Synthesis of Polycrystalline Bismuth Telluride by a Metal–Organo Complex Method

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Introduction

Bismuth, telluride, Bi_2Te_3, represents the parent compound of a family of technologically important semiconductor alloys which are used extensively in modern thermoelectric coolers. These alloys are normally made through metallurgical melt processing, i.e., the comelting of appropriate elements in an evacuated, sealed tube, followed by mixing and cooling of the melt.[1] The process is both equipment and labor intensive, and thermoelectric elements cut from the solidified alloys tend to be somewhat fragile. On the other hand, thermoelectric elements made from polycrystalline powders exhibit improved structural integrity, and are amenable to fabrication by automated production methods. These powders are commonly produced from the solidified melts by crushing and sieving.[2,3] Recently, Ritter reported a novel synthesis of polycrystalline bismuth telluride wherein bismuth and tellurium are coprecipitated as oxides in aqueous solution. The coprecipitated oxides are converted directly to fine Bi_2Te_3 powder through hydrogen reduction.[4] In another recent publication, Groshens and coworkers described a different approach to the synthesis of Bi_2Te_3 and related materials by means of elimination reactions conducted in hexane at −30 °C.[5]

The use of metal–organo complexes as a route to mixed-cation oxide powders has been extensively reported in the literature.[6–9] In essence, polybasic hydroxy acids are used to form water-soluble complexes of metal ions. Reportedly, these complexes are "fixed" in their state of homogeneous distribution during the formation of a solid, polymer-like composite, derived from concomitant esterification reactions with an added polyhydroxy alcohol. The desired metal oxides are generated from this composite through its controlled pyrolysis in an oxidizing environment. The categories of oxide powders prepared by this technique include titanates, zirconates, chromites, niobates, ferrites, and molybdates. Generally, these powders can be used directly for many advanced applications, thus eliminating the need for the repetitive ball-milling and calcining procedures commonly used in conventional processing.

In this paper, we report an unusual use of the metal–organo complex method to synthesize a *non-oxide* material, bismuth telluride, in fine-powder form.

Experimental Section

Materials and Procedures. Bismuth trioxide, Bi_2O_3 (99.55%), tellurium metal (99.999+%), DL-tartaric acid, nitric acid, and ethylene glycol were obtained from commercial sources and used as received. Water was doubly distilled.

X-ray powder diffraction (XRPD) and BET surface area measurements were conducted using standard, commercial instrumentation. Chemical analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN 37950-1610.

Synthesis of Bi_2Te_3. All operations described herein are conducted in an efficient fume hood to carry off toxic nitrogen oxides and possible organic pyrolysis products. Although we did not experience any excursions in our work, effective safety shielding is strongly prescribed. Since the synthesis involves solutions containing nitric acid and ethylene glycol, there is the possibility of forming *explosive* nitrate esters such as ethylene glycol dinitrate.[10]

Tellurium metal (0.06 mol) is dissolved in 300 mL of 6 M nitric acid at 25 °C, followed by the addition of 0.02 mol of bismuth trioxide. Upon complete dissolution of the oxide, 0.10 mol each of tartaric acid and ethylene glycol are added.

The metal ion–tartaric acid–glycol solution is heated slowly to about 90 °C, whereupon a vigorous evolution of nitrogen oxides takes place. After about 20 min, the gas evolution subsides, and the heating is continued near 100 °C to reduce the solvent volume. As the solution approaches about one-sixth of its original volume, the heat is reduced to minimize frothing. Subsequently, when essentially all of the solvent has been removed, a mixed-metal ion/polymer-like composite is formed with the concomitant evolution of additional nitrogen oxides. Further heating in air to about 350 °C produces a *char* which eventually undergoes ignition. Upon the cessation of fumes, the resultant cake is blanketed with nitrogen and cooled to room temperature. This procedure is designed to ensure complete removal of carbonaceous materials and to minimize the oxidation of the bismuth telluride. The caked product is pulverized and subsequently reduced in 0.1 MPa (1 atm) of hydrogen at 350 °C for 6 h.

Powder Identification. Elemental analysis of the black powder after hydrogen reduction is as follows. Calcd for Bi_2Te_3: Bi, 52.19; Te, 47.78. Found: Bi, 52.38; Te, 48.53. A comparison of its X-ray powder diffraction pattern with that of bismuth telluride in the literature is shown in Figure 1. With care in controlling the heating, yields of Bi_2Te_3 in the range 95–99%, based on the amounts of Bi_2O_3 and Te used, can be realized.

Typical equivalent spherical particle size estimated from BET surface area measurements is 100 nm.

Results and Discussion

The stages of the reaction chemistry of bismuth and tellurium species with the complexing agent are thought to be similar to those suggested originally by Pechini and elaborated upon later by Lessing.[6,9] Thus, it is postulated that the tartaric acid initially forms complexes with both the bismuth and tellurium moieties in solution. Both the carboxylic acid groups and the hydroxy groups of tartaric acid may participate in complex formation.[11] At temperatures above 100 °C, reactions between uncomplexed carboxylic acid groups and ethylene glycol lead to organic esters with the concomitant elimination of water. Heating to about 250 °C eliminates residual solvent and promotes the formation of an organic matrix, which is probably the result of polyesterification reactions. The matrix encapsulates the bismuth and tellurium species, thus producing a composite. X-ray powder diffraction on the composite suggests that the inorganic material present is predominantly Bi_2TeO_5, with possibly some Bi_2Te_3. A multiplicity of additional weak peaks in the pattern may arise from complex Bi–Te oxides which cannot be identified readily.

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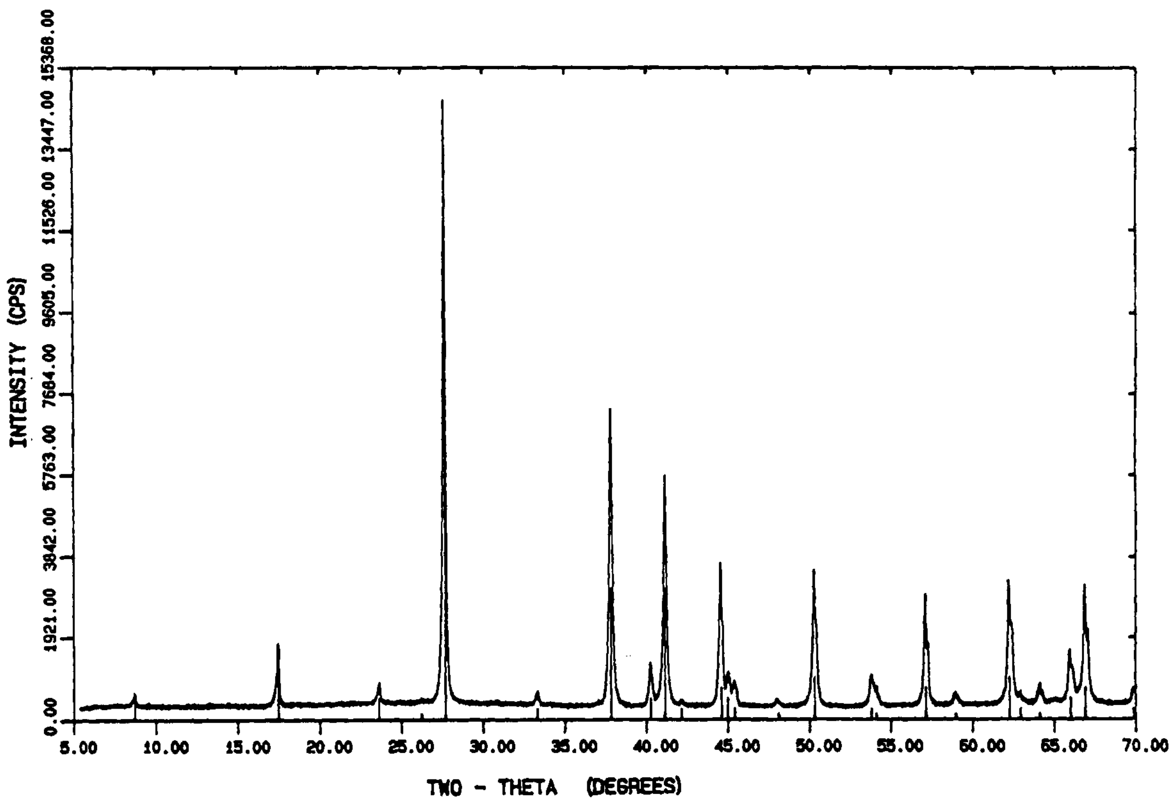

Figure 1. XRPD of powder after reduction at 350 °C in hydrogen for 6 h. Vertical lines depict reference Bi_2Te_3 pattern from the Joint Committee on Powder Diffraction Standards, JCPDS, Entry No. 15-863.

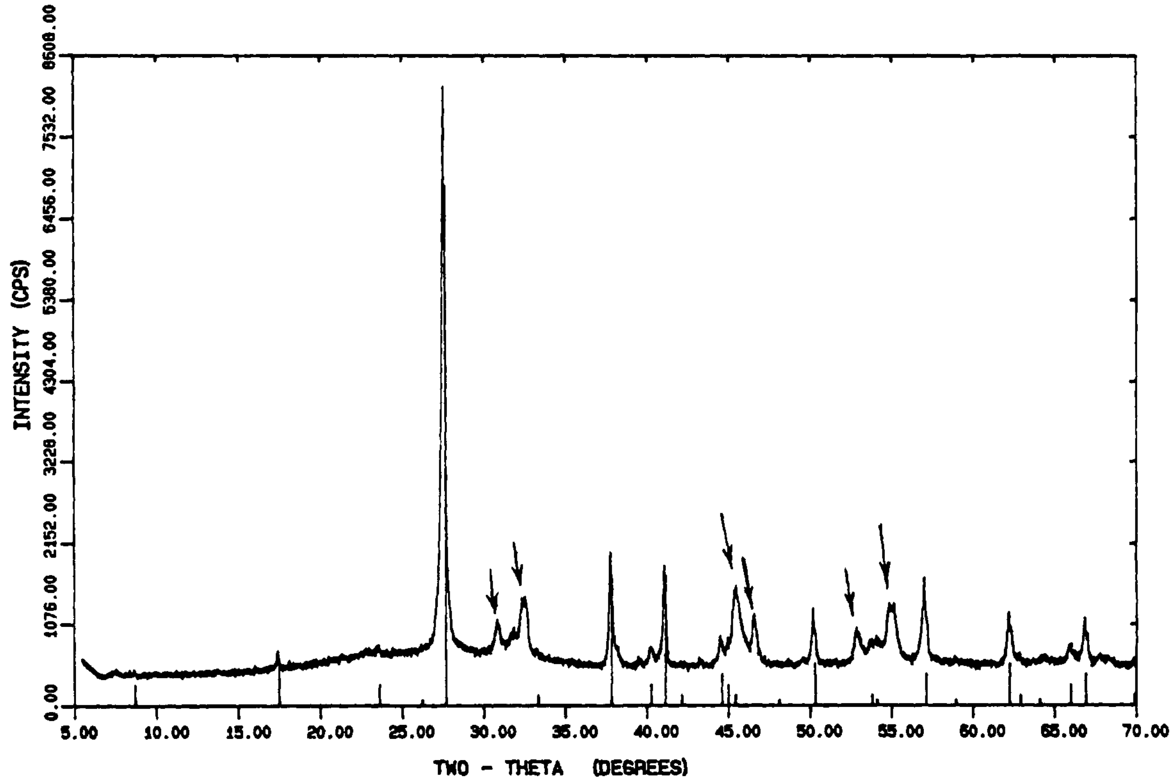

Figure 2. XRPD pattern of powder thermally processed in air and N_2. Vertical lines depict reference Bi_2Te_3, JCPDS, Entry No. 15-863. Arrows designate prominent peaks for Bi_2TeO_5, from JCPDS Entry No. 38-420.

As this composite is heated further in air, to about 350 °C, part of the residual organic material participates in the reduction of Te^{4+} to Te^{2-}, thus facilitating the formation of major amounts of bismuth telluride. The remainder of the organic matter is most probably eliminated as CO_2 and H_2O during subsequent ignition in the presence of atmospheric oxygen. In a final step, air is displaced with nitrogen to minimize the further formation of bismuth and tellurium oxides.

Conceptually, it should be possible to control these steps to obtain pure Bi_2Te_3. However, we found it difficult to determine the exact point at which to stop the oxidative processes. As a practical matter, it was decided to prolong heating in air and accept some oxidation of the Bi_2Te_3, so as to ensure the complete removal of carbonaceous matter. Both Bi_2Te_3 and Bi_2TeO_5 are easily identified in the XRPD of powder subjected to sequential thermal processing under air and N_2 as shown in Figure 2. Other oxides of tellurium and possibly of bismuth also may be present, but these are insufficiently crystallized to be identified by XRPD. Nevertheless, all of these oxides are readily converted to Bi_2Te_3 within a few hours in H_2 at 350 °C, as is shown by the XRPD in Figure 1. The metal−organo complex approach to Bi_2Te_3 is less labor intensive than the coprecipitation route published earlier[4] in that it avoids the separation, washing, and drying of precipitates.

In summary, bismuth telluride is synthesized by a simple metal−organo complex method using tartaric acid as the complexing agent in the presence of ethylene glycol. The identity of the product as Bi_2Te_3 is supported by chemical analysis and X-ray diffraction data.

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