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Universal and Solution-Processable Precursor to Bismuth Chalcogenide Thermoelectrics

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Thermoelectric materials convert thermal power into electrical power and vice versa. In practice, thermoelectric coolers and power generators are made by alternately arranging n- and p-type thermoelectric materials into modules. Thermoelectric devices have several advantages over traditional coolers and power generators such as no moving parts, no working fluid (e.g., steam or freon substitutes), and noiseless operation. Despite these attractive qualities, poor energy conversion efficiency and high cost have limited their widespread use.[1] The vast majority of thermoelectric research focuses on increasing device efficiency.[2−8] In contrast, there is little published work focused on decreasing the production cost of thermoelectric modules.[9,10] Here we present a solution-processing technique that could enable low-cost production of thermoelectric devices with efficiencies comparable to conventionally fabricated devices. Specifically, we describe a universal precursor that can be made to form any compound of the form $Bi_2Te_{3-x}Se_x$. This is of particular interest for applications near room temperature, for which $Bi_2Te_{3-x}Se_x$ is the best performing n-type thermoelectric material in use today.[1,11−13]

Solution-processed materials are extremely attractive due to their compatibility with established high-throughput manufacturing techniques such as casting, printing, and dip-coating. These benefits have made solution-processing an attractive emerging production route to low-cost electronics[14] and photovoltaics.[15] Our method involves hydrazine-mediated reduction of a bulk semiconductor to create a solution-processable precursor, in analogy to prior work[16,17] (*Caution: hydrazine is highly toxic and should be handled with extreme care*). These precursors are typically formed by mixing the metal-chalcogenide of interest with elemental chalcogen and hydrazine. This yields a mixture that can be solution-processed and then thermally decomposed into a polycrystal of its parent metal-chalcogenide. Using this chemistry, a number of applications have been demonstrated such as transistors, phase change memory, and photovoltaics.[16−18] This paper demonstrates the first use of this approach for thermoelectric applications.

Our route to the entire family of bismuth chalcogenide thermoelectric compounds is to first create a universal precursor based on bismuth sulfide (Bi_2S_3). This precursor is made by reacting bulk Bi_2S_3, sulfur, and distilled hydrazine (see Supporting Information). This results in a black viscous liquid that is a precursor suspension. Thermogravimetric analysis of the precursor indicates that the decomposition process is complete by 250 °C (Figure 1a). X-ray diffraction (XRD) of the precursor before and after decomposition (Figure 1b) also illustrates the structural metamorphosis. XRD analysis indicates that the decomposition product is a polycrystalline mixture of Bi_2S_3 and elemental Bi.

We demonstrate the extreme utility of this precursor by manipulating its decomposition product into pure-phase compounds of the generalized form, $Bi_2Te_{3-x}Se_x$. This is done by simply mixing appropriate amounts of selenium and/or tellurium with the precursor after its formation. During decomposition of these mixtures, the sulfur in the film is removed by the formation of gaseous byproducts. We use this approach to create the entire family of bismuth chalcogenide thermoelectric compounds: Bi_2Te_3, Bi_2Te_2Se, Bi_2TeSe_2, and Bi_2Se_3 (Figure 1b). This approach is similar to the preparation of precursors for

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(1) Bell, L. E. *Science* **2008**, *321*, 1457.
(2) Boukai, A. I.; Bunimovich, Y.; Tahir-Kheli, J.; Yu, J. K.; Goddard, W. A.; Heath, J. R. *Nature* **2008**, *451*, 168.
(3) Harman, T. C.; Taylor, P. J.; Walsh, M. P.; LaForge, B. E. *Science* **2002**, *297*, 2229.
(4) Heremans, J. P.; Jovovic, V.; Toberer, E. S.; Saramat, A.; Kurosaki, K.; Charoenphakdee, A.; Yamanaka, S.; Snyder, G. J. *Science* **2008**, *321*, 554.
(5) Hochbaum, A. I.; Chen, R. K.; Delgado, R. D.; Liang, W. J.; Garnett, E. C.; Najarian, M.; Majumdar, A.; Yang, P. D. *Nature* **2008**, *451*, 163.
(6) Hsu, K. F.; Loo, S.; Guo, F.; Chen, W.; Dyck, J. S.; Uher, C.; Hogan, T.; Polychroniadis, E. K.; Kanatzidis, M. G. *Science* **2004**, *303*, 818.
(7) Poudel, B.; Hao, Q.; Ma, Y.; Lan, Y. C.; Minnich, A.; Yu, B.; Yan, X.; Wang, D. Z.; Muto, A.; Vashaee, D.; Chen, X. Y.; Liu, J. M.; Dresselhaus, M. S.; Chen, G.; Ren, Z. *Science* **2008**, *320*, 634.
(8) Venkatasubramanian, R.; Siivola, E.; Colpitts, T.; O'Quinn, B. *Nature* **2001**, *413*, 597.
(9) Wang, R. Y.; Feser, J. P.; Lee, J. S.; Talapin, D. V.; Segalman, R.; Majumdar, A. *Nano Lett.* **2008**, *8*, 2283.
(10) Zimmer, A.; Stein, N.; Terryn, H.; Boulanger, C. *J. Phys. Chem. Solids* **2007**, *68*, 1902.
(11) Kutasov, V. A.; Lukyanova, L. N.; Vedernikov, M. V. In *Thermoelectrics Handbook Macro to Nano*; Rowe, D. M., Ed.; CRC Press: Boca Raton, FL, 2006.
(12) Scherrer, H.; Scherrer, S. In *Thermoelectrics Handbook Macro to Nano*; Rowe, D. M., Ed.; CRC Press: Boca Raton, FL, 2006.
(13) Snyder, G. J.; Toberer, E. S. *Nat. Mater.* **2008**, *7*, 105.
(14) Forrest, S. R. *Nature* **2004**, *428*, 911.
(15) Jayachandran, M.; Chockalingam, M. J.; Murali, K. R.; Lakshmanan, A. S. *Mater. Chem. Phys.* **1993**, *34*, 1.
(16) Mitzi, D. B.; Kosbar, L. L.; Murray, C. E.; Copel, M.; Afzali, A. *Nature* **2004**, *428*, 299.
(17) Mitzi, D. B. *Adv. Mater.* **2009**, *21*, 3141.
(18) Milliron, D. J.; Raoux, S.; Shelby, R.; Jordan-Sweet, J. *Nat. Mater.* **2007**, *6*, 352.

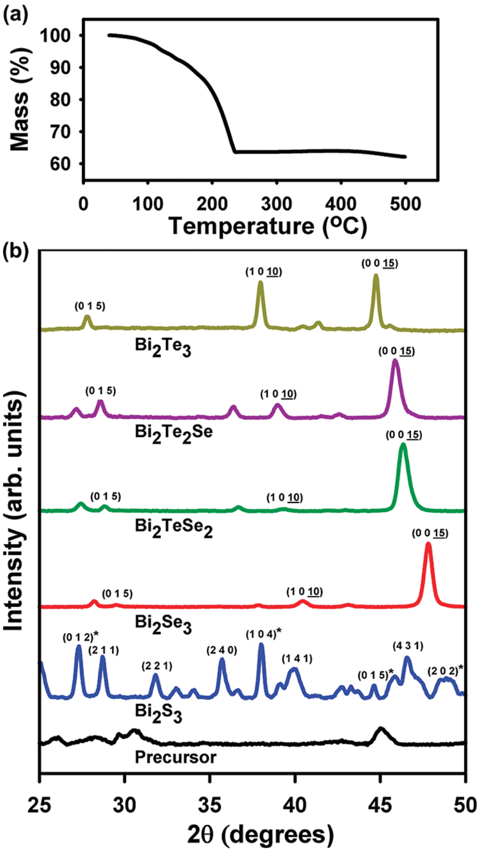

Figure 1. (a) Thermogravimetric analysis of the dried Bi_2S_3 precursor. The sample was heated at a rate of 2 °C/min. (b) X-ray diffraction patterns of the Bi_2Te_3, Bi_2Te_2Se, Bi_2TeSe_2, Bi_2Se_3, and Bi_2S_3 films and the undecomposed Bi_2S_3 precursor. The Bi_2S_3 film is a mixture of Bi_2S_3 and elemental Bi (peaks marked with *). All of the observed peaks in the X-ray diffraction patterns can be indexed by their respective JCPDS file, but for reasons of clarity, only select peaks are labeled. An expanded view of this figure that better illustrates the low intensity peaks is available in the Supporting Information. Peaks were indexed using JCPDS files: Bi, 01-085-1329; Bi_2S_3, 03-065-2435; Bi_2Se_3, 00-033-0214; Bi_2TeSe_2, 01-089-2007; Bi_2Te_2Se, 00-029-0248; Bi_2Te_3, 00-015-0863.

$CuInSe_2$ and $CuInTe_2$ which are made by mixing multiple chalcogenidometallate clusters.[19,20]

Thin films for characterization and transport measurements were made by spin-coating the precursors onto substrates. Bi_2Se_3 films were made by annealing the precursor at 250 °C for ∼30 min. To promote incorporation of tellurium into the compounds, the precursors for Bi_2Te_3, Bi_2Te_2Se, and Bi_2TeSe_2 were annealed at 400 °C for ∼30 min (when annealed at 250 °C, elemental Te peaks were observed in the XRD patterns). We note that the low decomposition temperatures of these precursors make this process compatible with flexible substrates such as high temperature plastics (e.g., kapton). The films were generally 300−800 nm thick after annealing. Rutherford backscattering spectrometry and energy dispersive X-ray spectroscopy confirm the presence of the indicated elements and the absence of residual sulfur (see Supporting Information).

The crystal structure of Bi_2Te_3 (which is isomorphous with Bi_2Se_3) is conveniently described as alternating layers of hexagonal monatomic planes.[12] The layers alternate as $-Te^{(1)}-Bi-Te^{(2)}-Bi-Te^{(1)}-$. In the case of $Bi_2Te_{3-x}Se_x$, Se preferentially substitutes into the $Te^{(2)}$ sites; after the $Te^{(2)}$ sites are filled, Se randomly substitutes into $Te^{(1)}$ sites.[12] The intense (0 0 $\underline{15}$) peaks in the XRD patterns (Figure 1b) indicate that our polycrystalline films preferentially orient with the *c*-axis perpendicular to the substrate. The precursor particle size and mass loss during decomposition cause the resultant films to possess roughness and porosity (see Supporting Information). The Bi_2Se_3 films were much smoother than the tellurium-containing compounds and had grain sizes in the range of ∼50 to 500 nm. Although the Bi_2Te_3, Bi_2Te_2Se, and Bi_2TeSe_2 films were rougher, their grains were much more developed and about an order of magnitude larger.

Having established this new chemical route to the bismuth chalcogenide family of compounds, we characterized their transport characteristics relevant to thermoelectric performance. The thermoelectric figure of merit, ZT, characterizes the energy conversion efficiency of a thermoelectric material and is given by the expression, $ZT = S^2\sigma T/k$. The symbols S, σ, k, and T denote the Seebeck coefficient (or thermopower), electrical conductivity, thermal conductivity, and absolute temperature, respectively. The best materials used in thermoelectric devices today are bulk semiconductors with ZT ∼ 1. Figure 2 shows the room temperature values of S, σ, and k for the films prepared in this work. The electrical conductivity and thermopower of the films were measured using top-contact parallel electrodes while the thermal conductivity was measured using the 3ω method.[21,22] Detailed measurement procedures and experimental uncertainty discussion are available in the Supporting Information.

All compounds exhibit a negative sign of thermopower, which indicates that these films are n-type semiconductors. The n-type behavior indicates that our synthesis generally leads to chalcogen-rich films. Even without extrinsic dopants, our films have remarkably high electrical conductivity; the electrical conductivities of optimally doped thermoelectric materials[12] are only a factor of ∼2 greater than our undoped Bi_2Se_3 and Bi_2TeSe_2. As the film changes from Bi_2Se_3 to Bi_2TeSe_2 to Bi_2Te_2Se, we observe a decrease in electrical conductivity and increase in thermopower, which is consistent with previous reports of the same materials prepared by high-temperature melt-processing.[23] The thermal conductivity of our materials is quite low and comparable to many plastics such as Teflon (k = 0.35 W m^{-1} K^{-1}).[24] To some extent the unusually low thermal conductivity can be explained by film porosity and crystal grain orientation. Nonetheless, it should be noted that these thermal conductivities are 2−3 times lower than a recent report[7] that demonstrates enhanced

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(19) Milliron, D. J.; Mitzi, D. B.; Cope, M.; Murray, C. E. *Chem. Mater.* **2006**, *18*, 587.

(20) Mitzi, D. B.; Copel, M.; Murray, C. E. *Adv. Mater.* **2006**, *18*, 2448.

(21) Borca-Tasciuc, T.; Kumar, A. R.; Chen, G. *Rev. Sci. Instrum.* **2001**, *72*, 2139.

(22) Cahill, D. G. *Rev. Sci. Instrum.* **1990**, *61*, 802.

(23) Fuschillo, N.; Bierly, J. N.; Donahoe, F. J. *J. Phys. Chem. Solids* **1959**, *8*, 430.

(24) Mills, A. F. *Basic Heat & Mass Transfer*; Prentice-Hall: Upper Saddle River, NJ, 1999.

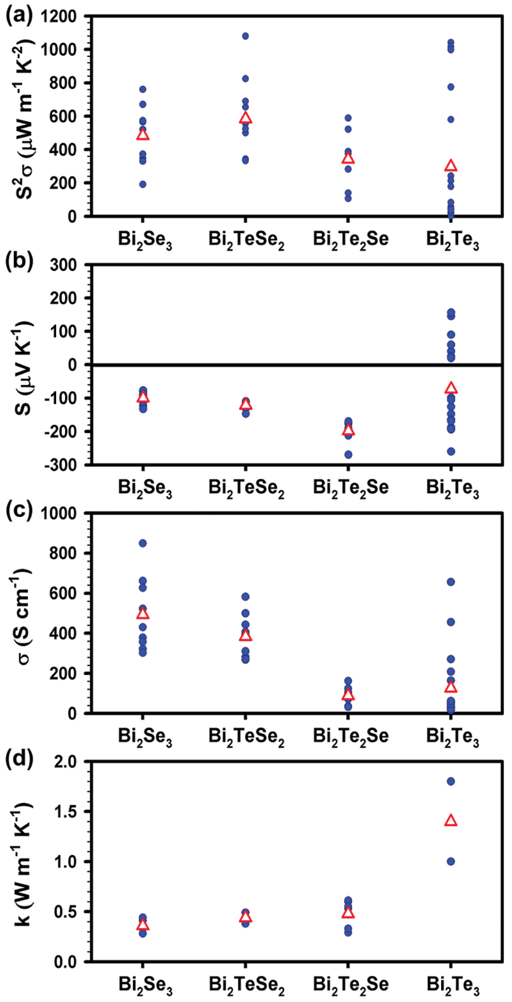

Figure 2. Room temperature transport properties of the films. The filled circles are measurements of individual samples and the open triangles indicate the average value. The measurement uncertainty on individual samples is approximately 7%, 30%, and 30% for S, σ, and k, respectively.

ZT in nanostructured Bi_2Te_3-based alloys via a reduction in thermal conductivity.

While we observe clear and consistent trends in the transport properties, sample-to-sample variations are considerable. It is well-known that metal-chalcogenide materials can accommodate a range of off-stoichiometric compositions and that this type of precursor chemistry can access these off-stoichiometric compositions.[17,18] Bi_2Te_3 exhibits the most variable transport properties, which we attribute to variations in tellurium content (see Supporting Information). Early reports[25] on Bi_2Te_3 show that varying Te content by just 3% can cause large changes in thermopower and electrical conductivity that are consistent with our observed property variations.

Based upon our room temperature transport measurements, we calculate a ZT of 0.40, 0.39, and 0.22 for Bi_2Se_3, Bi_2TeSe_2, and Bi_2Te_2Se, respectively. To our knowledge, this is the highest reported ZT for a fully solution-processed material with broad substrate compatibility.[9,10] These values are even more notable since no steps have been taken to optimize carrier concentration or alloying. As a result of film anisotropy and measurement directionality (cross-plane for thermal conductivity, in-plane for thermopower and electrical conductivity) we note that these values may overestimate ZT. Ideally all measurement directions would have been the same; however, measurements of in-plane thermal conductivity[21,26] and cross-plane thermopower[27] are pragmatically difficult. The ratio $k_{\text{in-plane}}/k_{\text{cross-plane}}$ of single crystal Bi_2Te_3[28,29] ranges from 1.5−2.5 and represents the maximum effects of anisotropy; this indicates that our ZT is at most overestimated by a factor of 2.5. We anticipate that anisotropy (and hence transport properties) will depend on film thickness due to changes in the substrate's overall influence on grain orientation. Since ZT depends only on the ratio, σ/k, the presence of film porosity does not introduce artifacts.

This work demonstrates a simple and universal, wet chemistry approach to prepare films of bismuth chalcogenide materials relevant to thermoelectric applications. There remain several opportunities for further work on these precursors for thermoelectric research. $Bi_{2-x}Sb_xTe_3$ is a commonly used p-type thermoelectric material[13] and could possibly be made by combining our precursor with the precursor for Sb_2Te_3.[17,30] Also, the thermoelectric performance of our n-type $Bi_2Te_{3-x}Se_x$ materials could be improved by tuning their carrier concentration. This could be done by introducing dopants and/or controlling the film's chalcogen content (either excess or deficiency). Lastly, recent reports have demonstrated that this type of precursor chemistry can be used to create nanocomposites.[17,30,31] This is especially promising because many of the best-performing thermoelectric materials are nanocomposites.[3,6−8] By further building on the foundation established here for precursor-derived bismuth chalcogenide films, thermoelectric materials that are simultaneously low-cost and high-efficiency could become a reality.

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Supporting Information Available: Detailed experimental procedures, supporting discussion, and additional figures (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Satterthwaite, C. B.; Ure, R. W. *Phys. Rev.* **1957**, *108*, 1164.

(26) Kurabayashi, K.; Asheghi, M.; Touzelbaev, M.; Goodson, K. E. J. Microelectromech. Syst. **1999**, *8*.

(27) Zeng, G. H.; Zide, J. M. O.; Kim, W.; Bowers, J. E.; Gossard, A. C.; Bian, Z. X.; Zhang, Y.; Shakouri, A.; Singer, S. L.; Majumdar, A. J. Appl. Phys. **2007**, *101*.

(28) Fleurial, J. P.; Gailliard, L.; Triboulet, R.; Scherrer, H.; Scherrer, S. *J. Phys. Chem. Solids* **1988**, *49*, 1237.

(29) Kaibe, H.; Tanaka, Y.; Sakata, M.; Nishida, I. *J. Phys. Chem. Solids* **1989**, *50*, 945.

(30) Kovalenko, M. V.; Scheele, M.; Talapin, D. V. *Science* **2009**, *324*, 1417.

(31) Tangirala, R.; Baker, J. L.; Alivisatos, A. P.; Milliron, D. J. Angew. Chem., Int. Ed. **2010**, in press.