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High-Pressure Synthesis and Thermal Transport Properties of Polycrystalline BAs$_x$ *

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Polycrystalline BAs$_x$ (x = 0.80–1.10) compounds with different boron-to-arsenic elemental molar ratios were synthesized by a high-pressure and high-temperature sintering method. Compared with other ambient-pressure synthesis methods, high pressure can significantly promote the reaction speed as well as the reaction yield. As the content of arsenic increases from $x = 0.91$ to 1.10, the thermal conductivity of BAs$_x$ gradually increases from 53 to 65 W·m^{-1}·K^{-1}. Furthermore, the temperature dependence of thermal conductivities of these samples reveals an Umklapp scattering due to the increasing phonon population. This work provides a highly efficient method for polycrystalline BAs synthesis.

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As Moore's law stated, when the price is constant, the number of transistors on an integrated circuit will be doubled every two years.[1] Although Moore's law was coming to an end in 2016, it does not prevent the density of transistors on the chip from increasing.[2] The more the transistors integrated per unit area of a chip, the higher the temperature they get. Therefore, high thermal conductivity materials are needed to promote the integrated circuit cooling and thus improve the device performance. For instance, graphite films with a maximum thermal conductivity value about 1900 W·m^{-1}·K^{-1} is widely used in smart phones for chip cooling.[3] In addition, the most commonly used heat dissipation material in industry is copper (thermal conductivity κ = 400 W·m^{-1}·K^{-1} at 300 K).[4] Silver has the highest thermal conductivity (κ = 434 W·m^{-1}·K^{-1} at 300 K) among all the metals,[4] but until now, materials with a thermal conductivity exceeding silver are rare. Diamond is the material with the highest thermal conductivity, but it is too expensive to use for massive industrial applications.[5]

In the past several years, BAs has been suggested as an interesting candidate for the high thermal conductivity materials. On the basis of first-principles calculations in 2013, Lindsay *et al.*[6] predicted that BAs has an extremely high thermal conductivity (over 2000 W·m^{-1}·K^{-1} at room temperature) similar to that of diamond. The calculation revealed that the ultrahigh thermal conductivity of BAs is mainly attributed to the large frequency gap between its acoustic and optic phonons and the bunching of its acoustic phonon dispersions, thus losing two important scattering channels, namely three acoustic phonons scattering and two acoustic phonons combining with one optic phonon scattering.[6] In 2015, Lv *et al.*[7] grew BAs single crystal by the chemical vapor transport (CVT) method but the measured thermal conductivity was only ∼200 W·m^{-1}·K^{-1}. By means of first-principles calculations and x-ray chemical analysis, that work attributed only one-tenth of the predicted value to the 2.8% arsenic vacancy defect. In 2017, Feng *et al.*[8] predicted that BAs has stronger four-phonon scattering than that of diamond, which reduces the predicted thermal conductivity value from 2200 to 1400 W·m^{-1}·K^{-1} at room temperature. In 2018, three groups independently grew high-quality BAs single crystal by the CVT method, the maximum thermal conductivity reached 1300 W·m^{-1}·K^{-1},[9–11] which is very close to that predicted by Feng *et al.*[8] and strongly confirmed the ultrahigh thermal conductivity of BAs.

To date, only the CVT method has been reported in the literature to grow BAs single crystals owing to the volatility of arsenic and the high melting point of boron.[12] Considering that the CVT method is prone to the absence of arsenic,[7] we believe that a high-pressure closed reaction environment can effectively avoid element volatilization, thus ensuring the ideal stoichiometric ratio. In this work, we have synthesized BAs$_x$ polycrystals by a high-pressure and high-

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temperature (HPHT) sintering method. We found that the HPHT method can not only significantly increase the reaction speed from 12 hours at ambient pressure to 30 min under high pressure, but also enhance the BAs yield. Though the boron and arsenic do not fully react according to stoichiometric ratio at the pressures that our high-pressure apparatus could provide ($\sim$5 GPa), the yield ratio of BAs to As impurity phase with HPHT enhances from 1.3 : 1 to 3 : 1.[13] In addition, we measured the thermal conductivities of BAs_x polycrystals with different molar ratios of boron to arsenic element, and found that, with the increasing As composition from 0.91 to 1.10, the thermal conductivity of BAs_x increases from 53 to 65 $\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$. To our knowledge, this is the first time that the thermal transport properties of polycrystalline BAs_x have been reported, although the measured thermal conductivity values are much less than those of single-crystal BAs samples most probably due to the grain boundary and/or defect scattering.

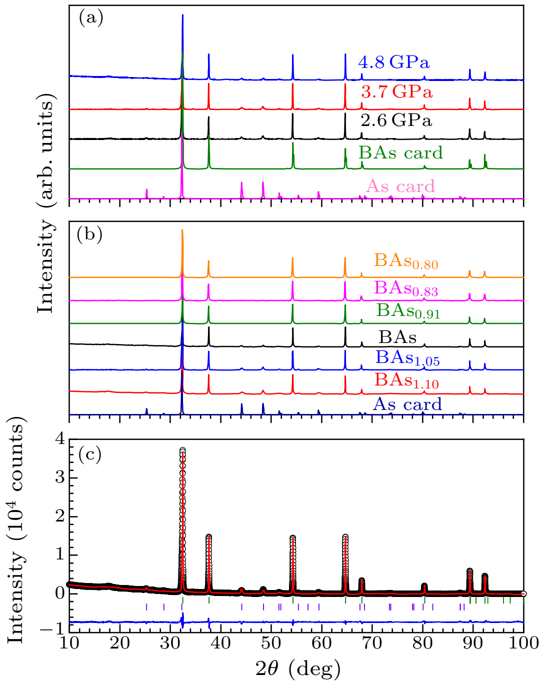

Fig. 1. (a) XRD patterns of the BAs sample with nominally equal molar ratio of boron to arsenic at different pressures. (b) XRD patterns of the BAs_x samples with different mixed molar ratios of boron to arsenic at room temperature. (c) Structure refinement results of the BAs sample with equal proportion of boron and arsenic. The observed (black circles), calculated (red line), and difference (blue line) patterns are shown. The top green ticks and bottom grape ticks show the allowed Bragg reflections with space group $Fm\bar{3}m$ (BAs) and $R\bar{3}m$ (As), respectively.

The polycrystalline BAs_x was synthesized using high purity (>99.99%) boron powders and arsenic polycrystalline lump as starting materials. First, appropriate stoichiometric boron and arsenic recipes with total mass of about 8 g were ball milled for four hours through high energy ball milling under argon protection in a SPEX Sample Prep 8000D Mixer/Mill. Second, the obtained powders were filled into a boron nitride capsule with 7 mm in diameter and 9 mm in length, and then loaded into a cubic-anvil-type high-pressure apparatus for HPHT treatment (2.6 to 4.8 GPa at 1273 K) for 30 min. The sample quality and crystal structure were characterized by powder x-ray diffraction (XRD) using a Huber diffractometer (Cu $K_{\alpha1}$ radiation, 40 kV, 300 mA). The diffraction data were collected in the angle (2θ) range from 10° to 100° with steps of 0.005°. Crystallographic parameters and phase fraction were analyzed by the Rietveld full-profile refinement using the GSAS program.[14] The thermal conductivity was calculated via $\kappa = D \cdot C_{\mathrm{p}} \cdot \rho$, where D is the thermal diffusivity, C_{p} is the heat capacity, and ρ is the measured density based on the Archimedes drainage method. For the thermal diffusivity tests, the samples were cut into 6-mm-diameter and 1.2-mm-thickness discs, and then coated with a thin layer of amorphous carbon. The thermal diffusivities were measured using a Linseis LFA 1000 apparatus in the presence of high-purity He (the diagram is shown in Fig. 2(a)). $\mathrm{BAs}_{0.80}$ and $\mathrm{BAs}_{0.83}$ samples are too fragile and could not be cut into 6-mm-diameter disc, so we have not measured their thermal conductivities. The scanning electron microscope (SEM) images were recorded using an S4800 SEM (Hitachi, Japan). The carrier type, carrier mobility and electrical resistivity were measured on Van der Pauw devices with an instrument model in HL5500PC at a constant magnetic field of 0.5 Tesla.

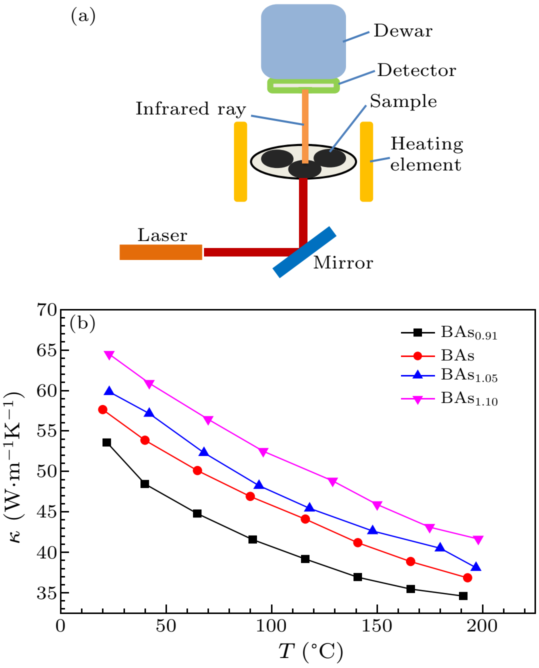

Fig. 2. (a) The diagram of the laser flash analysis (LFA). This apparatus calculates the thermal diffusion coefficient by detecting the heating time with an infrared detector. (b) Thermal conductivities of BAs_x samples with different molar ratios of boron to arsenic.

Some representative XRD patterns of BAs_x polycrystals prepared under high pressures are shown in

Figs. 1(a) and 1(b). Compared to the standard XRD cards of pure As and BAs, one clearly finds that the main phase of BAs is succeeded for preparation, while a small amount of As impurity phase is observed in some compositions. Figure 1(a) shows the as-made BAs (in nominal) at different pressures from 2.6 to 4.8 GPa, which is the maximum pressure for our HPHT apparatus. With increasing pressure, the diffraction intensity of impurity arsenic decreases slightly. This means that a higher pressure is favorable to crystallizing a more stoichiometric BAs sample, probably due to the smaller volatilization of As. We thus set the pressure at 4.8 GPa to prepare BAs_x with different As contents varying from $x = 0.80$ to 1.10, to clarify how the elemental molar ratios between arsenic and boron affect the yields of BAs. As shown in Fig. 1(b), as the As content gradually decreases, the diffraction intensity of As peaks considerably decreases. In particular, at $x = 0.91$, the impurity phase of As cannot be distinguished in the XRD pattern.

In order to determine the molar ratio of BAs to As impurity phase in the HPHT product with nominally equal proportion of boron and arsenic during the synthesis, we performed the Rietveld refinement on the XRD data using the GSAS program. The Rietveld refinement results are shown in Fig. 1(c), and the refined structural parameters of BAs and As are listed in Table 1. The lattice parameter of BAs we obtained is 4.7759 Å, which is very close to the reported value (4.777 Å).[15] According to the refined weight fraction (see Table 1), the molar ratio of BAs to As obtained in the current high-pressure product is about 3 : 1. In comparison, the molar ratio is only 1.3 : 1 for the reported synthesis of BAs photoelectrode heating at 1073 K for 12 h.[13] Obviously, the present high-pressure synthesis can prominently reduce the reaction time to 30 min and increase the production yield from 56.5% to 75%. High pressure is thus a more efficient method to prepare polycrystalline BAs, taking into account that pressurization can greatly accelerate the reaction rate by reducing the interatomic distances and increasing the contact area of reactants.

Table 1. Refined structure parameters of BAs and As at room temperature. BAs: space group $Fm\bar{3}m$, atomic sites As1 4*c* (0, 0, 0), B1 4*a* (0.25, 0.25, 0.75). As: space group $R\bar{3}m$, atomic sites As2 6*c* (0, 0, *z*).

Parameter	BAs and As
a_{BAs} (Å)	4.77590(1)
As2 (z)	0.2297(2)
$U_{\mathrm{iso}}(\mathrm{B1})/(100\,\mathrm{Å}^2)$	0.0266(12)
$U_{\mathrm{iso}}(\mathrm{As1})/(100\,\mathrm{Å}^2)$	0.00519(10)
$U_{\mathrm{iso}}(\mathrm{As2})/(100\,\mathrm{Å}^2)$	0.0416(14)
χ^2	0.2771
$R_{\mathrm{wp}}(\%)$	0.27
$R_{\mathrm{p}}(\%)$	0.13
Weight fraction (BAs)	0.77488
Weight fraction (As)	0.22512

To explore the relationship between the thermal conductivity and the molar ratio of boron to arsenic in our BAs_x samples, the thermal conductivity was measured. As shown in Fig. 2(b), thermal conductivities of $\mathrm{BAs}_{0.91}$, BAs, $\mathrm{BAs}_{1.05}$ and $\mathrm{BAs}_{1.10}$ samples decrease with increasing temperature, indicating Umklapp scattering due to increasing phonon population.[16] At 300 K, as the molar ratio of arsenic to boron increases from 0.91 to 1.10, the related thermal conductivity increases from 53 to 65 $\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$. On the one hand, as the proportion of arsenic increases, in general, the vacancy density of As in BAs_x samples decreases, therefore resulting in higher thermal conductivity for the As-enriched samples. On the other hand, the thermal conductivity of arsenic polycrystal ($\kappa = 27\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ at 300 K)[17] is higher than the thermal conductivity of boron polycrystal ($\kappa = 7\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ at 300 K),[18] resulting in the fact that the overall thermal conductivity of BAs_x compounds increases as the As content increases. Since our HPHT BAs_x samples are a mixture of B, As and BAs polycrystals, it is inferred that the intrinsic BAs polycrystal should have a thermal conductivity slightly higher than the measured values by LFA. If we consider that the components in the boron arsenide samples are connected in parallel to participate in the thermal transport process, given the thermal conductivity of As and B polycrystal, the intrinsic thermal conductivity of BAs polycrystal for the BAs sample is about 85 $\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ calculated by the formula $n_{\mathrm{total}} \cdot \kappa_{\mathrm{measured}} = n_{\mathrm{As}} \cdot \kappa_{\mathrm{As}} + n_{\mathrm{B}} \cdot \kappa_{\mathrm{B}} + n_{\mathrm{BAs}} \cdot \kappa_{\mathrm{BAs}}$ (where n denotes the molar ratio of each component with $n_{\mathrm{total}} = n_{\mathrm{As}} + n_{\mathrm{B}} + n_{\mathrm{BAs}}$). Note that the values of our polycrystalline BAs_x compounds are still far less than that of the single crystalline BAs. This is temporarily attributed to the strong grain boundary and/or defect scattering in polycrystals.

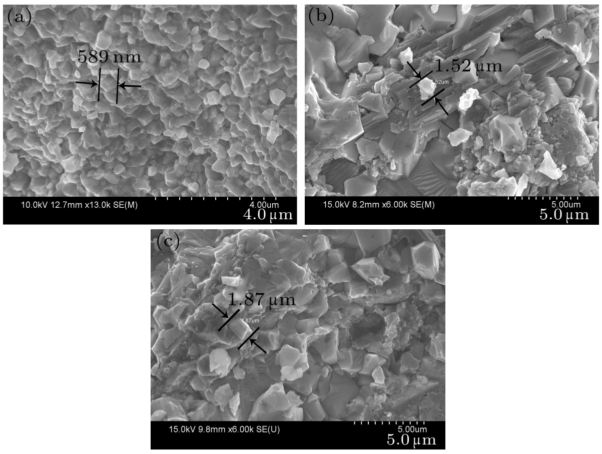

Fig. 3. SEM images of (a) $\mathrm{BAs}_{0.91}$, (b) BAs, and (c) $\mathrm{BAs}_{1.10}$.

To get deeper insight into the thermal conductivity data for different samples, we performed scanning electronic microscopy measurements and investigated the grain size distributions for BAs_x. The natural fracture surface of the boron arsenide samples were selected for the morphology comparison between different samples. The SEM images of the three samples ($\mathrm{BAs}_{0.91}$, BAs and $\mathrm{BAs}_{1.10}$) are displayed in Figs. 3(a), 3(b) and 3(c), respectively. For the $\mathrm{BAs}_{0.91}$ sample, the grain size is relatively uniform and about hundreds of nanometers. However, for the BAs and BAs$_{1.10}$ samples, the grain size is from dozens of nanometers to a few microns. In general, the larger the grain size in polycrystals, the less the influence of grain boundary scattering on the thermal conductivity. This is one of the reasons why the thermal conductivity of As-rich BAs$_x$ samples is slightly higher than that of the BAs$_{0.91}$ sample.

Furthermore, to shed more light on the transport mechanisms of the HPHT BAs$_x$ samples, we carried out the Van der Pauw measurements to investigate the carrier type, carrier mobility and electrical resistivity. The transport properties of the boron arsenide samples were measured at room temperature using square-shaped Van der Pauw patterns with sizes of 2–2.5 mm. The carrier concentration N_S, carrier mobility μ_mob, and electrical resistivity ρ are presented in Table 2. The electrical resistivities of BAs, BAs$_{1.05}$ and BAs$_{1.10}$ samples we measured are 0.76 mΩ·cm, 0.40 mΩ·cm and 0.29 mΩ·cm, respectively, while the reported electrical resistivity of BAs single crystal is 33 mΩ·cm.[19] Given that the electrical resistivity of As polycrystal and B polycrystal is 0.032 mΩ·cm and 10^3 mΩ·cm, respectively,[17,20] the much smaller resistivity of BAs$_x$ polycrystals is mainly due to the small resistivity of As impurity. The carrier concentrations of BAs, BAs$_{1.05}$ and BAs$_{1.10}$ are $4.66\times10^{20}\,\mathrm{cm}^{-3}$, $4.33\times10^{20}\,\mathrm{cm}^{-3}$ and $-1.10\times10^{23}\,\mathrm{cm}^{-3}$, respectively. Interestingly, we note that with the increasing As composition, the carrier type of BAs$_x$ switches from initially p-type to n-type, which may be due to contributions from excessive As in the As-rich product. The carrier mobility of BAs and BAs$_{1.05}$ polycrystals is very close to that of BAs single crystal ($\mu_\mathrm{mob} = 25.9\,\mathrm{cm}^2\cdot\mathrm{V}^{-1}\cdot\mathrm{s}^{-1}$ at 300 K),[9] but the carrier mobility of BAs$_{1.10}$ polycrystal is only $0.198\,\mathrm{cm}^2\cdot\mathrm{V}^{-1}\cdot\mathrm{s}^{-1}$, which may indicate that the rapid increasing of carrier concentration can strongly suppress the carrier mobility.[21]

Table 2. The carrier concentration N_S, carrier mobility μ_mob, and electrical resistivity ρ of BAs, BAs$_{1.05}$ and BAs$_{1.10}$.

	N_S (cm^{-3})	μ_mob (cm^2·V^{-1}·s^{-1})	ρ (mΩ·cm)
BAs	4.66×10^{20}	17.6	0.76
BAs$_{1.05}$	4.33×10^{20}	36.5	0.40
BAs$_{1.10}$	-1.10×10^{23}	0.198	0.29

In summary, we have prepared polycrystalline BAs$_x$ (x = 0.80–1.10) compounds with different elemental molar ratios of B and As by an HPHT sintering method. Though the reaction between B and As is inevitably reversible, we find that the HPHT method could greatly enhance the reaction speed and significantly increase the BAs yield of the product. The thermal conductivities of BAs$_{0.91}$, BAs, BAs$_{1.05}$ and BAs$_{1.10}$ samples increase from 53 to 65 W·m^{-1}·K^{-1} as the molar ratio of As to B increases, and the thermal conductivities of all the samples decrease with increasing temperature, indicating Umklapp scattering due to increasing phonon population. Although the thermal conductivity values of our polycrystalline BAs$_x$ compounds are much less than that of single crystalline BAs, we expect that the HPHT sintering method for high yield BAs polycrystal synthesis would pave the way for applications of BAs$_x$ compounds.

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