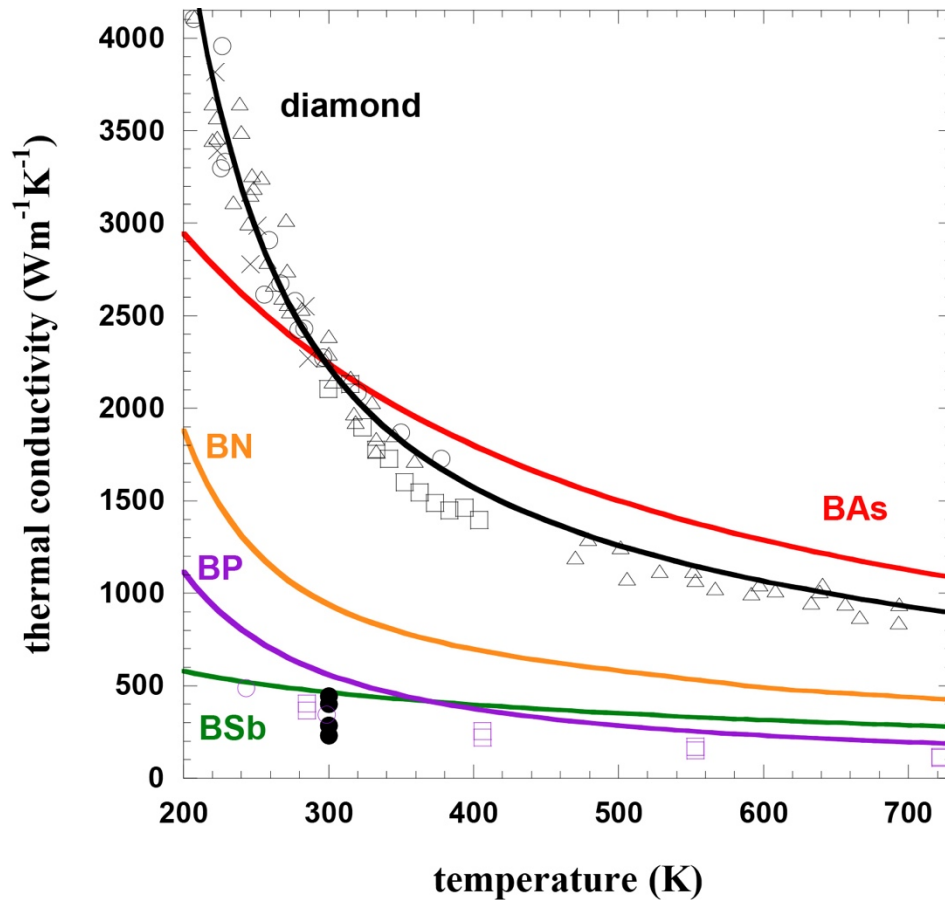


Figure 4 Calculated κ_{nat} vs temperature for cubic BN (orange), BP (purple), BAs (red), BSb (green), and diamond (black). [8]

The key principle for this new prediction is to introduce a large frequency gap between the acoustic and optic phonons (*a-o* gap) opened by a large mass ratio of the component elements (Figure 5). Specific for BAs, the bunching of the acoustic phonon dispersions also gives a high κ . In addition, the isotopically pure As atom gives relatively weak phonon-isotope scattering. In Figure 5, BAs has a large *a-o* frequency gap, which is absent in Si. Note that the near-zone center acoustic velocities for BAs and Si are similar. However, the three acoustic branches [two transverse (TA_1 and TA_2) and one longitudinal (LA)] are bunched closer to one another in BAs than are the corresponding branches in Si.

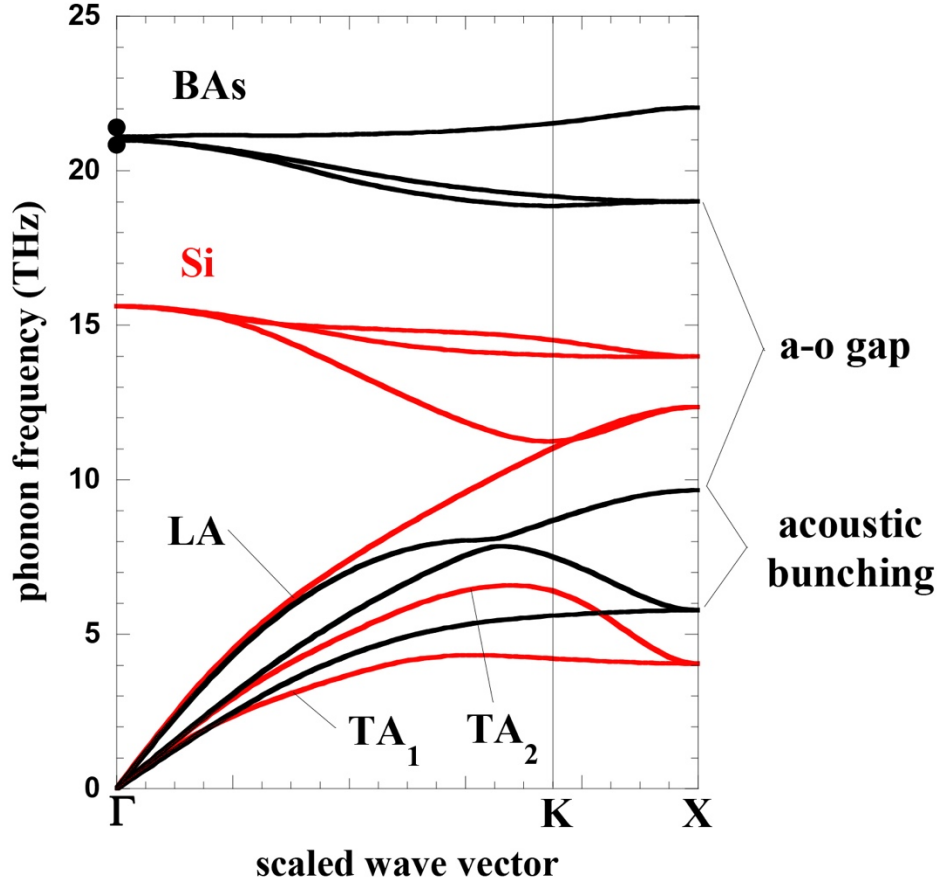


Figure 5 Phonon frequency vs scaled wave vector in the high symmetry $\Gamma \rightarrow K \rightarrow X$ direction for BAs (black) and Si (red) with experimental Raman data for BAs (black circles). [35]

1.5 Isotope Effect of BAs

Experimental achievements reported to date have generally been focused on BAs synthesized by using the naturally occurring boron isotope mixture $^{\text{nat}}\text{B}$ (19.9% ^{10}B and 80.1% ^{11}B) [36-39]. As a key factor that affects the lattice vibration, and thus the κ , isotopes have been found to have a significant influence on the κ of high κ materials such as diamond and cubic boron nitride [4,40]. Since ^{75}As is the only known stable arsenic isotope, we focus here on the effect of boron isotopes.

For BAs, the use of different pure isotopes is supposed to have a smaller effect on κ values than for BN [41]. Indeed, in the kinetic theory of thermal conductivity, κ is a sum over all phonon modes of a product of the phonon specific heat; the phonon transport lifetime that depends on the phonon-phonon, phonon-isotope, and electron-phonon scattering rates; and the square of the phonon (group) velocities. The acoustic phonons have the highest velocities and the isotope effect will be more strongly observed if they involve vibrations of isotopes. Since the atomic mass of As is much higher than that of B, As atoms dominate the heat-carrying acoustic phonons. Varying B isotopes in BAs changes the acoustic phonon dispersion and phonon velocities negligibly little. The two stable B isotopes, ^{10}B and ^{11}B , affect only the optical phonons. Under the three-phonon scattering mechanism, the RT κ of isotopically pure BAs ($^{\text{pure}}\text{BAs}$) is more than $3100 \text{ W m}^{-1} \text{ K}^{-1}$ [8,9], nearly 50% higher than that of $^{\text{nat}}\text{BAs}$ under the same assumption, which is shown in Figure 6. However, when four-phonon scattering processes are considered in the refined theoretical predictions [11], the RT κ value of $^{\text{pure}}\text{BAs}$ is only 20% higher than that of $^{\text{nat}}\text{BAs}$, departing significantly from the conclusion of the three-phonon processes [41].

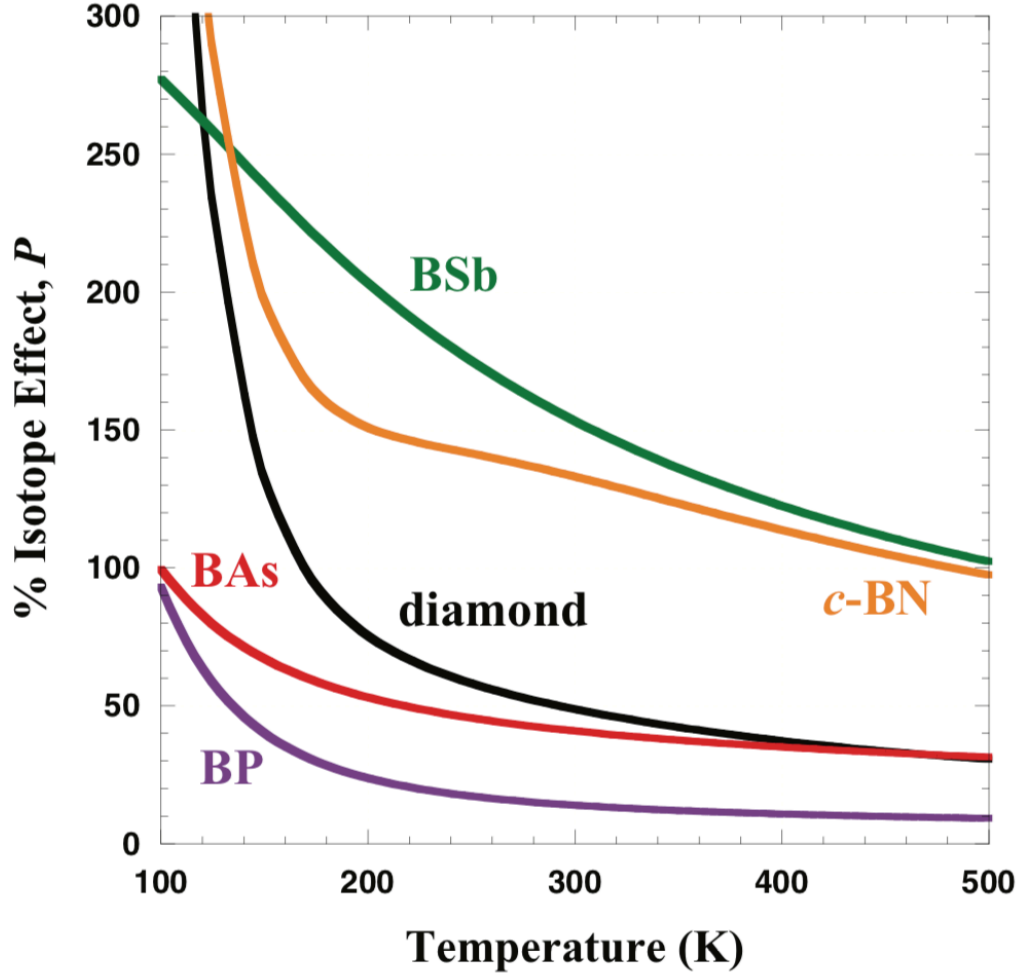


Figure 6 Calculated isotope effect, $P = 100(\kappa_{\text{pure}}/\kappa_{\text{nat}} - 1)$, as a function of temperature for c-BN (orange), BP (purple), BAs (red), BSb (green), and diamond (black). [9]

Not only theoretical analysis illustrates the importance of the isotope effect of boron arsenide, but also recently the experimental results give us the direct fact that cBN, BAs and BP have the isotope effect which nearly satisfies the three- and four-phonon scattering calculation. The experimental data of BAs in Figure 7 is from our crystals.

Figure 8 displays the phonon dispersion and phonon density of states (pDOS) of ^{10}BAs and ^{11}BAs as calculated using DFPT. Notably, the upper nondegenerate branch of the ^{10}B optical phonon dispersion in Figure 8 crosses no ^{11}B optical branches whereas the doubly degenerate lower branch has a few crossovers with the ^{11}B dispersion.

Another interesting feature of the phonon dispersion in BAs is an overbending of the upmost optical phonon branch, i.e., the frequency of the phonons at any wave vector on the nondegenerate optical branch is higher than that of the Γ -phonon. The effect is clearly seen in the pDOS where the Γ -phonon frequency lays between the pDOS of nondegenerate and doubly degenerate phonon branches [42]. A similar overbending effect has been found in diamond [11] but not in Si and Ge. As we show further the overbending of the upmost optical phonon branch in BAs is essential for the observed phonon isotope effects. From Figure 8, we can see the gap between optical phonon and acoustic phonon in ^{10}BAs is larger than that of ^{11}BAs . Thus, the thermal conductivity of ^{10}BAs should be greater than ^{11}BAs .

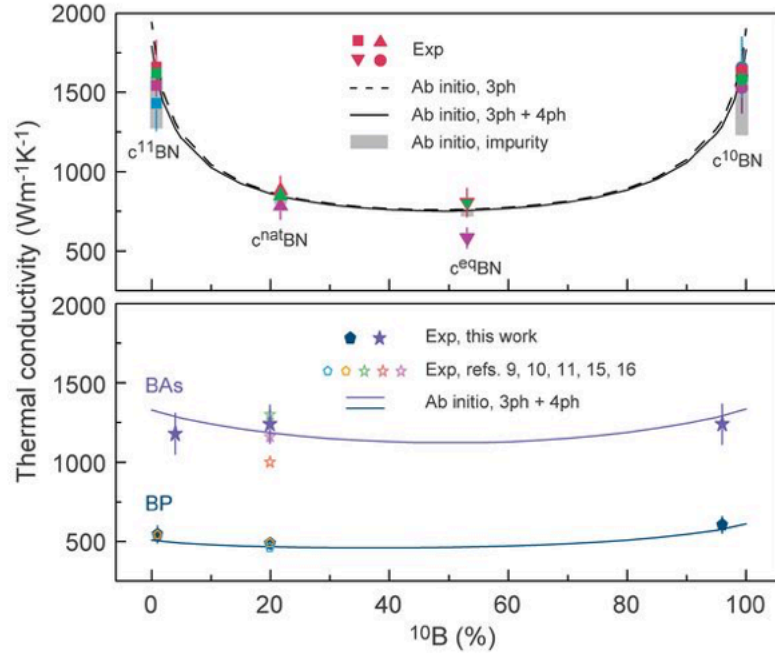


Figure 7 Computed thermal conductivities κ of ideal (top) cBN and (bottom) BAs and BP crystals, compared with measured values as a function of isotope composition for three $c^{10}\text{BN}$, two $c^{11}\text{BN}$, one $c^{\text{nat}}\text{BN}$, and two $c^{\text{eq}}\text{BN}$ crystals. [41]

Therefore, understanding the isotope effects on the κ value of BAs would help to confirm the correctness of the four-phonon processes in the prediction of κ by first-principles calculations.

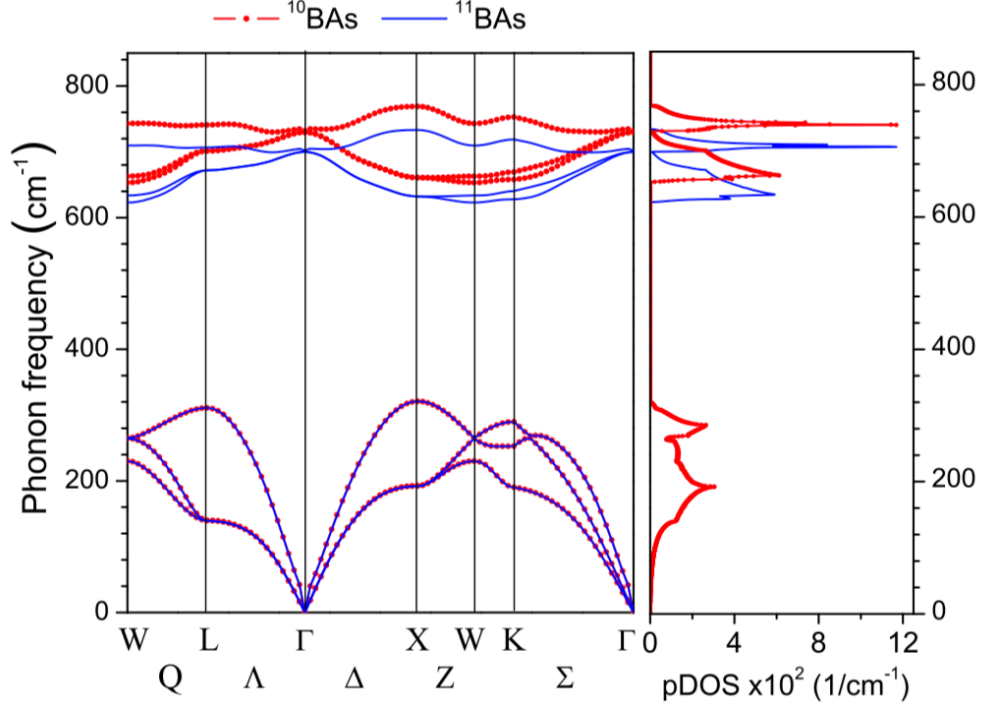


Figure 8 DFPT calculated phonon dispersion and phonon density of states in ^{10}BAs and ^{11}BAs . pDOS is normalized to $3N_{\text{cell}} = 6$. [42]

1.6 Outlines of This Work

Here we report another significant property of the lattice dynamics of cubic BAs: the isotope effect of BAs. We successfully synthesized isotopically pure BAs single crystal (1 mm - 5 mm) which is a magnitude higher than the largest reported size (200 μm) [15] and similar to the size (2 mm) in the paper of Fei *et al.* [30]. The detailed studies on the growth of single crystals of BAs with different isotopic ratios demonstrate that the κ of isotopically pure BAs is at least 10% higher than that of BAs grown from natural B which is very close to the theoretical 3- and 4- phonon scattering theory. Raman spectroscopy of phonons involving

isotopes was tested and analyzed. We expect these results will help to clarify the influence of isotopes on the thermal properties of BAs single crystals.

In this dissertation, a brief introduction to high thermal conductivity material researches and single crystal growth techniques is first presented. Then the characterization techniques and measurement methods are shown in the following chapter. The next chapter focuses on the BAs single crystal growth process, after which the results and discussions come. At last, this dissertation ends with my summaries.

CHAPTER 2 CHARACTERIZATION AND MEASUREMENT

2.1 Thermal Conductivity Measurement

Over the past two decades, ultrafast laser-based transient thermoreflectance (TTR) method is a reliable, powerful and efficient technique for characterizing thermal properties of a large variety of samples including both thin films with a thickness down to ~ 20 nm and bulk materials. In particular, the time-domain thermoreflectance (TDTR) technique has been applied for measuring materials with thermal conductivity values ranging from a high end at $\sim 2000 \text{ W m}^{-1} \text{ K}^{-1}$ (like diamond and graphite) to as low as $0.03 \text{ W m}^{-1} \text{ K}^{-1}$ (e.g., disordered WSe_2 films). The heat capacity of new materials and the thermal conductance of various solid/solid interfaces have also been frequently measured using TDTR. As a pump-probe technique, TDTR has many advantages over other thermal conductivity measurement techniques. For example, it requires minimal sample preparation and no delicate design of electrical heaters or temperature sensors, and it works equally well in regular ambient conditions or through the window of a vacuum chamber. Significant efforts have been devoted to advance the TDTR technique itself as well as its applications in thermal and phonon property characterization of various kinds of samples.

Samples are usually coated with a thin metal film acting as a transducer (see Figure 9 A for an illustration), whose surface reflectance changes linearly with temperature when the temperature rise is small (typically $<10\%$ of the absolute temperature or $<10 \text{ K}$, whichever is smaller). The TDTR method measures the thermoreflectance response as a function of delay time between the arrival of the pump and probe pulses on the sample surface, where the pump beam deposits a periodic heat flux on the sample surface and the probe beam detects the corresponding temperature change through the reflectance change (Figure 9 B shows the set

up). The acronyms PBS, BS, EOM, and $\lambda/2$ stand for polarizing beam splitter, beam splitter, electro-optic modulator, and half-wave plate, respectively.

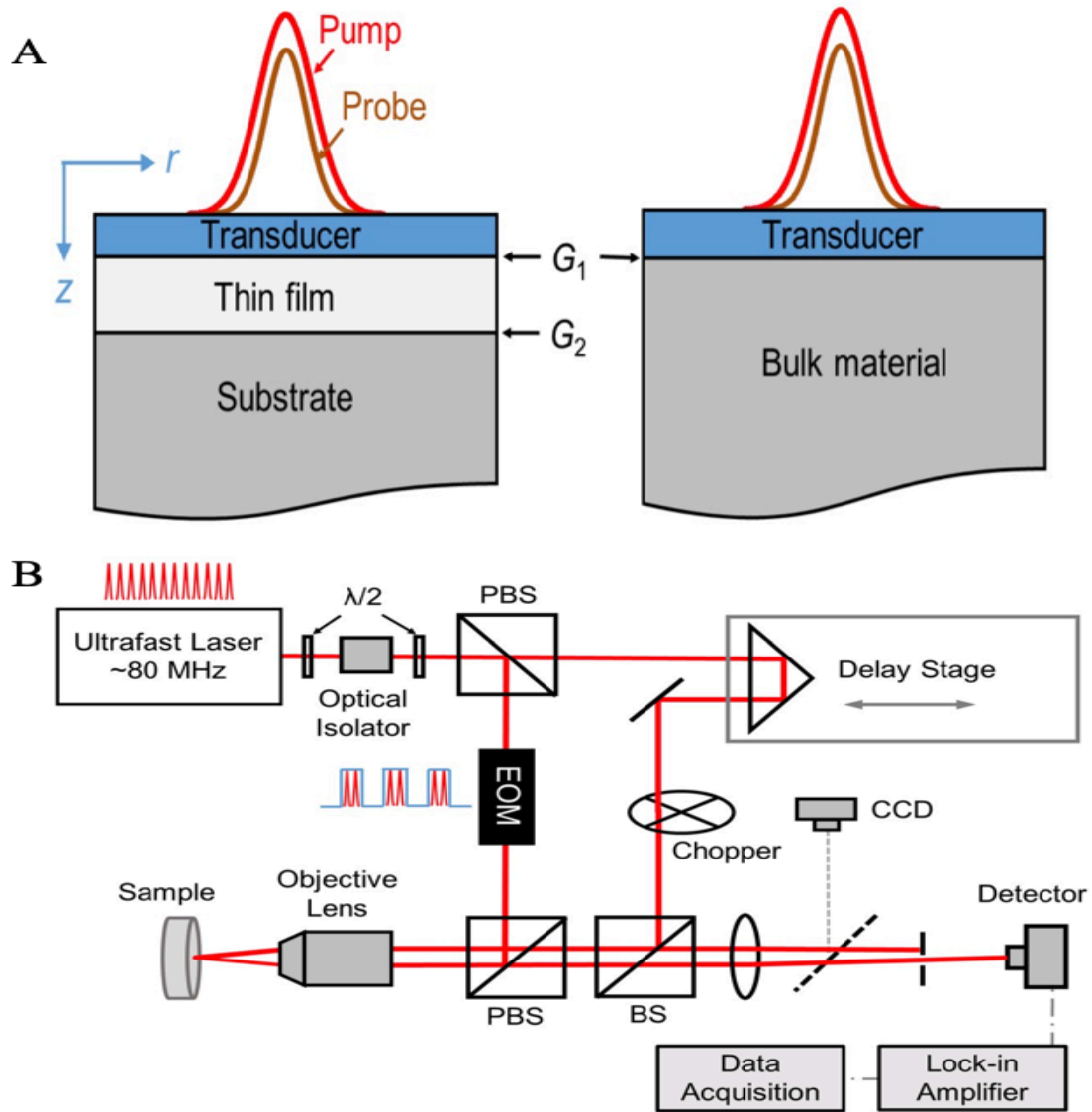


Figure 9 (A) Typical sample configurations of thin film and bulk materials measured using the TDTR technique with concentric pump and probe beams. (B) Schematic of a typical transient thermorefectance setup. [43]

2.2 Phase and Microstructure Characterization

X-ray diffraction spectroscopy analysis of pellets and powder was conducted on a PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro). Microstructures were characterized by scanning electron microscopy (SEM Leo 1525 Gemini FEG, Zeiss and FE-SEM, LEO 1525).

Crystals are regular arrays of atoms, whilst X-rays can be considered as waves of electromagnetic radiation. Crystal atoms scatter incident X-rays, primarily through interaction with the atoms' electrons. This phenomenon is known as elastic scattering; the electron is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. In the majority of directions, these waves cancel each other out through destructive interference, however, they add constructively in a few specific directions, as determined by Bragg's law:

$$2d\sin\theta = n\lambda$$

Where d is the spacing between diffracting planes, θ is the incident angle, n is an integer, and λ is the beam wavelength. The specific directions appear as spots on the diffraction pattern called reflections. Consequently, X-ray diffraction patterns result from electromagnetic waves impinging on a regular array of scatterers. These diffracted X-rays are then detected, processed and counted.

scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the detected

signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector (Everhart-Thornley detector). The number of secondary electrons that can be detected, and thus the signal intensity, depends, among other things, on specimen topography.

2.3 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique typically used to determine vibrational modes of molecules, although rotational and other low-frequency modes of systems may also be observed. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified.

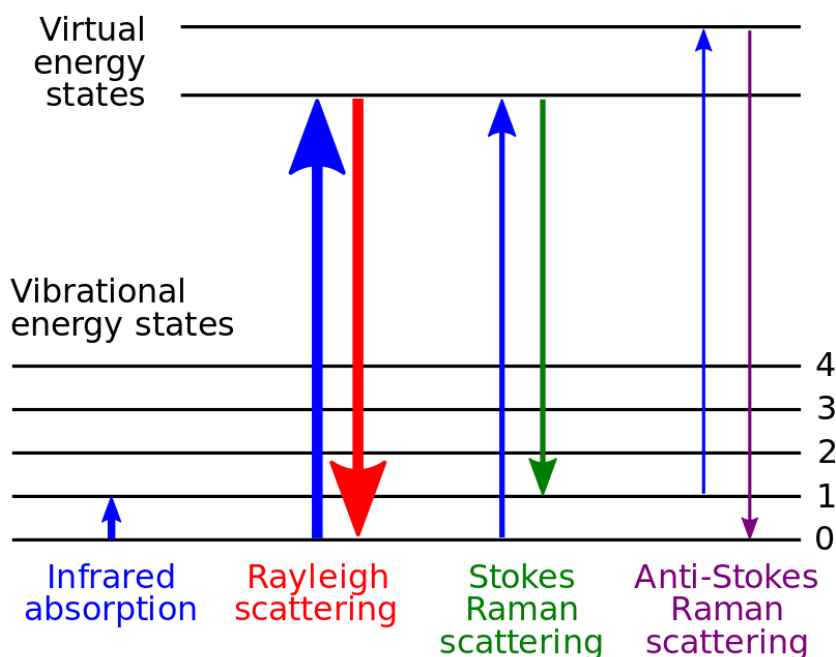


Figure 10 Energy-level diagram showing the states involved in Raman spectra.

Raman spectroscopy relies upon the inelastic scattering of photons, known as Raman scattering. A source of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range is used, although X-rays can also be used. The laser light interacts

with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The energy shift gives information about the vibrational modes in the system (Figure 10).

We used high-resolution Raman spectroscopy to study the phonon dynamics of BAs samples with boron isotope content. The Raman spectroscopy of BAs samples was measured using a Horiba JY T64000 triple spectrometer excited by a 632 nm laser at 294 K [42]. The spectroscopy was collected in a back-scattering configuration with the incident and scattered light directions normal to the large face of the crystals. The Raman spectroscopy of all BAs samples shown in Figure 33.

2.4 Hall Measurement

Hall effect measurements have been valuable tools for material characterization since Edwin Hall discovered the phenomenon in 1879. Essentially, the Hall effect can be observed when the combination of a magnetic field through a sample and a current along the length of the sample creates an electrical current perpendicular to both the magnetic field and the current, which in turn creates a transverse voltage that is perpendicular to both the magnetic field and the current (Figure 11). The underlying principle is the Lorentz force, that is, the force on a point charge due to electromagnetic fields. The “right-hand rule” we all learned in our introductory physics classes allows us to determine the direction of the force on a charge carrier based on its direction of motion and the direction of the applied magnetic field.

Hall effect measurements are used in many phases of the electronics industry, from basic materials research and device development to device manufacturing. Users include integrated circuit producers, particularly their technology and their process development groups. Crystal manufacturers also use this measurement technique, as do researchers in university- and

industry-based labs. For example, nanotechnology researchers studying graphene, a single-atom-thick, crystalline form of carbon, determined recently that the material demonstrated the quantum Hall effect; therefore, the electrons flowed through the crystal with relativistic effects.

A Hall effect measurement system can actually be used to determine quite a few material parameters, but the primary one is the Hall voltage. Other important parameters such as carrier mobility, carrier concentration, Hall coefficient, resistivity, magnetoresistance, and conductivity type are all derived from the Hall voltage measurement. With the addition of some other instruments, I-V characterization curves can be created with a similar test setup.

Hall effect measurements are useful for characterizing virtually every material used in producing semiconductors, such as silicon (Si) and germanium (Ge). They're often used in characterizing thin films of these materials for solar cells/photovoltaics, as well as organic semiconductors and nanomaterials like graphene.

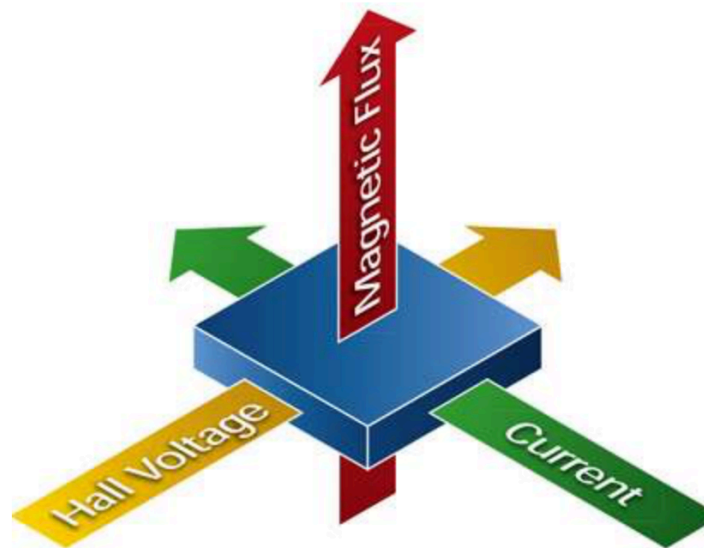


Figure 11 Illustration of Hall effect.

2.5 Heat Capacity Measurement

Heat capacity is the fundamental thermodynamic parameter, which always is used to obtain enthalpy, entropy and Gibbs energy. These thermodynamic parameters are critical for chemical reaction, phase equilibrium, material synthesis and design.

The heat-capacity measurement system is manufactured by Quantum Design (QD). QD's physical properties measurement system (PPMS) employs a thermal-relaxation calorimeter that operates in the temperature range of 1.8–395 K.

2.6 Optical Measurement

Optical spectroscopy is based on the Bohr-Einstein frequency relationship $\Delta E = E_2 - E_1 = h\nu$. The relationship links the discrete atomic or molecular energy state E_i with the frequency of electromagnetic radiation. The proportionality constant h is Planck's constant (6.626×10^{-34} J s). Ultraviolet-visible spectroscopy (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible regions of the electromagnetic spectrum. This means it uses light in visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions of electrons from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out

in solutions but solids and gases may also be studied. It is a good method to calculate the band gap of semiconductors through absorption spectroscopy.

2.7 Photoluminescence Mapping and Time-Domain Thermo-Photoluminescence (TDTP) Measurement

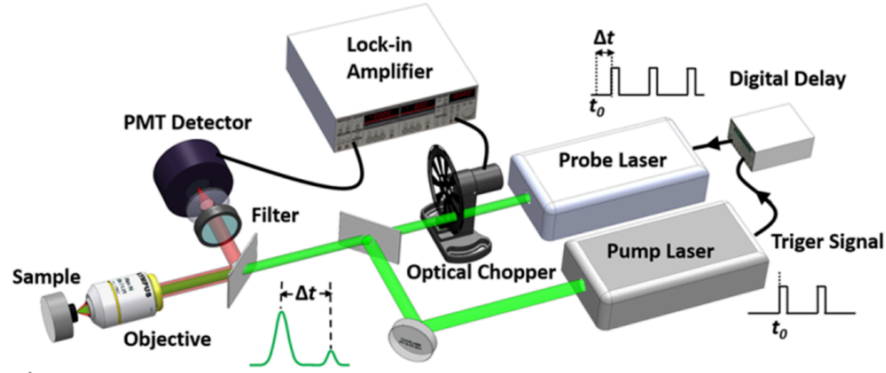


Figure 12 The schematic of pump-probe time-domain thermo-photoluminescence (TDTP). [44]

Photoluminescence mapping is a technique used for noncontact inspection of semiconductor wafers. The material is illuminated by an excitation source that stimulates photoluminescence; the resulting spectrum is analyzed, yielding information about the purity and lattice quality of the compound. TDTP (Figure 12) uses a pump pulse (527 nm, 140 ns) to generate localized heat in a sample, and a weak time-delayed probe pulse (527 nm, 100 ns) to monitor the temperature and heat transfer dynamics. κ is obtained by fitting the measured temperature data to the known analytical/numerical solutions. However, there are very distinct differences between TDTP and TDTR. Instead of ultrafast femtosecond or picosecond lasers used in TDTR, TDTP uses nanosecond lasers which are much cheaper and accessible. The local heat in the material is directly generated by the material's optical absorption of the pump pulse, so there is no metal film coated on the surface as in TDTR. The temperature of the

sample is obtained by its temperature-dependent PL. To eliminate the PL excited by the pump, the probe pulses are modulated and the PL is detected at the probe modulation frequency.

PL-mapping provides a nearly real-time image of crystal quality and κ over mm-sized crystal surfaces; while TDTP allows us to pick up any spot on the sample surface and measure its κ using nanosecond laser pulses. These new techniques reveal that the apparent single crystals are not only non-uniform in κ , but also are made of domains of very distinct κ . Because PL-mapping and TDTP are based on the band-edge PL and its dependence on temperature, they can be applied to other semiconductors, thus paving the way for rapid identification and development of high- κ semiconducting materials.

CHAPTER 3 ISOPOTICALLY PURE BORON ARSENIDE SINGLE CRYSTALS GROWTH PROCESS

This part will give you a general information of the different growth methods which we used for growing BAs single crystals with increasing size and better quality. All the image results for crystals will be presented in Chapter 4.

3.1 Source Materials Preparation

^{10}B (boron powder, $\geq 96\%$ atomic ^{10}B , crystalline, particle size: from 0.425 mm to 4.75 mm, 99.9% metals basis, Alfa Aesar), ^{11}B (boron powder, $\geq 96\%$ atomic ^{11}B , crystalline, particle size: less than 0.15 mm, 99.9% metals basis, Alfa Aesar), and $^{\text{nat}}\text{B}$ (boron powder, crystalline, particle size: from 0.425 mm to 4.75 mm, 99.9999% metals basis, Alfa Aesar) were used as different boron sources. Manually mixed B powders of 20% ^{10}B and 80% ^{11}B (denoted $^{10}\text{B}_{0.2}^{11}\text{B}_{0.8}$), and 50% ^{10}B and 50% ^{11}B (denoted $^{10}\text{B}_{0.5}^{11}\text{B}_{0.5}$) were also prepared as boron sources for comparison with results obtained from natural boron. As (arsenic polycrystalline lump, 2-8 mm, puratronic 99.99999+% metals basis, Alfa Aesar) and I_2 (Iodine, resublimed crystals, puratronic 99.9985% metals basis) were also used for samples preparation.

3.2 Basic Knowledge of Source Materials

Boron (B) is a chemical element with a very high melting point (2349 K) and boiling point (4200 K) which makes it very difficult to handle during the whole experiment system. Its high hardness makes it tough to cut and weigh accurately. Its density is 2.08 g/cm^3 . When exposed to air, Boron can be oxidized to form B_2O_3 which is a condensed film to block the reaction during crystal growth. Boron has two naturally occurring isotopes, ^{11}B and ^{10}B ,

which means ^{10}B is an isotope of boron with 5 neutrons and atomic mass of 10 and ^{11}B is an isotope of boron with 6 neutrons and atomic mass of 11. Natural boron has 19.9 % ^{10}B and 80.1 % ^{11}B . We will use the equation to present the mass of an average atom:

$$\text{Atomic mass} = (\%_1)(\text{mass}_1) + (\%_2)(\text{mass}_2) + \dots$$

And thus, the boron's atomic mass is 10.8.

Arsenic is a chemical element with the symbol As and the atomic number 33. Arsenic is a common n-type dopant in semiconductor electronic devices. It is also a component of the III-V compound semiconductor gallium arsenide. Arsenic and its compounds, especially trioxide, are used in the production of pesticides, treated wood products, herbicides, and insecticides. The sublimation point of As is 887 K and the melting point is 1089 K which is in the range of the temperature of our crystal growth period. Meanwhile, during the crystal growth, there are both liquid As and As vapor both. The density of liquid As is 5.22 g cm⁻³, which similar to the density of crystal BAs (5.22 g cm⁻³), but by the experience of growing crystals of BAs, we can clarify that the density of liquid As is a little bit smaller than solid BAs crystals, which makes BAs grow in the liquid As. Arsenic has high vapor pressure in the sealed tube and easy to react with air to form As₂O₃, which is a toxic chemical and can be fatal. So, when handling the arsenic, we should be careful enough in the fume hood and in the glove box.

Iodine (I₂) is a chemical element with the symbol I and the atomic number 53. It readily sublimates with gentle heat and its boiling point is 457 K. Iodine can react with boron at high temperature. The reaction is a significant one for our crystal growth and can be listed here: $2\text{B (s)} + 3\text{I}_2\text{ (g)} \xrightarrow{\Delta} 2\text{BI}_3\text{ (g)}$. It helps get the gas phase of boron to continue for the chemical vapor transport method.

There is an important point here, which is c-BAs will have the irreversible decomposition to form icosahedral boron arsenide ($B_{12}As_2$) at the temperature 1193.15 K. During the crystal growth, we have to control the temperature no higher than 1193.15 K. Otherwise, the crystals will have very low quality.

The tube we used is made of quartz, which is SiO_2 . Boron will react with SiO_2 at some temperature, which is the main side reaction during the chemical vapor transport process. Boron reacts with SiO_2 to form B_2O_3 . As I mentioned above, B_2O_3 is a compound which blocks BAs growth.

3.3 Single Crystal Growth Basic Process

All the source materials were weighed with proper calculated amounts in the grove box which were all put into a quartz tube with the appropriate length for the experiment. Then the sealed tube was put into a three-zone furnace, which was set as a cold zone, hot zone and cold zone (which are marked as zone 3, zone 2, zone 1 shown in Figure 13) as the sequence. The temperature and position were set. The suitable ratio of the source materials, temperature, position and tube length were finally found by lots of trials. The temperature we used is 1063 K (cold zone) and 1163 K (hot zone). After several weeks, the furnace was cooled down to room temperature naturally. Finally, the tubes were taken out for observing and collecting the BAs crystals. The following part shows different experiments and thoughts we did to grow better crystals steps by steps.

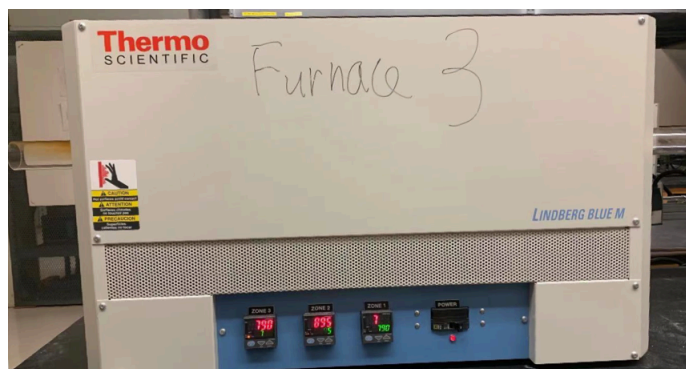


Figure 13 The three-zone furnace we used for single crystal growth with a proper temperature gradient set.

3.3.1 Source Materials Put at Cold Side

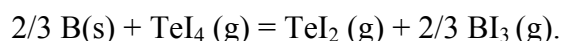
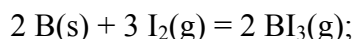
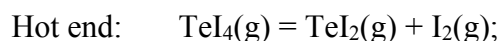
At the very beginning, when isotope boron (^{10}B and ^{11}B), arsenic and iodine were put into the sealed tube, the primary thing we thought was the position that the source materials should be. After discussion, we put them in the cold zone of the furnace. Normally, the crystals were grown at the lowest temperature. And by changing the position of the tube when putting it into a three-zone furnace, we first time got some crystals.

3.3.2 Use BAs Precursor

Through the experience of chemical vapor transport single crystal growth, one idea came up, which was that we could try to make isotopically pure BAs precursors first. Using precursor was the method that most crystal growth did in the chemical vapor transport method. Boron (^{10}B and ^{11}B) and arsenic were put into a sealed tube and heated in a box furnace for several days to let boron react with arsenic completely to perform BAs precursor. And then the precursor and iodine were put together into the three-zone furnace for single crystal growth. The best ratios of different source materials and tube lengths were found. Normally, it is called a two-step CVT growth method.

3.3.3 Use Another Transport Agent (TeI₄)

In order to make crystals grow larger and have better quality, we began to alter the source materials. Boron and arsenic were our target materials. We tried to replace transport agent I₂ with TeI₄. It was also a good way to take research on the effect of transport agents. When the TeI₄ used, the chemical reaction of the CVT growth can be as follows:



TeI₄ could be decomposed into TeI₂ and I₂. When heating the sealed tube filled with our materials, TeI₄ decomposed first and boron reacted with both TeI₄ and I₂ to form the BI₃ gas phase, which could decrease the reaction rate of the whole growth period. All the other steps were the same in the chemical vapor transport process.

3.3.4 Add Quartz Plate

Every time we took out the cooling tubes, we observed and concluded the crystals' size and position they grew. The best-looking and largest crystals were grown at the very bottom of the tubes in the cold side. After observing the nucleation position of the crystals, we were thinking if we could provide a fixed position for them to start growing and grow larger and larger along with that position. So, when loading the materials, we cut a very small quartz plate (2 cm long) and put it at the growth side to let the single crystals grow from the edge of the plate. We were trying to control the nucleation position and growth direction.

3.3.5 Add Quartz Fiber

When thinking more about the quartz plate, we observed that the growth mostly started from the sharp edge of the plate. But the quartz plate we used was too large and took so much space in the tube that prevents the crystals from growing bigger. When crystals grew from the edge of the plate and stopped when touching the inner surface of the tube. If we could decrease the width of the quartz plate as thin as possible, taking an imagination, which means the limit was that we shrunk a 3-D plate into a 2-D line (or even a 1-D dot, which is difficult to realize) with only a sharp edge. To make it happen, we created a quartz fiber to satisfy it. The quartz fiber was a straight long thin line made from quartz. We used the fiber instead of the plate.

3.3.6 Arc Melting of Boron Source

All the methods above we used were some creative designs for chemical vapor transport. From now on, I would discuss and display the problems and methods we found for isotope boron sources. After the crystal growth, when the tubes were taken out, we observed there was always some boron left at the hot end, which implied only a little boron participated in the reaction during the growth and caused the small size and low quality of the isotope crystals. Because the isotope boron source (^{10}B and ^{11}B) was the powder which was totally different from the natural boron source (Table 1 shows the exact difference between isotope boron source and natural boron source). The main problems were the size and purity difference of the boron source. Natural boron sources were small particles, even though Table 1 shows the ^{10}B and $^{\text{nat}}\text{B}$ are in the same particle size range. Essentially, ^{10}B was about 0.425 mm and $^{\text{nat}}\text{B}$ was about 4.75 mm. And the purity of $^{\text{nat}}\text{B}$ was much higher than isotope boron. But these boron sources were the best quality source materials in the market. So, when we

could not buy better materials, we had to improve the isotope boron source or change the isotope boron source morphology to satisfy the environment of the experiments. Boron powder was supposed to react faster with I_2 because of its larger surface area. Here what we were trying to do was to change the morphology of the boron sources to become similar to the natural boron sources. First, we used the arc melting method to melt boron powders directly to become bigger boron particles as natural boron. Arc Melting method is used for melting metals typically to form alloys. Heating is via an electric arc struck between a tungsten electrode and metals placed in a depression (crucible) in the copper hearth. In vacuum arc melting the chamber is evacuated and then backfilled with argon gas. Essentially it is an additional processing step to improve the quality of metal. Arc melting method was supposed to be very useful to melt boron and change the shape to what we need. But as I mentioned before, the melting point of boron is very high causing increasing difficulties during the process. For our experiment, when boron was put in the air, which could also react with oxygen to form B_2O_3 , a dense oxide membrane, preventing the crystal growth. Especially, when I was performing the arc melting method, it took me a very long time to proceed the melting process. Moreover, When I put 0.2 g isotope boron, only 0.02 g boron could be melted. It was barely 10 % efficiency. Even though the method itself worked, but it was a kind of a waste of source materials.

Table 1 Differences of ^{11}B (^{11}B), ^{10}B (^{10}B) and natural boron ($^{\text{nat}}\text{B}$).

	^{11}B (%)	^{10}B (%)	Impurity (%)	Size (mm)
$^{\text{nat}}\text{B}$	80.1	19.9	0.0001	0.425 - 4.750
^{10}B	4.0	96.0	0.1	0.425 - 4.750
^{11}B	96.0	4.0	0.1	<0.150

3.3.7 Use BAs Ingot

Besides using arc melting, I had tried induction, which was also a method to melt boron directly. What I had done here is to change the morphology of isotope boron powders directly to become larger particles. But obviously, it did not work efficiently. If it was a challenge to transform them directly, I was thinking of other ways to improve them indirectly. As One new batch had been taken out, I observed that there were some boron chunks left every time at the hot end which illustrated boron didn't react completely. And some boron sources even remained the same shape as I put. But in other prospects, that big boron chunk could be regarded as boron particles. Then we chose the remaining boron chunks as our new boron source. The advantage was that it was a big boron chunk which satisfied the requirement for boron powders to become larger particles and could slow down the reaction during the crystal growth. The disadvantage was that it contained B_2O_3 and some impurities when put in the air for a long time. It was a creative trial for the BAs crystal growth. Several experiments with different amounts of big born chunks were processed to find the best ratios.

3.3.8 Use BAs Small Crystals

Using boron chunks was a good way to change the morphology of the boron source, but it introduced lots of impurities to decrease the thermal conductivity of BAs single crystals. For the next step, we were thinking of a new method to change the size and the purity of the boron source, which was collecting the BAs small crystals from the previous batches as a new boron source. The small crystals were relatively clean and were small particles, not powders anymore. They should have a parallel reaction rate as natural boron particles. This method was more like the two-step chemical vapor transport method. The first step, we had grown small BAs crystals. The second step, we put BAs crystals as boron source and mixed them

with a proper amount of I_2 in sealed tubes to do the crystal growth. The results showed the exact good crystals as we expected. And this method gave us the best thermal conductivity values.

3.3.9 Put Source Materials in Different Sides

As we mentioned before, both liquid As and As vapor played an important role in the sealed tube during the crystal growth. And the previous trial gave us the enlightenment that the transparent and big crystals were grown at the very bottom which was in the liquid As at the cold end of the tube. For the new experiment this time, we separated the arsenic and boron at two sides when transfer tubes before putting into the three-zone furnace, which was that we put the arsenic at the cold side which was the crystals growth side to make more liquid arsenic happen there and put boron and iodine at the hot side to let them react completely at a higher temperature. Because of the operation of the separation manually, the three source materials could not be divided totally. We tried our best to put more arsenic only at the cold end.

3.3.10 Prevent Direct Contact from Boron and Quartz

As I listed in basic knowledge, boron reacts with quartz tube (SiO_2) to form B_2O_3 , which will prevent crystal growth processing. In order to remove or weaken this side effect, several trials were found to improve the problem. The most efficient method was to decrease the possibility of contact between boron and quartz. Carbon coating and BN crucible were used here. Carbon coating was made by ourselves only at one side of the tube we used. To simplify, we coated carbon at the position where we put the boron source, which provided a layer between the quartz and boron to prevent direct contact. But it introduced a new impurity carbon. Later, a BN crucible was brought in to replace carbon. BN crucible provided a

flexible way for us to handle the position of the boron source. Meanwhile, it gave extra boron for us to participate in the crystal growth. But the result was not as good as we thought.

3.3.11 Change the Amount of Iodine

Since we knew the biggest differences between the isotope boron source and natural boron source were size and purity. We had tried several methods to purify the boron source directly, but none worked. To change the morphology of the isotope boron source, we tried arc melting, using ingot and using BAs crystals. All the effort we put in here was to alter the reaction rate during the crystal growth periods. Since several methods were tried to change the boron source to adjust the reaction rate, on another hand, we could decrease or increase the amount of iodine to control the reaction rate. Firstly, we thought when growing isotope BAs, the powders had a larger surface area and the reaction rate should be too fast. Then we decreased the amount of iodine for several trials. But the fact was that because of the impurity, almost all boron sources remained the same shape as we put on the hot end, which meant boron did not react totally. Then we increased the amount to let more reactions happen. Different amount of iodine was used here to make a comparison of the effect of transport agent.

3.3.12 Mix Boron Source Manually

Boron has two stable isotopes as ^{10}B and ^{11}B . The ratio in natural boron is 80.1% ^{11}B and 19.9% ^{10}B . We mixed isotope boron source manually using 80.1% ^{11}B and 19.9% ^{10}B (denoted $^{10}\text{B}_{0.2}^{11}\text{B}_{0.8}$), which was the same as natural boron. At the same time, 50% ^{11}B and 50% ^{10}B (denoted $^{10}\text{B}_{0.5}^{11}\text{B}_{0.5}$) was made for a comparison. It was good for Raman spectroscopy measurement.

3.4 Handle the Samples

After several weeks of growth period, the furnace was naturally cooled down to room temperature. And the sealed tubes were taken out, we saw clearly that there were some source materials left at the hot side and crystals were covered by solid arsenic at the cold side. Normally, we were using two methods below to clean the crystals.

3.4.1 Acid Washing

After breaking the tubes, all the materials inside were taken into a beaker in a fume hood. *Aqua regia* (HCl: HNO₃ = 3: 1) was used to help remove the impurities and excess As residues on the surface of the crystals. After two days of reaction, only crystals and boron were left in the acid. At last, the crystals were picked out and measured.

3.4.2 Vaporize Arsenic

There was an obvious drawback to using acid washing. *Aqua regia* was a very strong acid and could destroy the surface of crystals which would decrease the thermal conductivity value. So, we had to develop a none chemical reaction method to remove all the residues without damaging the as-grown BAs. Then we chose to vaporize the impurities and arsenic at the cold side. We reversed the two sides of the tube and put it into the three-zone furnace for one more day. To simplify, the crystals covered by solid arsenic were put at the hot end and arsenic would be transfer to the cold end through the temperature difference.

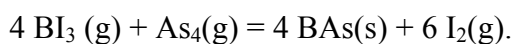
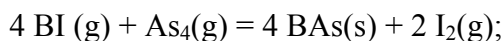
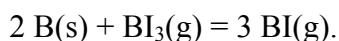
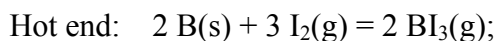
These two methods had their pros and cons. Acid washing gave us crystals with the smooth and shiny surfaces but relatively low thermal conductivity. Vaporizing arsenic directly gave us crystals with a rough surface but relatively high thermal conductivity.

CHAPTER 4 RESULTS AND DISCUSSIONS

This part will give you a general idea of the results of different growth methods which we mentioned in Chapter 3. Raman spectroscopy and thermal conductivity value will be present.

4.1 Chemical Reactions in Chemical Vapor Transport

In 2006, Dumont and Monteil reported a thermodynamic calculation that deduces the endothermic behavior of the formation reaction of BAs [45]. Our CVT method to grow isotopically pure BAs single crystals prefers the hot-to-cold direction, and the main processes which are more likely to occur are listed as follows:



4.2 Adjust Tube Length and Temperature

In this process, I_2 was treated as a transport agent and the amount of it kept constant, which helped continuously make isotopically pure BAs. By carefully adjusting the growth parameters like amount of source materials, temperature gradient, position of the tubes and vapor pressure, BAs crystals can be grown at the cold end of the quartz tube. At the very beginning, we grew some small bulk crystals with many defects. After changing the parameters, several experiments were set to help us better control the growth period and find a

suitable environment for the process. The results of different tube lengths are shown in Table

2. The results of different temperature gradients are shown in Table 3.

Table 2 The influence of different tube lengths during the isotopically pure BAs single crystal growth.

Tube lengths/ cm	Experimental results of ^{10}BAs or ^{11}BAs crystals
9	Many grey crystals only
10	Many grey crystals and a few dark reddish crystals
11	Many large reddish thin transparent crystals
12	Many large reddish thin transparent crystals
13	Many small dark reddish crystals
14	Some bulk grey crystals
15	No ^{10}BAs or ^{11}BAs
16	No ^{10}BAs or ^{11}BAs

Table 3 The influence of different temperature gradients during the isotopically pure BAs single crystal growth.

Temperature gradient $\Delta T / ^\circ\text{C}$	Experimental results of ^{10}BAs or ^{11}BAs crystals
70	Many small grey bulk crystals
80	Many large grey bulk crystals
90	A few small dark reddish crystals
100	Many reddish and transparent crystals up to 3 mm in size
110	Many reddish and transparent crystals up to 3 mm in size
120	A few reddish crystals and many large grey bulk crystals

130	A few small gray bulk crystals
140	A few small gray bulk crystals

4.3 Optical Images of Crystals

4.3.1 Source Materials Put at Cold Side

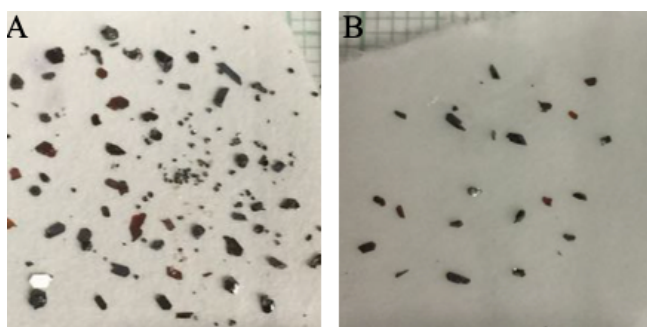


Figure 14 Optical images of isotopically pure boron arsenide. (A) ^{10}BAs ; (B) ^{11}BAs .

These were the results of our first batch. After all the parameters were fitted, we got the crystals with a length of 200 micrometers or less than 1 mm. The color for most crystals was grey and thermal conductivity for them was only $200 \text{ W m}^{-1} \text{ K}^{-1}$. The crystals were like thick plates. The results indicated that putting all materials at the cold end was not a good way to process crystal growth. Because when all materials were gathered at the cold end, there was nowhere for crystals to grow, which mostly happened at the lowest temperature.

4.3.2 Use BAs Precursor

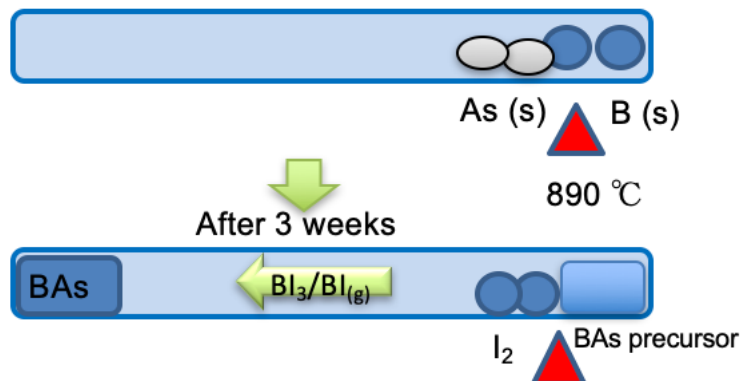


Figure 15 A simple schematic diagram for the precursor and crystal formation.

A simple schematic diagram was shown in Figure 15, which illustrates how we grew the BAs crystals and how we made the precursor. During making the boron arsenide precursor, we found that the so-called precursor is difficult to react with, even we heated the boron and arsenic for more days. For the first step, boron and arsenic were put into a box furnace for 3 days, but we observed the ingot we got from the heated tube, it was not typical for the precursors of other crystals. When using the so-called precursor as source materials, the results were shown in Figure 16. The size and the number of crystals were very small, which were only less than 1 mm. Using the precursor method is suitable for most crystals in CVT, but it was not a good way for boron arsenide.

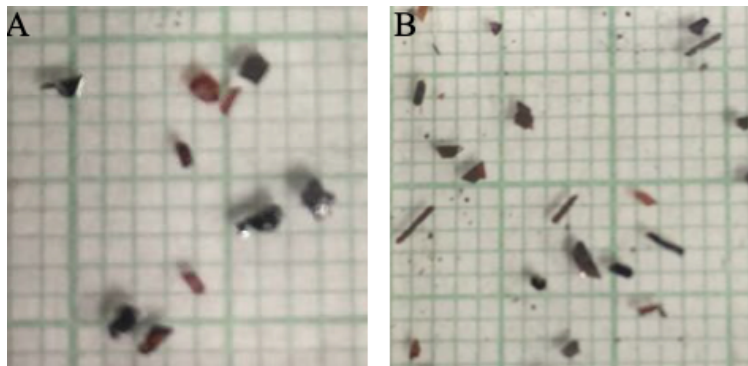


Figure 16 Optical images of isotopically pure BAs crystals grown by BAs precursor on a scale paper with 1 mm per grid. (A) ¹⁰BAs; (B) ¹¹BAs.

4.3.3 Use Another Transport Agent Tellurium Tetraiodide (TeI_4)

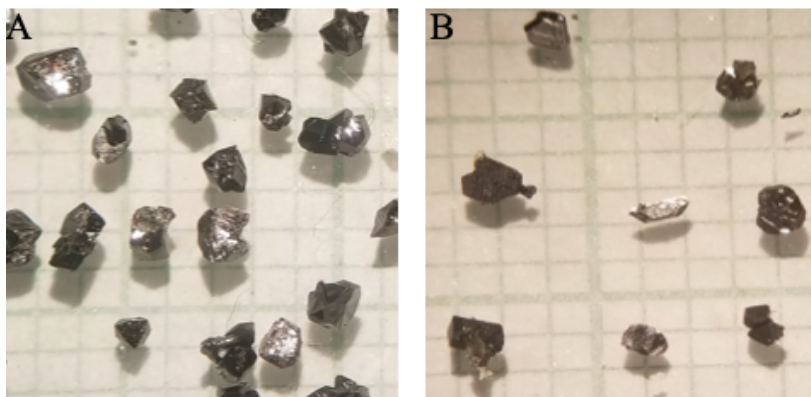


Figure 17 Optical images of Isotopically pure BAs crystals grown by transport agent TeI_4 on a scale paper with 1 mm per grid. (A) ^{10}BAs ; (B) ^{11}BAs .

As I analyzed in Chapter 3, TeI_4 would slow down the reaction rate of the whole crystal growth period. But on the other hand, TeI_4 itself introduced some impurities into boron arsenide crystals, which was tellurium. All the crystals were grey and less than 1.5 mm. They were bulk crystals, not like the thick plate crystals before. They had lower thermal conductivity. Using TeI_4 as a transport agent was not a proper way to improve the crystal growth.

4.3.4 Add Quartz Plate



Figure 18 Optical images of quartz plate we used on a scale paper with 1 mm per grid.

A 3 mm thick quartz plate was shown in Figure 18. We added a quartz plate at the cold end of the tube, hoping the plate provides a nucleation position for crystals starting to grow. It satisfied our expectations. Crystals were observed to grow on the plate or at the very bottom of the tube. The optical photo was shown in Figure 19. It was our first time to grow very thin reddish plate crystals as shown in upright of Figure 19 B. That piece had a smooth surface, even though the size was still 1 mm. But it seemed that we were finding a proper way to improve the chemical vapor transport process.

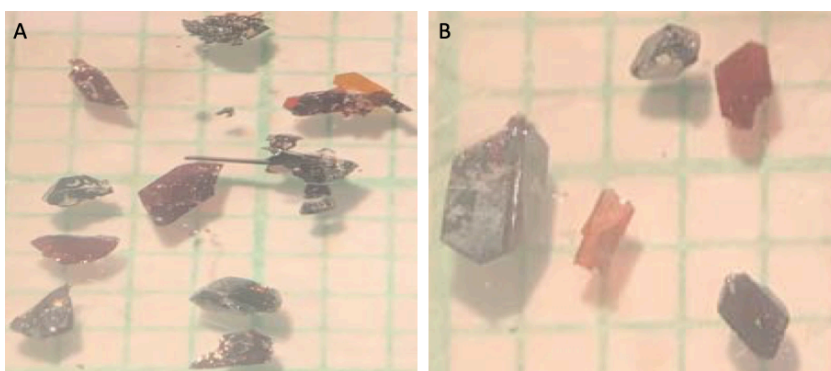


Figure 19 Optical images of isotopically pure BAs crystals grown by a quartz plate on a scale paper with 1 mm per grid: (A) ^{10}BAs ; (B) ^{11}BAs .

4.3.5 Add Quartz Fiber

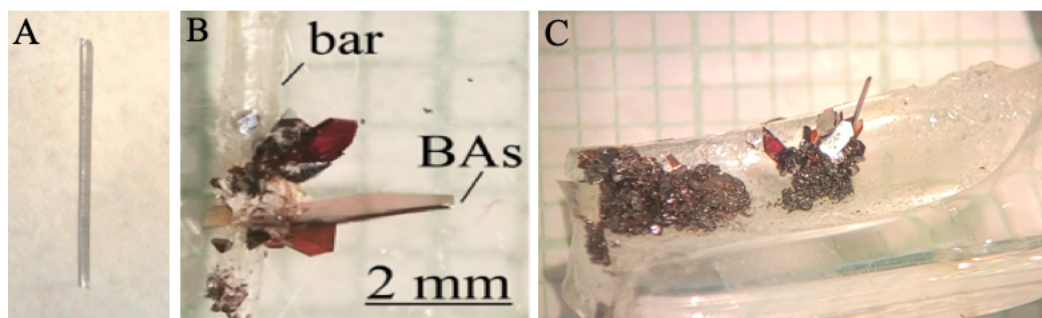


Figure 20 (A) the optical images of quartz fiber; (B) BAs crystals grown along with the fiber; [49] (C) BAs crystals grown from the bottom of the tube.

A 5 mm quartz fiber was put at the cold end shown in Figure 20 A. Figure 19 gave us the definition of the thin plate (3 D). As I discussed in Chapter 3, when shrinking the dimension,

the perfect condition was a 2 D line without any thickness. We realized it by using the fiber shown in Figure 20 A which worked very well in the following experiments. Fiber gave crystals a good and suitable position for them to start growing. And we clearly observed the orientation of the crystals from Figure 20 B and C. Some crystals were grown from the end of the fiber where was very closed to the coldest end. They grew from a point and continuously grew vertically along with the fiber. Meanwhile, some crystals grew from the bottom of the inner tube, which was also grown vertically from a point along the inner tube. The orientation was found for crystal growth. For the next step, we tried to adjust the position of fiber to leave more space for crystals to start growth vertically and it worked obviously in natural BAs crystal growth.

4.3.6 Arc Melting of Boron Source

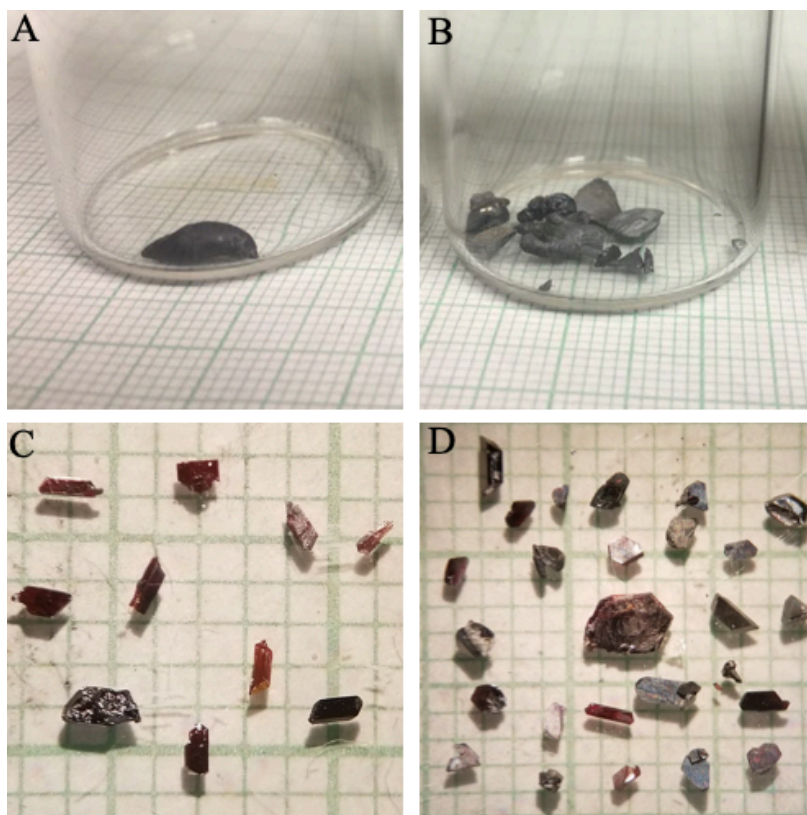


Figure 21 (A) Arc melted ^{10}B ; (B) Arc melted ^{11}B ; (C) Optical image of ^{10}BAs ; (D) Optical image of ^{11}BAs . All crystals are on a scale paper with 1 mm per grid.

Arc melting method worked better than the methods above. But as I indicated, the melting process itself was quite tough to handle and waste of boron source materials. The arc melted isotope boron source was displayed in Figure 21 A and B. It was obvious to see that the surface of the arc melted boron source lost the shiny surface as the boron powder. It was analyzed to be B_2O_3 . It was the first time for us to change the morphology of boron powders, but the cost was large. The crystals grown by arc melting method were shown in Figure 21 C and D. The size of crystals ^{11}BAs was larger and reached 3 mm long. When we looked carefully and compared it with the crystals before, we observed that the surfaces of the crystals were not shiny and flat, which looked like some impurities coated on the surface. And

the thermal conductivity was not good. But we grew some reddish and thin crystals, which was also a good sign to further improve the growth process.

4.3.7 Use BAs Ingot

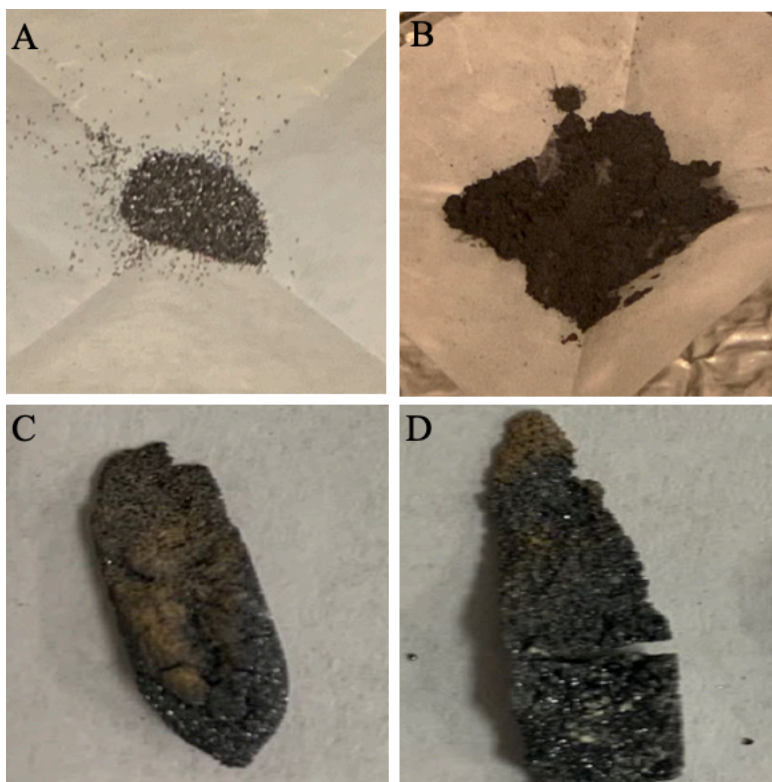


Figure 22 (A) Source materials we used of ^{10}B powders, which looked like very tiny particles; (B) Source materials we used of ^{11}B powders, which looked like thin sands; (C) ^{10}B ingot we got from previous batches; (D) ^{11}B ingot we got from previous batches.

Using ingot was like the improvement of the method we did of using BAs precursor. Figure 22 shows the optical image of the isotope boron source and ingot we made. We clearly saw the source materials were transferred from powders to big chunks. The results grown by this method were shown in Figure 23. The size of ^{10}BAs was grown bigger by 3 mm and the quality of ^{11}BAs looked better, especially the one piece at the left lower corner in Figure 23 B. The surface was reddish, smooth and transparent, which we could even see the grid of scale

paper through the light. And the thermal conductivity should be high, which was sent for measurement.

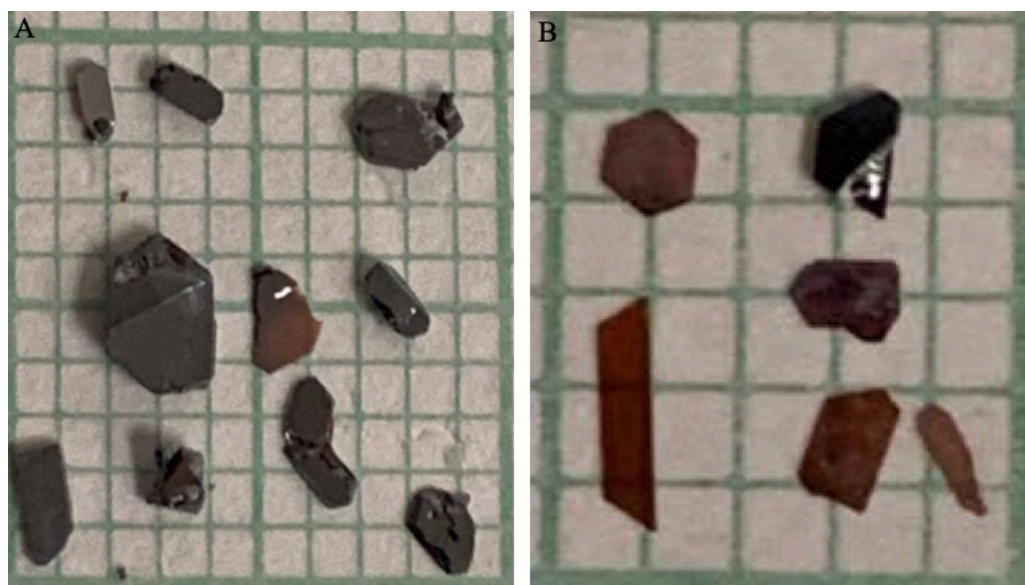


Figure 23 Optical images on a scale paper with 1 mm per grid: (A) ^{10}BAs crystals we got from the ^{10}BAs ingot; (B) ^{11}BAs crystals we got from the ^{11}BAs ingot.

4.3.8 Use BAs Small Crystals

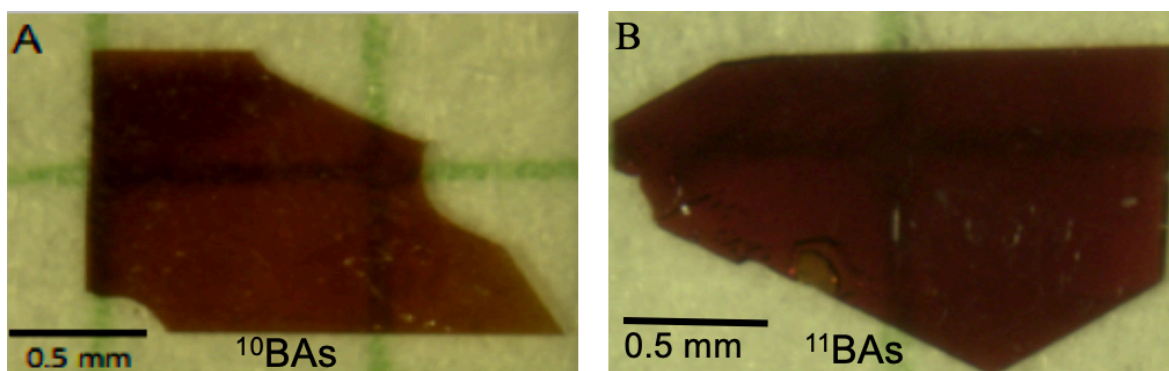
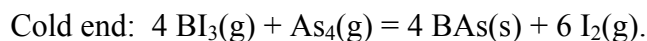
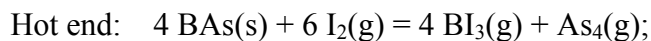


Figure 24 Optical images on a scale paper with 1 mm per grid: (A) ^{10}BAs single crystal; (B) ^{11}BAs single crystal.

All the previous results gave us positive signs to grow large crystals. Here comes the demand for higher quality, which is reflected by the thermal conductivity value. Using BAs small crystals was a good method to grow better quality crystals of isotopically pure BAs. The BAs small crystals were treated as seeds to supply the growth substrates and starting points.

On the other hand, the BAs small crystals were much cleaner and bigger than the original boron powder source. When as-grown BAs were used as new source materials, a different set of reactions occurs:



The results are shown in Figure 24 A and B respectively, ^{10}BAs and ^{11}BAs single crystals with dimensions of $2.0 \times 1.0 \times 0.1 \text{ mm}^3$ were obtained within a two (or three)-week growth time. The transparency and dark reddish color of the single crystals clearly show that their RT band gap is around 1.78 eV, which matches recent calculations [46-48]. This batch gave us the best crystals up to now. And the thermal conductivity value would be shown in Table 5.

4.3.9 Prevent Direct Contact from Boron and Quartz Tube

Preventing direct contact from boron and quartz tube could decrease the reaction between boron and quartz and decrease the impurities involved. Here we used two main methods to realize it, which were using BN crucible and using carbon coating to cover the tube. The results were shown in Figure 25. There were some problems during the operations. The first was that the diameter of the BN crucible was small and it was hard to put all the boron sources in. Meanwhile, we had to manually adjust the position of the source materials. When we were shaking the tubes, the boron powder spread everywhere. And the boron in the small BN crucible almost remained after growth, which meant most boron did not react during the growth. For carbon coating, carbon was successfully coated at the bottom of the tube where we put the boron powder source, but it introduced carbon as impurities. The results in Figure 25 were not good as before.

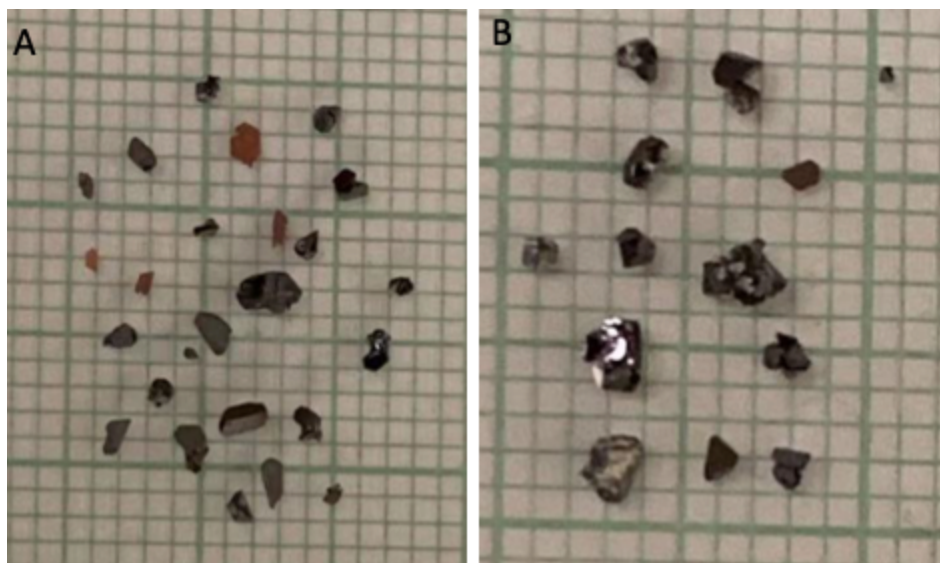


Figure 25 (A) ^{10}BAs crystals grown by BN crucible; (B) ^{10}BAs crystals grown by carbon coating. All crystals are on a scale paper with 1 mm per grid.

4.3.10 Change the Amount of Iodine

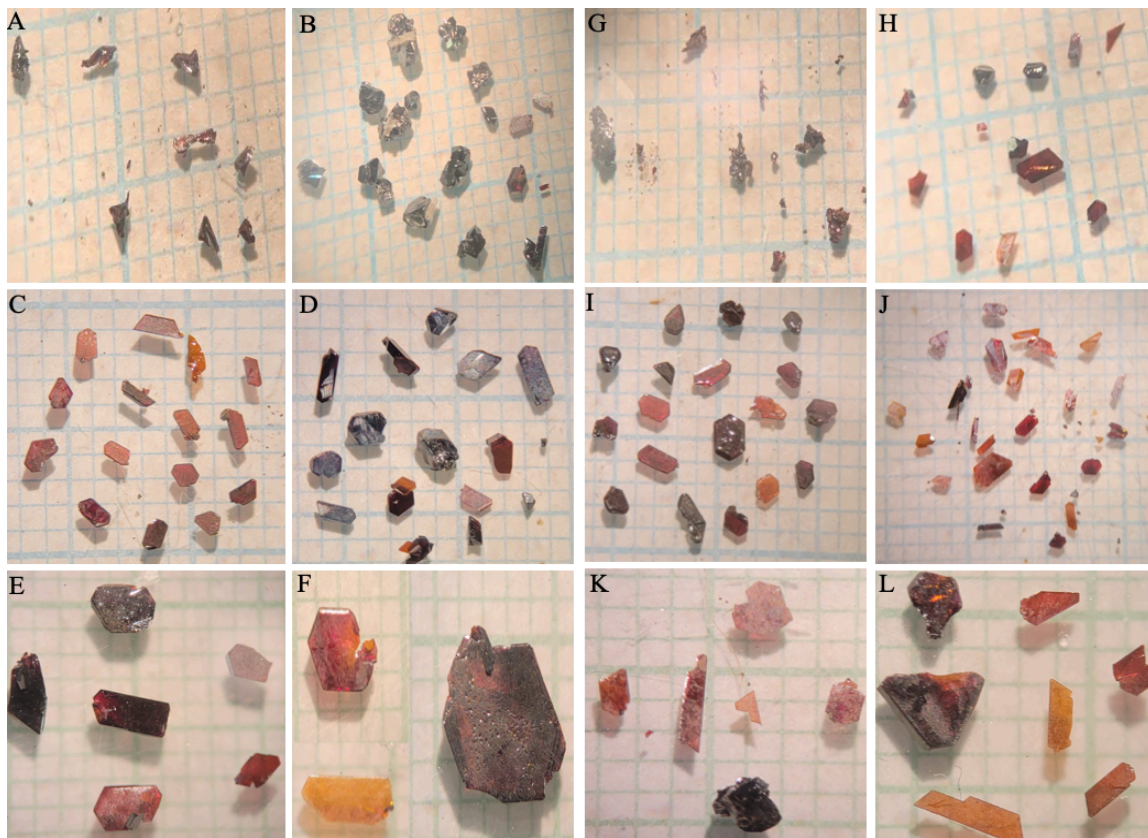


Figure 26 Optical images of A-F: ¹⁰BAs by an increasing amount of I₂; G-L: ¹¹BAs by an increasing amount of I₂. All crystals are on a scale paper with 1 mm per grid.

Here we presented crystals results with different amounts of transport agent I₂ in Figure 26. It was obvious to see the larger and larger crystals with the increasing amount of I₂. The best ¹⁰BAs crystal we got reached 5 mm and was the reddish and thin plate. By calculation, the pressure of the tube could hold was 40 atm. It was not safe to try more I₂ which would cause an explosion and leave a blank here of the results using more I₂. If we could find suitable tubes with larger diameters and calculated pressure by changing the amounts of different parameters for the future, more amount of I₂ would be experienced.

4.3.11 Mix Boron Source Manually

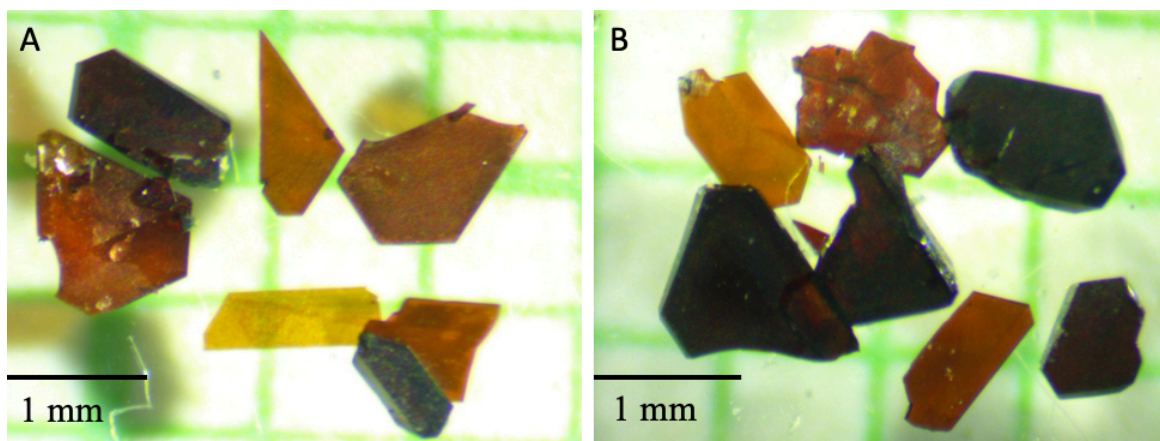


Figure 27 Optical images of (A) $^{10}\text{B}_{0.2}^{11}\text{B}_{0.8}\text{As}$; (B) $^{10}\text{B}_{0.5}^{11}\text{B}_{0.5}\text{As}$ single crystals. All crystals are on a scale paper with 1 mm per grid.

For comparison, we manually mixed the two isotope boron sources with different ratios. Here we presented the crystals results of different ratios of boron sources. We mixed isotope boron source manually using 80.1% ^{11}B and 19.9% ^{10}B , which was the same as natural boron and the crystals were marked as $^{10}\text{B}_{0.2}^{11}\text{B}_{0.8}\text{As}$. At the same time, 50% ^{11}B and 50% ^{10}B crystals (marked as $^{10}\text{B}_{0.5}^{11}\text{B}_{0.5}\text{As}$) were made for comparison. The crystals were not as big as natural boron arsenide (marked as $^{\text{nat}}\text{BAs}$) and only had 1-2 mm long with the dark reddish and transparent surfaces. The following Raman spectroscopy would show some interesting research.

4.3.12 Two Clean Methods

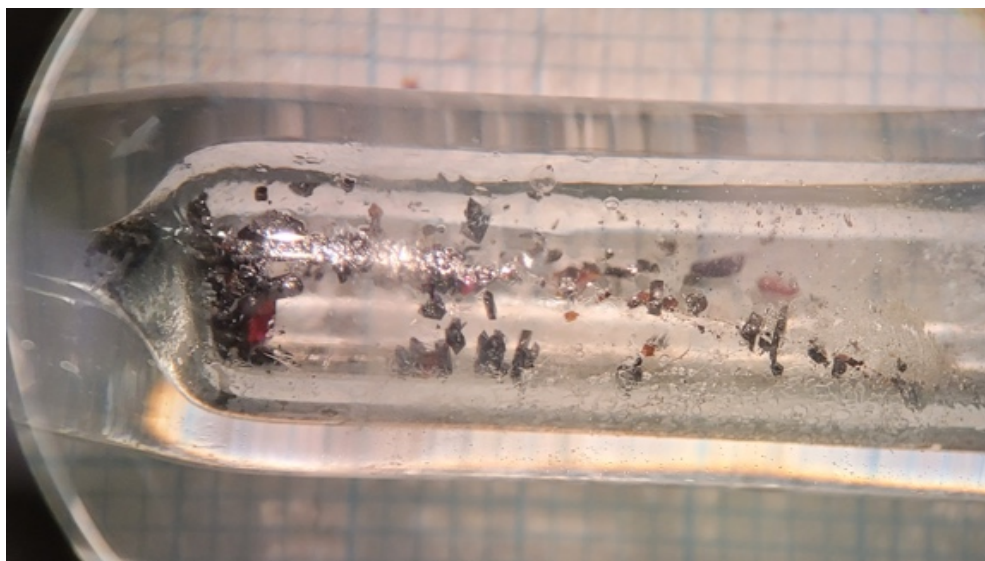


Figure 28 The tube of crystal growth side without acid washing.

Two clean methods had their advantages and the results were totally different. Figure 28 gave us the direct observation of where crystals grew. This was the optical image of the bottom of the tube at the cold temperature side. At the very bottom, we could see some reddish crystals and some crystals grew along the inner surface of different positions of the tubes.

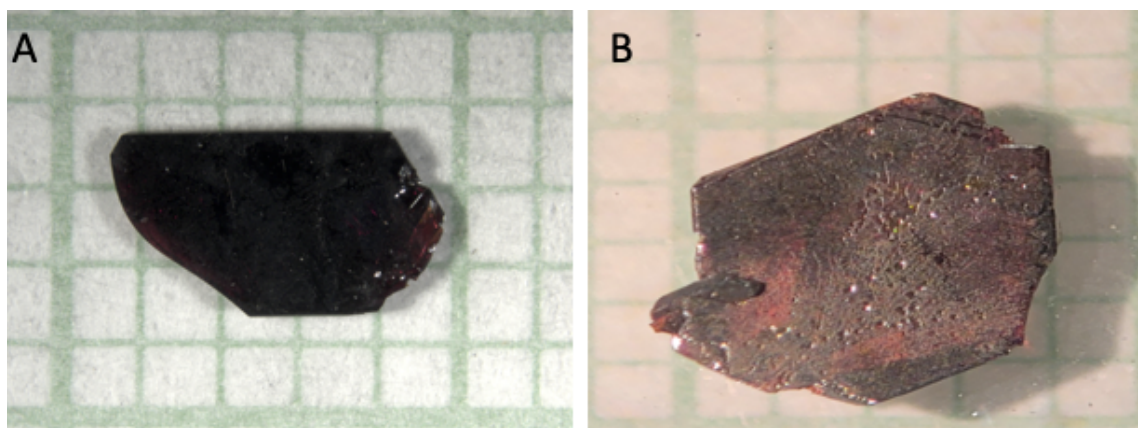


Figure 29 Optical images of (A) ^{10}BAs crystal with acid washing; (B) ^{10}BAs crystal without acid washing. Both crystals are on a scale paper with 1 mm per grid.

Figure 29 shows the surface difference of the ^{10}BAs crystals. Here two largest crystals of ^{10}BAs with two clean methods were put to compare the surface. Both were 4 – 5 mm. In Figure 29 A, the surface of the crystal with acid washing was very clean, smooth and shiny. In Figure 29 B, the surface was very irregular and had some holes on it. The acid-washed crystals were supposed to be of some damages on thermal conductivity measurement. When we polished the surface during measurement for the ones without acid washing, the thermal conductivity would be higher than before.

4.3.13 Comparison of Crystals with Different Colors and Thickness

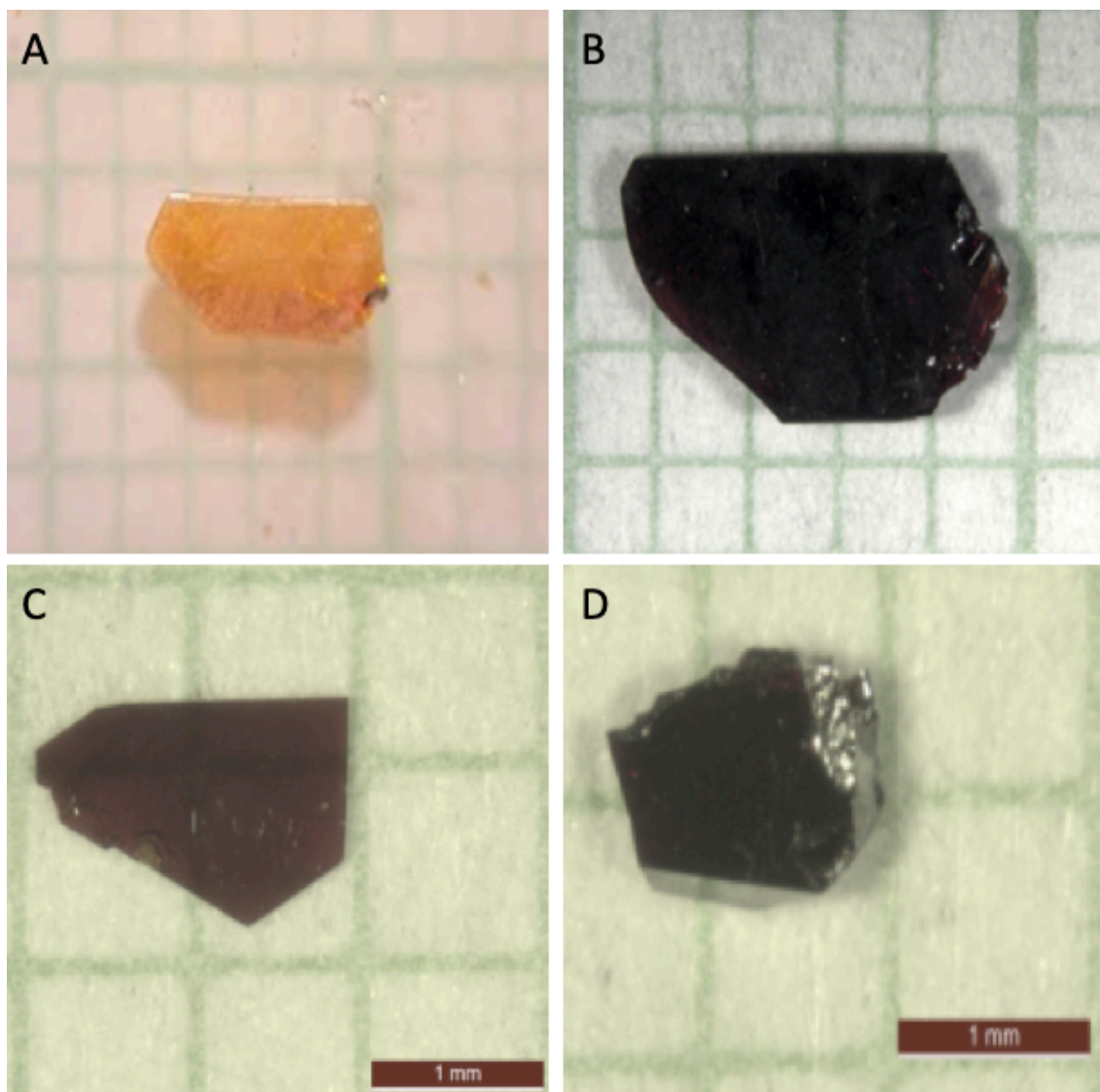


Figure 30 Optical images of ^{10}BAs with different colors. All crystals are on a scale paper with 1 mm per grid.

To summary up, we totally got four main kinds of crystals which were shown in Figure 30. The first one was the thinnest one with transparent and yellowish color in Figure 30 A. The second one was the dark reddish one with some thickness in Figure 30 B. The light could go through. The third one was reddish, transparent and very thin crystals in Figure 30 C which held the highest thermal conductivity value. The last one was grey and bulk crystal and very

thick in Figure 30 D. Four types of crystals could be grown in one batch at different positions. Usually, Figure 30 A and C were found at the very bottom of the tube and had good value for thermal conductivity measurement (the yellowish ones were easy to be broken and hard to measure). Figure 30 B was more likely to be found close to the bottom of the tube.

4.4 SEM and XRD Measurements for Crystals

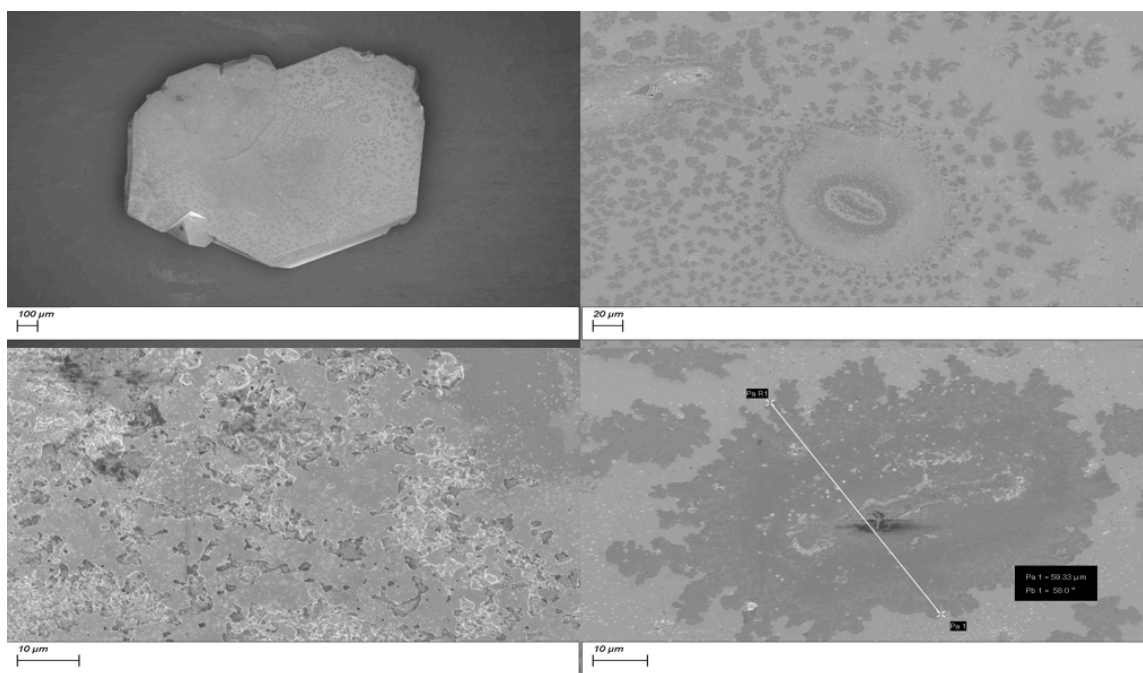


Figure 31 SEM images of ^{10}BAs crystals after cleaning with *aqua regia*. ^{10}BAs crystals with poor quality and central radiative cracks, irregular facets, and plenty of holes.

Figure 31 showed the delicate surface of ^{10}BAs after acid washing. There were two reasons for hole existence. One was from the crystal growth itself, combining different factors like impurities and growth positions made the ^{10}BAs crystals imperfect. The other one was that we used *aqua regia* to remove the impurities on the surface of the crystals and did some damages to them. Same situation as ^{11}BAs did. Even though the crystals grown with lots of cracks, the thermal conductivity was not bad as shown in Table 5. It indicated that there would have a further improvement of the crystals and thermal conductivity values.

X-ray diffraction analysis was performed on the crystals for structural characterization. The shiny flat surface with the light grey metallic luster of the as-grown crystals was found to be the (111) facet in Figure 32.

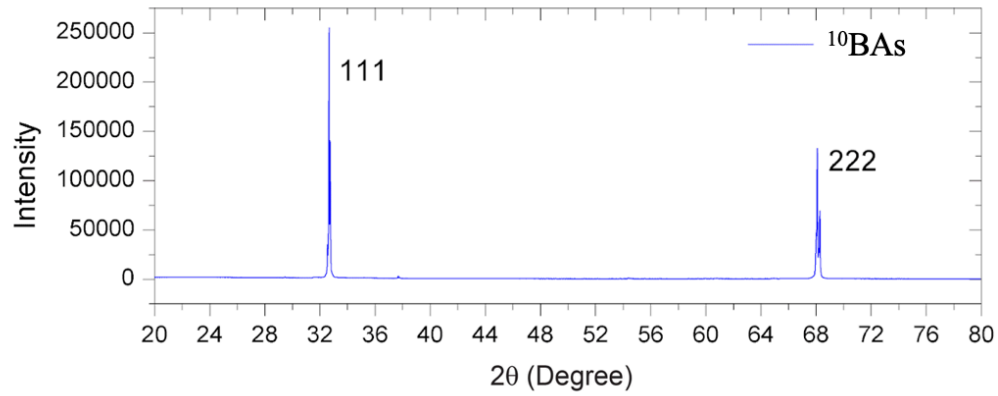


Figure 32 X-ray diffraction pattern taken from a shiny and flat surface on a selected ¹⁰BAs single crystal.

4.5 Raman Spectroscopy

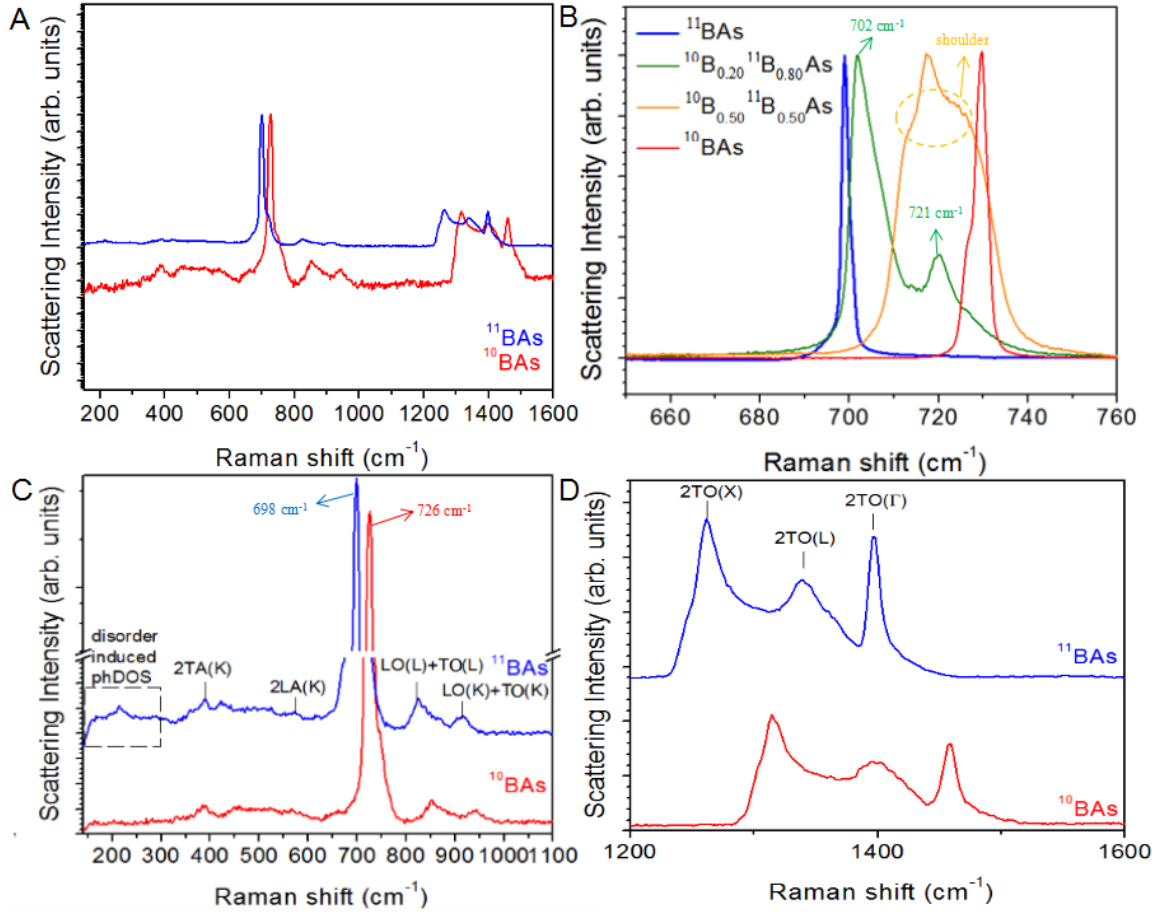


Figure 33 (A) Raman spectroscopy for ^{10}BAs and ^{11}BAs samples; (B) Expanded view of Raman spectroscopy in $650 - 760 \text{ cm}^{-1}$ for BAs samples with different boron-source ratios (pure ^{10}BAs , $^{10}\text{B}_{0.20}^{11}\text{B}_{0.80}\text{As}$, $^{10}\text{B}_{0.50}^{11}\text{B}_{0.50}\text{As}$, and pure ^{11}BAs); (C) Raman spectroscopy for ^{10}BAs and ^{11}BAs samples at low frequency; (D) Raman spectroscopy for ^{10}BAs and ^{11}BAs samples at high frequency.

This section is a reprint of my paper (Sun, H.; Chen, K.; Gamage, G. A.; Ziyadee, H.; Wang, F.; Wang, Y.; Hadjiev, V. G.; Tian, F.; Chen, G.; Ren, Z., Boron isotope effect on the thermal conductivity of boron arsenide single crystals. *Materials Today Physics* **2019**, 11 100169.)

The Raman spectra of all BAs samples shown in Figure 24 are displayed in Figure 33. BAs has only one phonon that is active in the first-order Raman scattering and seen as a single

Raman peak because of its very small LO-TO splitting [42]. In Figure 33 B the experimental Raman peak for ^{10}BAs is at 726 cm^{-1} , close to the calculated value of 729 cm^{-1} , and that of ^{11}BAs is at 698 cm^{-1} , which is also in good agreement with the calculated value of 699 cm^{-1} [42] as listed in Table 4. In the mixed $^{10}\text{B}_{(1-x)}^{11}\text{B}_x\text{As}$ ($x = 0.8$ or 0.5) samples, the frequency of this phonon changes as ω_x is approximately equal to $[(1-x)\cdot m(^{10}\text{B}) + x\cdot m(^{11}\text{B})]^{-0.5}$, where $m(^{10}\text{B})$ and $m(^{11}\text{B})$ are the masses of the respective boron isotopes and x is the portion of ^{11}B in the isotope mixture. This expression provides a good approximation to the positions of the sharp peaks in Figure 33 B. In boron mixed isotope samples with prevailing ^{11}B content, there also exists isotope disorder that relaxes the Raman selection rules, such that ^{10}B vibrations from other points of the Brillouin zone become Raman active and produce Raman bands in addition to the main Raman peak. These vibrations originate in the area of overlapping of ^{10}BAs and ^{11}BAs phonon density of states (phDOS) [42]. The overlapping of frequencies and wavevectors of ^{10}B and ^{11}B vibrations is maximized in the $^{10}\text{B}_{0.5}^{11}\text{B}_{0.5}\text{As}$ sample, which in turn produces a broad Raman band (two shoulders) around the main peak with frequency $\sim[0.5\cdot m(^{10}\text{B}) + 0.5\cdot m(^{11}\text{B})]^{-0.5}$. New modeling approaches, however, are needed to reveal completely the origin of this band.

Table 4 Comparison between experimental Raman peak position and calculated Raman peak position.

	Experimental Raman peak position / cm^{-1}	Calculated Raman peak position / cm^{-1}
^{10}BAs	726	729
^{11}BAs	698	699

The Raman scattering from phonons is a two-photon process in which incoming laser light is exciting electrons in the material, which in turn results in emission (Stokes) or absorption (Anti-Stokes) of phonons via electron-phonon coupling. Laser excitations can also produce Raman scattering from electronic excitations, known as electronic Raman scattering (ERS). It has been most notable in doped semiconductors as p-doped Si. Electronic Raman scattering has been observed also in a number of BAs samples. ERS produces a scattering background and a Fano lineshape of the Raman peaks in BAs. The appearance of ERS correlates with the hole concentration in BAs and it is found detrimental to the thermal conductivity [42]. We attribute this effect to the enhanced phonon scattering due to electron-phonon coupling. In BAs, the absence of ERS is notably manifested by the appearance of several second-order Raman bands seen clearly in Figure 33 C and D. The assignment of the harmonics and combinational Raman bands in Figure 33 is straightforward given the phonon dispersion in Ref. [42].

For BAs samples, a subtle Raman detail may provide additional information on the crystal quality. Even a slight structural disorder may relax the Raman scattering selection rules and produce a first-order Raman scattering band that resembles part or the whole phonon density of states. We present such an example in Figure 33 C (dashed rectangle) in which the phDOS of acoustic modes around 200 cm^{-1} becomes Raman active.

One of the most surprising results is that the thermal conductivity of ^{10}BAs is found consistently higher than that of ^{11}BAs although within a relatively small margin. While the difference in thermal conductivity between mixed and pure boron isotope BAs is due to the enhanced phonon-isotope scattering rate as also confirmed by a number of DFT simulations, the difference in thermal conductivity between pure isotope samples remains an enigma.

There should not be a notable difference between pure isotope BAs if only three-phonon scattering is taken into account. Indeed, all substantial terms in thermal conductivity presented as a sum over all phonon modes involve only acoustic modes as the large energy gap between acoustic and optical phonons forbids phonon-phonon scattering that involves optical (boron) modes. Recent DFT simulations have shown that four-phonon scattering is strong in BAs and have to be included in the calculations of thermal conductivity. The four-phonon scattering mechanism extends the scattering configurations to the involvement of optical, only boron contained, modes. Here we see a possibility for producing slightly higher thermal conductivity in ^{10}BAs than in ^{11}BAs : ^{10}B optical branches are shifted at higher frequencies than those of ^{11}B , which may close some scattering channels and reduce the four-phonon scattering rate in ^{10}BAs . Therefore, the pure isotope effect in BAs is giving experimental evidence for the significance of four-phonon scattering.

4.6 TDTR Measurements

Table 5 Thermal conductivity of isotopically pure BAs.

Composition	Label in Figure 24	Highest κ ($\text{W m}^{-1}\text{K}^{-1}$)	Lowest κ ($\text{W m}^{-1}\text{K}^{-1}$)	Calculated κ ($\text{W m}^{-1}\text{K}^{-1}$) [41]
^{10}BAs	Figure 24 A	1260	689	1374
^{11}BAs	Figure 24 B	1180	381	1331
$^{\text{nat}}\text{BAs}$		1160	640	1188

This section is a reprint of my paper (Sun, H.; Chen, K.; Gamage, G. A.; Ziyadee, H.; Wang, F.; Wang, Y.; Hadjiev, V. G.; Tian, F.; Chen, G.; Ren, Z., Boron isotope effect on the thermal conductivity of boron arsenide single crystals. *Materials Today Physics* **2019**, 11 100169.)

The time-domain thermoreflectance (TDTR) method [50-52] was used to measure the κ of the grown ^{10}BAs and ^{11}BAs samples. TDTR has been validated to effectively measure a material's thermal conductivities, especially for mm- or μm -scale samples, where traditional heat transport measurements cannot be applied due to the near-zero temperature difference over a short length. A set of TDTR measurements was taken following the previously reported procedure [30], where the diameters ($1/e^2$) of the pump and probe laser spots are 58 μm and 9 μm , respectively. Pump intensity was modulated by an electro-optic modulator (EOM) at a 3-MHz frequency. An 82 nm thick aluminum coating was deposited to the surface of each BAs crystal. κ values for each sample are measured on many spots and the highest and lowest values together with the calculated values are summarized in Table 5. The highest RT κ obtained from ^{10}BAs (Figure 24 A) is $1260 \pm 130 \text{ W m}^{-1} \text{ K}^{-1}$, higher than that of the $^{\text{nat}}\text{BAs}$ sample ($1160 \pm 130 \text{ W m}^{-1} \text{ K}^{-1}$) measured by the same method [30], which shows that isotopically pure ^{10}BAs exhibits slightly higher κ as compared to $^{\text{nat}}\text{BAs}$ and the measured κ agrees with the predicted value assuming 4-phonon scattering. The highest RT κ of ^{11}BAs ($1180 \pm 130 \text{ W m}^{-1} \text{ K}^{-1}$) (Figure 24 B) is smaller than that of ^{10}BAs . For comparison, we also grew BAs single crystals by hand-mixing B isotopes in different ratios. Unfortunately, the highest κ values obtained from the as-prepared $^{10}\text{B}_{0.2}^{11}\text{B}_{0.8}\text{As}$ (Figure 33 C) and $^{10}\text{B}_{0.5}^{11}\text{B}_{0.5}\text{As}$ (Figure 33 D) crystals are less than $300 \text{ W m}^{-1} \text{ K}^{-1}$, much lower than expected, which is probably due to the extra step of manual mixing of different B isotopes and some unknown

reasons, further studies are in progress. Each spot was measured at least 30 times to guarantee accuracy.

We also use TDTR measurement to measure the thermal conductivity of ^{nat}BAs. Figure 34 shows the temperature dependent κ measurements in the paper of Tian *et al.* [38], comparing the measured values with the theoretical calculations. In Figure 38, Calculated κ versus temperature for BAs (black) and diamond (green) included only three-phonon scattering (dashed lines) and both three- and four-phonon scattering (solid lines). We measured κ for diamond by TDTR (green diamonds) and measured κ 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 κ for BAs (blue and red solid lines, respectively), and reported measured κ 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 steady state and lock-in Raman measurement results were calculated by propagating random errors at 95% confidence and systematic errors. FDTR - Frequency domain thermoreflectance. This was the first time we had obtained highest κ of BAs for one single point in a sample with the value of $1160 \pm 130 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature.

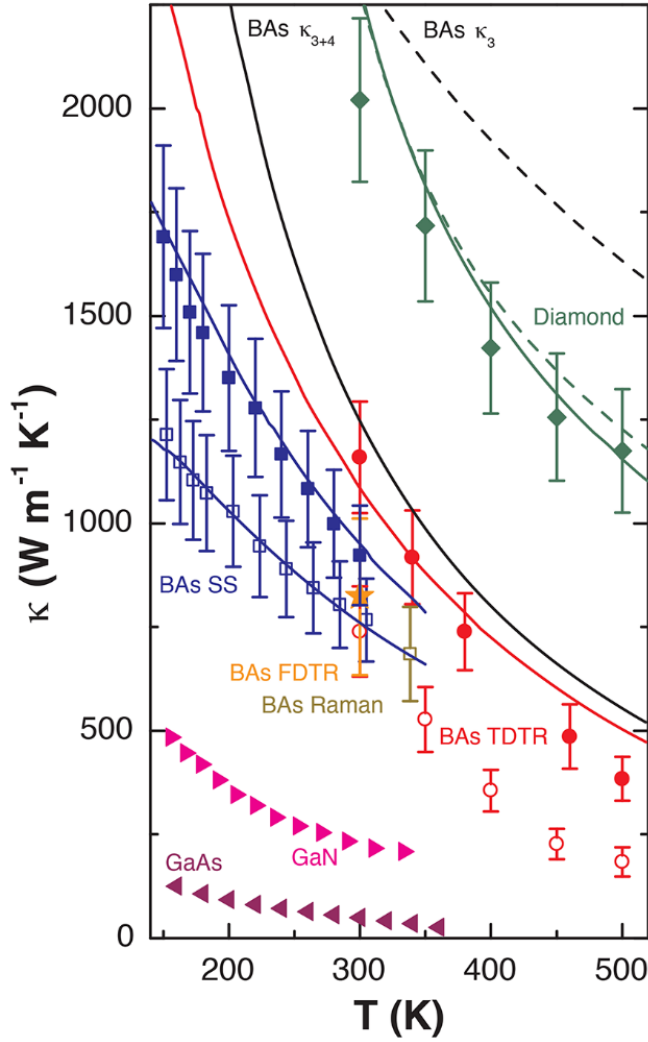


Figure 34 Measured thermal conductivity of BAs in comparison with theoretical calculations and other crystals. [38]

4.7 Heat Capacity

Temperature-dependent C_p measurement is very useful to study lattice properties, phase transitions and thermodynamic calculations. Hamid et al. [53] did high-temperature C_p measurements to calculate enthalpy (H), entropy (S) and Gibbs energy (G) of BAs. heat capacity (C_p) measurement was carried out using the Quantum Design PPMS system. The results are shown in Figure 35.

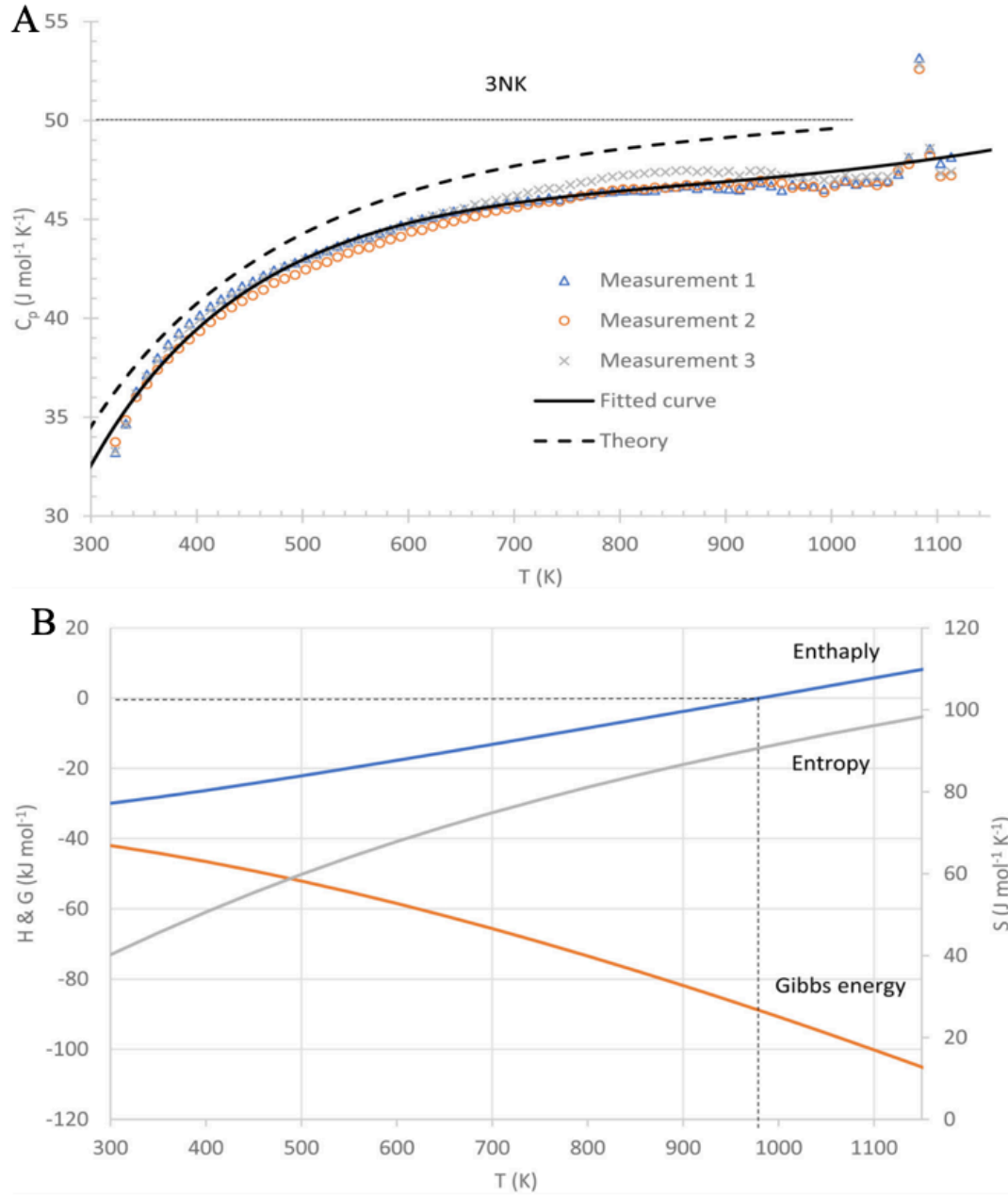


Figure 35 (A) C_p measured data and its fitted curve compared with calculated data. The uncertainty of the C_p measurement is 5%; (B) Enthalpy, entropy, and Gibbs free energy of BAs with respect to temperature. [53]

4.8 Comparison of Isotope Effect of Different High Thermal Conductivity Materials

We define the isotope effect as $P = (\kappa_{\text{pure}} / \kappa_{\text{nat}} - 1) \times 100\%$, where κ_{pure} and κ_{nat} represent the κ of enriched and natural isotope abundances, respectively. In contrast, previous

experimental efforts only reported a small isotope effect on other substances. For example, the influence was $P \approx 10\%$ for Si [54], 20% for Ge [55], 5% for GaAs [56], 15% for GaN [57], and 50% for diamond [58]. Isotope effects of 43% and 58% were measured for hBN [59] and graphene [60], respectively. However, first principles calculations for hBN [59] and graphene [61, 62] found much smaller isotope effects of only $\sim 15\%$. Furthermore, the smaller theory values for graphene were within the range of the large error bars in experiment [60].

Unlike cBN, the effect of four-phonon scattering is strong for BAs at all boron isotope compositions because three- and four-phonon scattering dominates over the entire frequency range (Figure 36 B). We theoretically and experimentally determined the isotope effect for κ at room temperature in BP, cBN and BAs. We found that the uncertainty between our measured, calculated κ and reference κ (Figure 36 A, bottom) [41] was consistent. The κ we measured were 600 ± 90 , 540 ± 50 , and 490 ± 50 W m⁻¹ K⁻¹ for ¹⁰BP (96% ¹⁰B), ¹¹BP (96% ¹¹B), and ^{nat}BP (19.9% ¹⁰B and 80.1% ¹¹B), respectively, and were 1650 ± 160 , 1660 ± 170 , and 880 ± 90 W m⁻¹ K⁻¹ for ¹⁰BN (99.3% ¹⁰B), ¹¹BN (99.2% ¹¹B), and ^{nat}BN (21.7% ¹⁰B and 78.3% ¹¹B), respectively. The phonon-isotope scattering had much smaller effects on BP and BAs (Figure 36 A).

The strong inverse correlation between the isotope effect on κ and the atomic mass ratio is driven mainly by the decrease phonon-isotope scattering rates from cBN to BP and BAs (Figure 36 B). In these three compounds, heat is carried mainly by acoustic phonons. The large relative mass difference between ¹⁰B and ¹¹B leads to considerable mass fluctuations in c^{nat}BN, ^{nat}BP, and ^{nat}BAs. With increasing pnictogen-to-boron mass ratio, the vibration amplitudes of the isotopically mixed B atoms decrease sharply for acoustic phonons throughout the Brillouin zone. In BP and BAs, the heavier pnictogens determine the acoustic

phonons, while the mass fluctuation at B sites becomes increasingly invisible, resulting in weak phonon-isotope scattering (Figure 36 B). In cBN, the small mass difference between B and N results in large displacements on the B sites for acoustic phonons, which significantly increases the phonon-isotope scattering intensity, leading to shorter phonon lifetimes and lower thermal conductivity (Figure 36 B). The small isotope effect for BAs results not only from the weak phonon-isotope scattering but also from a competition with four-phonon scattering (Figure 36 B). Under only three-phonon scattering, a 40% isotope enhancement of κ was calculated for BAs, in contrast with the much smaller P of 12% upon including four-phonon scattering. [41]

Here are some brief explanations of Figure 36. For Figure 36 A is the computed thermal conductivities κ of ideal (top) cBN and (bottom) BAs and BP crystals, compared with measured values as a function of isotope composition for three c¹⁰BN, two c¹¹BN, one c^{nat}BN, and two c^{eq}BN crystals. For cBN, the effect of oxygen impurities is indicated with the gray bars. For Figure 36 B is the comparison of various phonon scattering rates in cBN, BP, and BAs with natural B at 300 K obtained from ab initio simulations. Phonon-isotope scattering rates are inversely correlated with the pnictogen-to-boron mass ratio. Four-phonon scattering is weaker than both three-phonon and phonon-isotope scattering in cBN but exceeds phonon-isotope scattering at all frequencies of interest in BAs. For Figure 36 C is the measured and calculated κ of cBN crystals versus temperature. The solid lines are calculations for the measured B isotope compositions and the dashed lines are for 100% ¹⁰B or ¹¹B. Literature data for cBN, BP, BAs, and diamond with natural isotopes are also plotted. For Figure 36 D is the calculated κ accumulation with phonon MFP for cBN at 100, 300, and 500 K.

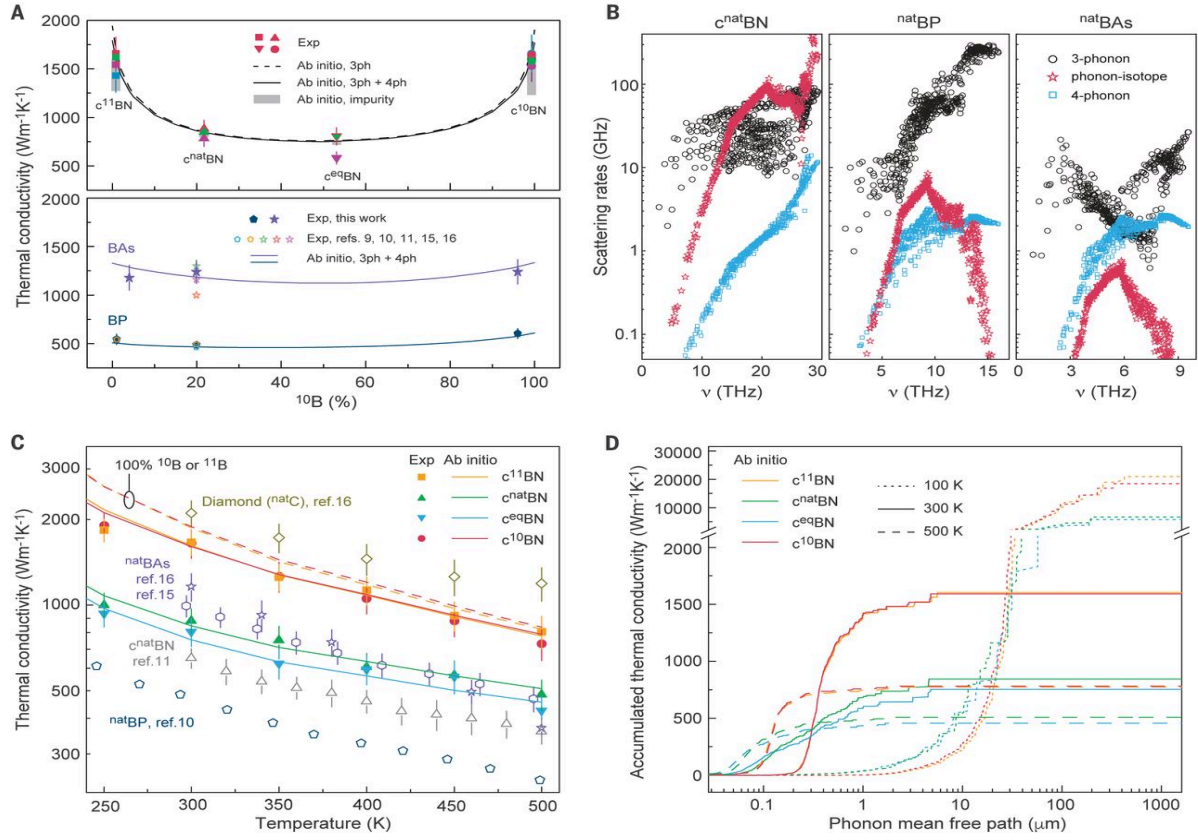


Figure 36 Isotope effect and temperature dependence of heat transport in cubic boron pnictides. [41]

CHAPTER 5 SUMMARY

Recently, theoretical calculations on the III-V compounds BAs reported exhibiting an ultrahigh room temperature thermal conductivity of $2000 \text{ W m}^{-1} \text{ K}^{-1}$ including only 3-phonon scattering processes. When 3- and 4- phonon scattering processes are involved, calculation shows the BAs room temperature thermal conductivity close to $1200 \text{ W m}^{-1} \text{ K}^{-1}$. For the isotopically pure BAs, when considering 3- and 4- phonon scattering processes, ^{10}BAs should have the largest thermal conductivity value of around $1400 \text{ W m}^{-1} \text{ K}^{-1}$ and ^{11}BAs can reach more than $1300 \text{ W m}^{-1} \text{ K}^{-1}$.

In summary, based on these predictions, I systematically researched the single crystal growth of isotopically pure BAs in this dissertation to prove and realize the thermal conductivity value which was obtained to be the maximum of $1260 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature for ^{10}BAs . The BAs samples grown from the ^{10}B source consistently exhibit higher thermal conductivity than those from ^{11}B . Both pure isotope BAs have higher thermal conductivity than that of natural or mixed isotope B. Besides the single crystal growth, I also enhanced the CVT growth by introducing different novel designs to help get better crystals. The thermal conductivity of BAs single crystals grown with different boron isotopes was characterized by TDTR and the structures were analyzed by Raman spectroscopy. Raman spectrometry displays an obvious change in the phonon frequency of the isotopically pure BAs and indicates that B isotopes affect the phonon interactions.

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LIST OF PUBLICATIONS

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