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A Novel Synthesis of Polycrystalline Bismuth Telluride

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With the planned phase-out of chlorofluorocarbon (CFC) refrigerants within this decade, considerable interest has developed in alternative refrigeration and cooling technologies. It is possible that alternatives to CFC liquid−gas expansion systems such as solid-state thermoelectric devices could easily develop into a substantial future technology.

Thermoelectric cooling devices based upon the Peltier effect have been used for many years in specialized applications. At present, these units do not achieve the performance currently available with CFCs. Typically, CFC systems operate near 40% of Carnot efficiency while the best thermoelectric systems reach only about 10% of Carnot efficiency.[1] Nonetheless, a significant thermoelectric cooling industry based on the Peltier effect has already developed.

Certain semiconductor materials, particularly bismuth telluride-based alloys, are the materials of choice in modern thermoelectric coolers. These alloys are commonly made through metallurgical melt processing,[2] i.e., by comelting appropriate amounts of the pure elements in sealed vessels at temperatures above 600 °C, mixing, and then subjecting the melts to controlled cooling. This batch-processing approach is both equipment and labor intensive, while thermoelectric elements cut from the solidified alloys tend to be somewhat fragile. An alternative approach, amenable to *automated* production, is the fabrication of thermoelectric elements from polycrystalline powders.[3,4] These powders are commonly obtained by crushing the solidified melts and sieving the resultant particulate material. Polycrystalline thermoelectric elements offer improved structural integrity, although they generally exhibit some degradation in thermoelectric performance due to the anisotropic nature of the matieral.

As a step toward the development of an alternative route for the preparation of polycrystalline, Bi/Te-based thermoelectric materials, this publication describes a novel synthesis of the parent compound, bismuth telluride, Bi_2Te_3. This method provides a simple, two-step process for the preparation of fine-particle bismuth telluride. The process features the room-temperature coprecipitation of a bismuth telluride precursor in aqueous media, followed by its conversion to Bi_2Te_3 through hydrogen reduction. For scale-up to production levels, the coprecipitation reaction lends itself to continuous powder synthesis through the use of a chemical flow reactor.[5]

A very recent publication by Groshens et al. describes another approach to the synthesis of Bi_2Te_3 and related materials by means of elimination reactions conducted in hexane at −30 °C.[6]

Experimental Section

Materials and Procedures. Bismuth trioxide, Bi_2O_3 (99.95%), tellurium metal (99.999+%), and nitric acid were obtained from commercial sources and used without further purification. Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37950-1610.

Synthesis of the Bi_2Te_3 Precursor. A bismuth/tellurium solution is prepared by dissolving 0.44 mol of tellurium in 300 mL of 6 M nitric acid with warming to about 60 °C and stirring. Since toxic nitrogen oxides are released during this process, it must be performed in an efficient fume hood. After Te dissolution is complete, an amount of bismuth trioxide, Bi_2O_3, calculated to give Bi:Te = 2:3 is slowly and quantitatively added. The final clear, colorless Bi/Te solution is cooled to 25 °C.

A solution consisting of 370 mL of concentrated aqueous ammonia diluted with 370 mL of distilled water is added to dropwise to the Bi/Te solution at 25 °C with rapid stirring. The resultant fine, white precipitate is separated by centrifugation, thoroughly washed three times with distilled water, and dried over silica gel. The equivalent spherical particle size estimated from BET surface area measurements[7] is 27 nm. Anal. Calcd for the Bi_2Te_3 precursor, $Bi_2Te_3O_9{\cdot}xH_2O$ ($x = 1$): Bi, 43.39; Te, 39.76. Found: Bi, 43.88; Te, 39.35.

Synthesis of Bi_2Te_3. Weighed quantities of the dried precursor powder are heated to 275 °C in 0.1 MPa (1 atm) of flowing hydrogen for 12 h. Calculated weight loss for the conversion of $Bi_2Te_3O_9{\cdot}xH_2O$ ($x = 1$) into Bi_2Te_3 is 18.69%. For the chemically analyzed precursor, the measured weight loss upon H_2 reduction at 275 °C is 18.78%.

Powder Identification. Anal. Calcd for the black powder resulting from hydrogen reduction of the precursor, Bi_2Te: Bi, 52.19; Te, 47.78. Found: Bi, 52.67; Te, 48.46. A comparison the X-ray powder diffraction pattern of this compound with that of bismuth telluride is shown in Figure 1. The overall yield is 92% of that expected from the amounts of Bi_2O_3 and Te used.

Differential thermal analysis (DTA) of both commercially obtained and chemically synthesized Bi_2Te_3 powders was performed with automated commercial instrumentation, using an alumina reference powder under a N_2/5% H_2 atmosphere. Both materials exhibited simple, sharp melting behavior at 582.1 and 582.8 °C, respectively.

The Bi_2Te_3 powder exhibits a typical equivalent spherical particle size, estimated from BET measurements, of about 100 nm.

Results and Discussion

A consideration of the reaction chemistry relevant to the coprecipitation of Bi and Te described herein leads to the proposition that the white precursor is most likely a hydrated, very intimate mixture of bismuth and tellurium oxides. The precursor weight loss and analytical results are consistent with the formulation $Bi_2O_3{\cdot}3TeO_2{\cdot}xH_2O$ where $x = 1$. Alternatively, the more complex formulation $Bi_2Te_3O_y(OH)_z{\cdot}xH_2O$ is also a possibility and cannot be ruled out entirely. However, for either formulation, the end result of chemical reduction by hydrogen will be bismuth telluride.

A schematic representation of the two-step chemical process for the simplest case follows:

$$2Bi^{3+} + 3TeO_3^{2-} \xrightarrow[H_2O]{OH^-} \underset{\text{white precursor}}{Bi_2O_3{\cdot}3TeO_2{\cdot}xH_2O} \tag{1}$$

$$Bi_2O_3{\cdot}3TeO_2{\cdot}xH_2O \xrightarrow[275\ ^\circ C]{H_2} \underset{\text{black}}{Bi_2Te_3} + (9 + x)H_2O \tag{2}$$

In summary, a novel, simple coprecipitation route to a bismuth telluride precursor has been developed. The precursor is reduced by hydrogen, to fine-particle (100 nm) bismuth telluride.

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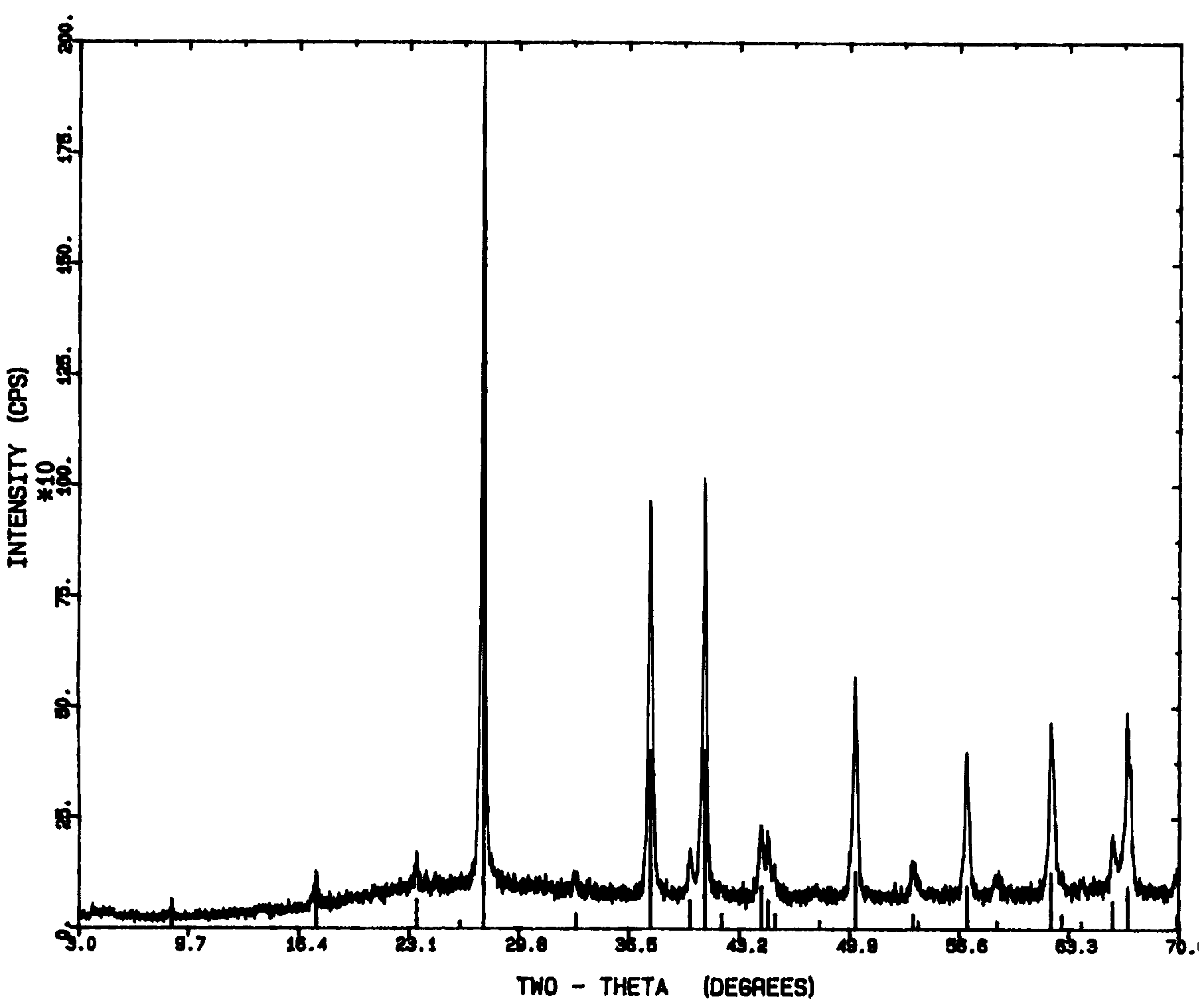

Figure 1. X-ray powder diffraction pattern for chemically generated bismuth telluride. The reference pattern from the Joint Committee on Powder Diffraction Standards, No. 15-863, for bismuth telluride is depicted with vertical lines.

Identification of the product as bismuth telluride is supported by elemental and X-ray analyses as well as by melting point data.

This approach offers several advantages over alternative processes for generating polycrystalline Bi_2Te_3 powders. These advantages include (1) precursor synthesis at 25 °C, in aqueous solution, from commonly available chemicals, (2) easy scale-up to continuous precursor production using a chemical flow reactor, (3) bismuth telluride synthesis with >90% yield at a temperature some 350 °C lower than that used in melt processing, and (4) elimination of the crushing and sieving steps necessary after melt processing, since the new approach yields a fine powder directly.

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