Synthesis of Fine-Powder Polycrystalline Bi−Se−Te, Bi−Sb−Te, and Bi−Sb−Se−Te Alloys

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Introduction

Solid state thermoelectric cooling devices based upon the Peltier effect are being considered as alternatives to systems requiring gaseous chlorofluorocarbon refrigerants and as modular cooling units for electronic circuits. Materials for the active elements in modern thermoelectric coolers are selected from a family of bismuth telluride-based alloys having the general compositions $Bi_2Se_xTe_{3-x}$, $Bi_{2-x}Sb_xTe_3$, and $Bi_{2-x}Sb_xSe_yTe_{3-y}$.[1] Bismuth−antimony−tellurium and bismuth−selenium−tellurium systems exhibit complete solid solubility, and thus, a wide range of compositions is possible.[2] The development of specific compositions that maximize thermoelectric performance as indicated by high figures-of-merit has been the subject of intensive investigations.[3]

In current practice, these alloys are made through metallurgical melt processing, i.e., appropriate amounts of the pure elements are comelted above 650 °C, mixed, and subjected to controlled cooling in sealed vessels.[4] This batch processing approach is both equipment and labor intensive, while thermoelectric elements fabricated from the solidified melts tend to be somewhat fragile.[5] Thermoelectric elements made from polycrystalline powders are more robust and can be fabricated by automated production methods. Polycrystalline powders are normally derived from the solidified melts by standard crushing and sieving procedures.

We have reported previously on two aqueous solution syntheses methods for generating the parent compound, bismuth telluride, Bi_2Te_3, directly in polycrystalline, fine-powder form.[6,7] We now describe modifications to these methods which facilitate the synthesis of fine-powder, polycrystalline Bi−Se−Te, Bi−Sb−Te, and Bi−Sb−Se−Te alloys. While the exact compositions of the alloys used in present-day thermoelectric devices are proprietary, our compositions were selected to be representative of this class of materials.

Experimental Section

Materials and Procedures. Elemental bismuth (99.5%), selenium (99.99%), antimony (99.5%), and tellurium (99.99%); bismuth trioxide, Bi_2O_3 (99.99%); selenium dioxide, SeO_2 (99.999%); and antimony trioxide, Sb_2O_3 (99.0%) were obtained from commercial suppliers in powder form of 325 mesh or smaller. DL-tartaric acid; 16 M nitric acid; 15 M ammonium hydroxide; and ethylene glycol were also obtained from commercial suppliers and used in the as-received condition. Water was doubly distilled.

X-ray powder diffraction (XRPD) using Cu Kα radiation, $\lambda = 0.154\,06$ nm, was conducted using standard, commercial instrumentation. The phase detectability limits by XRPD were estimated to be about 2 wt % for the described Bi−Sb−Se−Te materials. The effects of instrumental errors on peak positions were minimized through the use of an external calibrant, LaB_6, NIST SRM 660.[8] Refinements of the diffraction data were accomplished with a published least-squares fitting program specified for a hexagonal crystal system and a rhombohedral Bravais lattice.[9] Initial *a* and *c* values were selected from the Joint Committee on Powder Diffraction Standards (JCPDS) entry 29-247 for Bi_2SeTe_2.

Surface area measurements were conducted using standard, commercial BET instrumentation using nitrogen as the working fluid. Chemical analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN 37950-1610.

All operations described herein were conducted in an efficient fume hood to carry off toxic nitrogen oxides, ammonia fumes, volatile selenides, and possible organic pyrolysis products. Since some of the procedures involve solutions containing nitric acid and ethylene glycol, there is the possibility of forming *explosive* nitrate esters such as ethylene glycol dinitrate.[10] Thus, effective safety shielding is strongly prescribed. However, we did not experience any excursions in our work.

After a consideration of the scale of the reactions and the sensitivity of the balance used to weigh out the solid reactants, we estimated that our combined weighing and transfer errors were less than 0.1%. This level of uncertainty is relevant to all of the initial alloy compositions. Typically, alloy yields, based upon the amounts of starting materials taken, were from 88 to 92% of the theoretical yields.

Synthesis of $Bi_2Se_xTe_{3-x}$. For $x = 1$, 0.040 00 mol of Te metal powder was dissolved in 400 mL of 6 M nitric acid with the evolution of nitrogen dioxide. After the metal had dissolved completely, 0.020 00 mol of bismuth trioxide was added and dissolved with stirring. The hydrous oxides of Bi and Te were coprecipitated by the dropwise addition of 15 M ammonium hydroxide with constant stirring. An excess of 15 M ammonium hydroxide, 10% beyond the molar amount required for neutralization of the acid, was added to ensure that the slurry was alkaline. The resultant fine, white precipitate was separated by centrifugation and was washed with several portions of distilled water until the odor of ammonia was no longer detectable. The coprecipitated hydrous oxide precursor was air-dried to constant weight.

From the results of earlier work, the composition of the dried powder was taken as $Bi_2O_3{\cdot}2TeO_2{\cdot}H_2O$ (fw = 803.16).[4] Sufficient SeO_2 was combined with a weighed quantity of the $Bi_2O_3{\cdot}2TeO_2{\cdot}H_2O$ to give Bi:Se:Te = 2:1:2 using a mortar and pestle. The resultant powder was heated in 0.1 MPa (1 atm) of flowing hydrogen at 300 °C for 6 h and at 350 °C for an additional 6 h. Equivalent spherical particle size for the powder estimated from BET data was 500 nm.

Samples of $Bi_2Se_xTe_{3-x}$ with $x = 0.3$ and $x = 0.5$ were also prepared using this method.

Synthesis of $Bi_{0.5}Sb_{1.5}Te_3$. A 0.030 00 mol quantity of Te metal powder and 0.005 000 mol of Bi_2O_3 were sequentially dissolved in 300 mL of 12 M nitric acid. Antimony trioxide, in the amount of 0.015 00 mol, was added to the solution and thoroughly dispersed with continued stirring. At this point, Sb_2O_3 has only partial solubility in this medium. Subsequently, 0.05 mol each of tartaric acid and ethylene glycol were added to the dispersion. The system was heated slowly to about 90 °C, whereupon the 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 approached about one-sixth of its original volume, the heat was reduced to minimize

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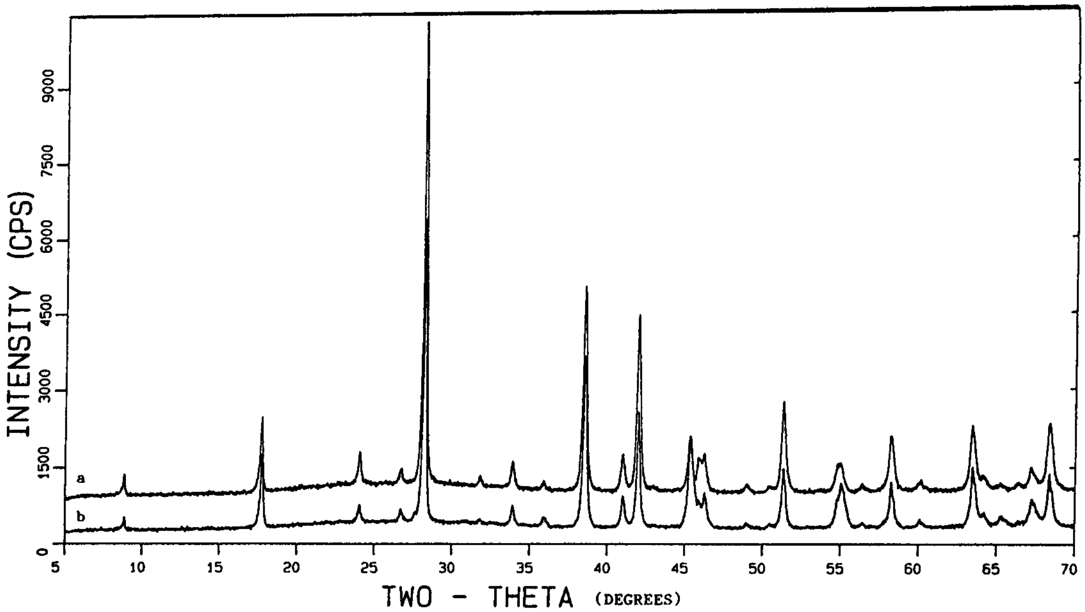

Figure 1. (a) XRPD pattern of chemically synthesized Bi_2SeTe_2. (b) XRPD pattern of Bi_2SeTe_2 prepared by melt processing.

frothing. Subsequently, when essentially all of the solvent had been removed, a mixed-metal ion/polymer-like composite was formed with the concomitant evolution of additional nitrogen oxides. Further heating in air up to about 350 °C produced a *char* which eventually underwent ignition. Upon the cessation of fumes, the resultant cake was blanketed with nitrogen and cooled to room temperature. The char was pulverized and heated under 0.1 MPa (1 atm) of flowing hydrogen at 300 °C for 6 h and at 400 °C for an additional 6 h. Equivalent spherical particle size for the powder estimated from BET data was 420 nm.

Synthesis of $Bi_{2-x}Sb_xSe_yTe_{3-y}$ for $x = 0.2$ and $y = 0.15$. Antimony trioxide in the amount of 0.002 000 mol was dissolved in 200 mL of 16 M nitric acid, followed by the addition of 300 mL of water. A 0.018 00 mol portion of Bi_2O_3 was dissolved in this solution with stirring followed by the dissolution of 0.057 00 mol of Te powder. The mixed-element hydrous oxides were coprecipitated from the resultant colloidal dispersion by the dropwise addition of 15 M ammonium hydroxide under constant stirring. An excess of ammonium hydroxide, 10% beyond the molar amount required for neutralization of the acid, was added to ensure that the slurry was alkaline. The resultant fine, white precipitate was separated by centrifugation and was washed with several portions of distilled water until the odor of ammonia was no longer detectable. The powder was air-dried to constant weight.

The composition of the coprecipitated oxides was estimated to be $0.9Bi_2O_3 \cdot 0.1Sb_2O_3 \cdot 2.85TeO_2 \cdot H_2O$ (fw = 921.37). Using a mortar and pestle, a weighed quantity of this material was thoroughly combined with sufficient SeO_2 to give the composition $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$. The resultant powder was heated in 0.1 MPa (1 atm) of flowing hydrogen at 300 °C for 6 h and at 400 °C for 6 h. Equivalent spherical particle size for the powder estimated from BET data was 1300 nm.

Synthesis of XRPD Reference Materials by Melt Processing. Stoichiometric amounts of the pure elements were flame-sealed, under vacuum, into 75 mm long sections of 300 × 9 mm i.d. fused silica tubes. The remaining 225 mm tube sections were left attached and used as arbors for rotating the tubes horizontally at about 20 rpm within a tube furnace. The elements were thus mixed for 4 h in the molten state at a temperature of 800 °C. The temperature was subsequently reduced to about 385 °C, and the resultant ingots were annealed for 20 h. Upon cooling to 25 °C, the ingots were removed and pulverized using a borosilicate glass mortar and pestle. In this manner, powders were obtained to produce reference XRPD patterns for Bi_2SeTe_2, $Bi_{0.5}Sb_{1.5}Te_3$, and $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$.

Powder Identification. Elemental analyses of the powders after hydrogen reduction expressed in weight percentages are as follows. Anal. Calcd for Bi_2SeTe_2: Bi, 55.57; Se, 10.50; Te, 33.93. Found: Bi, 56.08 ; Se, 9.95; Te, 32.47. Anal. Calcd for $Bi_2Se_{0.3}Te_{2.7}$: Bi, 53.16; Se, 3.01; Te, 43.82. Found: Bi, 53.52; Se, 2.88; Te, 44.52. Anal. Calcd for $Bi_{0.5}Sb_{1.5}Te_3$: Bi, 15.60; Sb, 27.26; Te, 57.14. Found: Bi, 16.33; Sb, 23.20; Te, 57.53. Anal. Calcd for $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$: Bi, 48.47; Sb, 3.14; Se, 1.53; Te, 46.86. Found: Bi, 47.59; Sb, 2.75; Se, 1.70; Te, 48.78.

Table 1. Unit Cell Parameters for Bi_2SeTe_2

	a	std error	*c*	std error
chemically synthesized	4.3032	0.0005	30.013	0.005
melt processed	4.3041	0.0005	29.997	0.004
JCPDS No. 29-247[a]	4.28		29.86	

[a] Calculated from the single-crystal data of Bland and Basinski: Bland, J. A.; Basinski, S. J. *Can. J. Phys.* **1961**, *39*, 1040.

Results and Discussion

Due to the relatively high water solubility of SeO_2 (about 38 g/100 mL at 14 °C[11]), the quantitative introduction and retention of Se^{4+} in the coprecipitation and washing of Bi−Te precursors presented a challenge. As an alternative, we tried the metal−organo complex (MOC) method, used previously to synthesize Bi_2Te_3.[7] Unfortunately, the reductive environment indigenous to this process converted all of the Se^{4+} to Se^{2-}.[12] The Se^{2-} was effectively volatilized from the system as H_2Se. During this procedure, H_2Se was readily detected by its characteristic, offensive odor.

The simplest approach to the syntheses of Bi−Se−Te alloys consisted of coprecipitating a Bi−Te hydrous oxide precursor and subsequently dry-blending it with fine particle SeO_2. Evidently, the reduction of SeO_2 and the subsequent diffusion of Se into Bi−Te at 350 °C under hydrogen were favorable for the quantitative conversion of this system to Bi_2SeTe_2. The identity of this material was confirmed by elemental analysis and from XRPD data summarized in Figure 1 and Table 1.

An examination of the elemental analysis data for $Bi_2Se_xTe_{3-x}$ materials with $x = 0.3$ and $x = 1.0$ showed that the Bi percentages were slightly high, while the values for Se were somewhat low. However, the sum of the values for Bi, Se, and Te are 100.9 and 98.50, respectively. These results indicate that, to within 1 or 2%, a satisfactory accounting for the elements was achieved. Discussions with the analyst indicated that it was difficult to obtain consistently clean separations between

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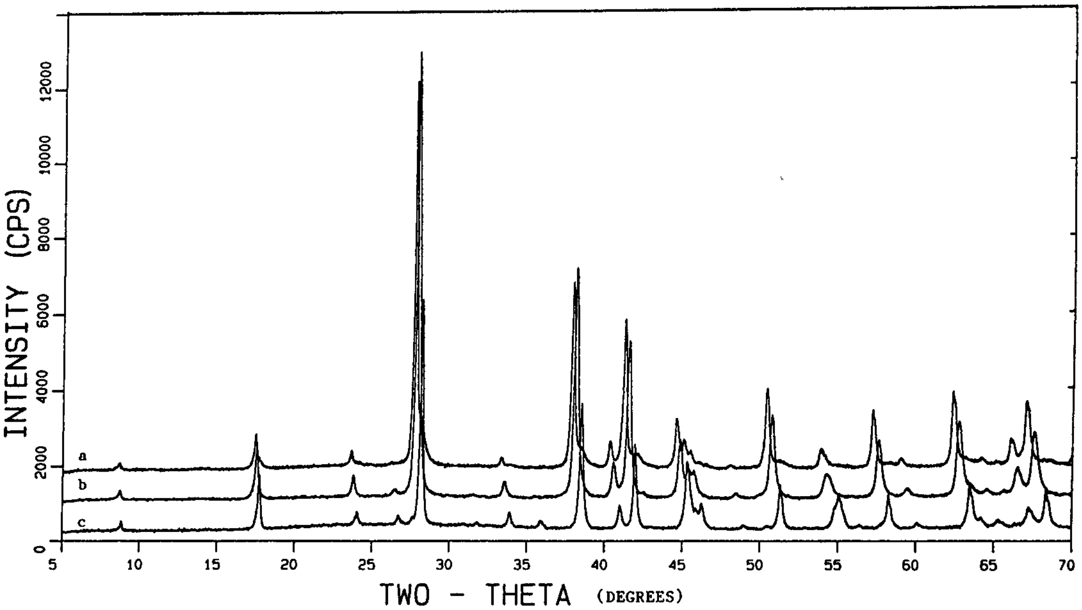

Figure 2. (a) XRPD pattern of chemically synthesized $Bi_2Se_{0.3}Te_{2.7}$. (b) XRPD pattern of chemically synthesized $Bi_2Se_{0.5}Te_{2.5}$. (c) XRPD pattern of Bi_2SeTe_2 prepared by melt processing.

Table 2. Unit Cell Parameters for $Bi_2Se_xTe_{3-x}$

x	*a*	std error	*c*	std error
0.3	4.3704	0.0003	30.424	0.002
0.5	4.3449	0.0004	30.278	0.003
1.0	4.3401	0.0005	29.997	0.004

the heavy, group 5A and 6A elements. This problem was manifested in the elemental analyses for all of the alloys treated in this paper.

A comparison of the XRPD pattern for our chemically synthesized Bi_2SeTe_2 with material of the same composition prepared by melt processing is shown in Figure 1. Further, a comparison of the refined cell parameters for these compounds is given in Table 1. It is apparent that, within the stated uncertainties, they are identical. However, the respective *a* and *c* values for Bi_2SeTe_2 from the JCPDS entry NO. 29-247 differ significantly from our values, since they were calculated from single-crystal data.

The two other compositions of $Bi_2Se_xTe_{3-x}$, with $x = 0.3$ and $x = 0.5$, were examined by XRPD. Figure 2 depicts a comparison of the diffraction patterns of these two compounds with that of melt-processed Bi_2SeTe_2. The evident, general shift of peaks to lower 2Θ values as *x* decreases is consistent with an expansion of the crystalline lattice as Se is replaced by the larger Te species.[13] Table 2 shows the expected increase in lattice parameters as the Se content is decreased.

As mentioned above, dry-blended $Bi_2O_3{\cdot}2TeO_2{\cdot}H_2O/SeO_2$ was cleanly converted to Bi_2SeTe_2 at 350 °C under hydrogen. In contrast, the XRPD pattern of a $0.25Bi_2O_3{\cdot}3TeO_3{\cdot}H_2O/0.75Sb_2O_3$ dry-blend reduced under analogous conditions showed a significant fraction of unreacted Sb_2O_3. Subsequently, we developed two alternative ways in which to introduce Sb^{3+} chemically into a Bi−Te system, depending upon the final composition desired.

Experimentally, we determined that Sb_2O_3 has a limited, but useful solubility of about 0.3 g/100 mL in 16 M HNO_3. Generally, when the desired alloy contained less than 4% Sb by weight, it was practical to coprecipitate a Bi−Sb−Te hydrous oxide precursor following the procedure given for the synthesis of $Bi_{2-x}Sb_xSe_4Te_{3-y}$ for $x = 0.2$ and $y = 0.15$ in the Experimental Section.

When the desired alloy required much more than 4% Sb by weight, the coprecipitation approach became unwieldy in the handling of large volumes of concentrated nitric acid and ammonium hydroxide. Hence, the MOC method was adapted to synthesize $Bi_{0.5}Sb_{1.5}Te_3$. During the MOC process, the dissolution of Sb_2O_3 in 12 M HNO_3 was assisted by a reaction temperature near 100 °C and by the presence of tartaric acid.[11]

An examination of the elemental analysis data shows that the Bi and Te percentages are somewhat high, while the value for Sb is low. The sum of the values for Bi, Sb, and Te is 97.1, indicating that an accounting for the elements was achieved within 3%.

No literature XRPD pattern for $Bi_{0.5}Sb_{1.5}Te_3$ was found. Figure 3 shows the XRPD pattern for the Bi−Sb−Te material and that of the $Bi_{0.5}Sb_{1.5}Te_3$ reference material prepared by melt processing. Table 3 shows the *a* and *c* values obtained from the XRPD data. A comparison of respective *a* and *c* values suggests that some small compositional differences may exist between the Bi−Sb−Te materials prepared by the different methods. Unfortunately, from the data on hand, we are unable to state unequivocally, whether both, or only one of the preparations may be off of the intended stoichiometry. For this reason, the parameters reported in Table 3 are considered to be tentative.

Since the four-component alloy $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ contained <4% Sb, its Bi−Sb−Te hydrous oxide precursor was readily coprecipitated as described in the synthesis of $Bi_{2-x}Sb_xSe_4Te_{3-y}$ for $x = 0.2$ and $y = 0.15$ in the Experimental Section. The stoichiometric amount of SeO_2 was dry-blended with this precursor, and the mixture was reduced in hydrogen. The variations between calculated and found values in the elemental analysis data for the resultant alloy reflect the analytical separation problem indigenous to combinations of the heavy group 5A and 6A elements. Bismuth and Sb are low, while Se and Te are higher than expected. However, the sum of the values is 100.8, indicating a satisfactory accounting for the elements within 1%. No literature reference XRPD patterns were found for Bi−Sb−Se−Te materials. Figure 4 shows the XRPD pattern for the Bi−Sb−Se−Te material and that of the $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ reference material prepared by melt processing. The mismatch of peak intensities suggests that the chemically synthesized material may have some preferred orientation. Table 4 shows the respective *a* and *c* values

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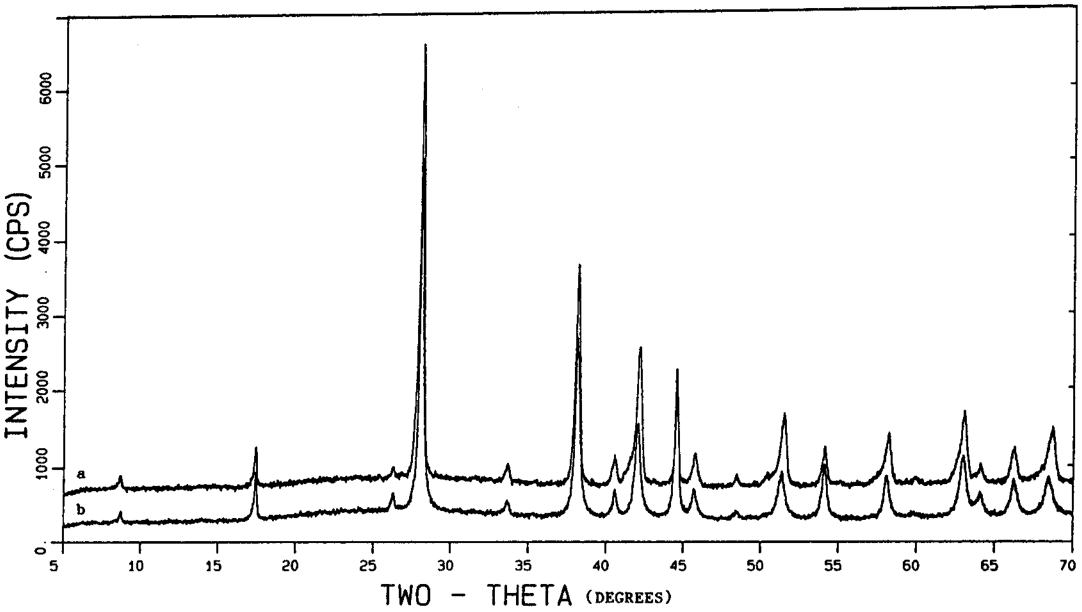

Figure 3. (a) XRPD pattern of chemically synthesized $Bi_{0.5}Sb_{1.5}Te_3$. (b) XRPD pattern of $Bi_{0.5}Sb_{1.5}Te_3$ prepared by melt processing.

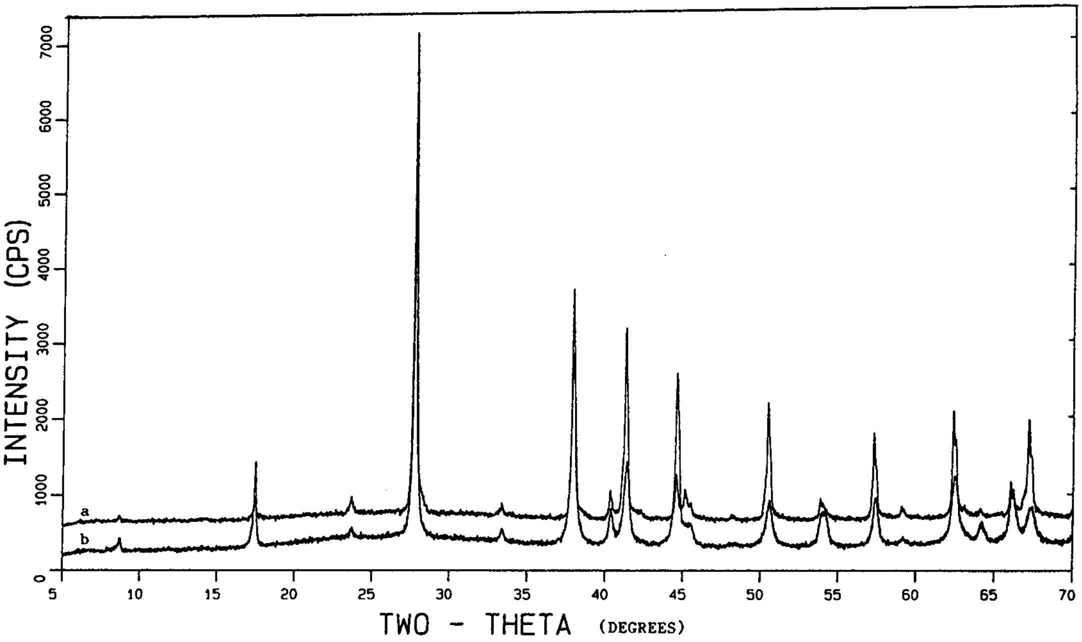

Figure 4. (a) XRPD pattern of chemically synthesized $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$. (b) XRPD pattern of $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ prepared by melt processing.

Table 3. Unit Cell Parameters for $Bi_{0.5}Sb_{1.5}Te_3$

	a	std error	*c*	std error
chemically synthesized	4.2842	0.0008	30.524	0.006
melt processed	4.2936	0.0006	30.532	0.007

Table 4. Unit Cell Parameters for $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$

	a	std error	*c*	std error
chemically synthesized	4.3688	0.0005	30.466	0.004
melt processed	4.3621	0.0007	30.512	0.006

obtained from X-ray data refinement. Again, a comparison of the values suggests possible small differences in composition between the complex alloys produced by the different methods. Thus, we consider the values in Table 4 to be tentative.

In summary, representative, polycrystalline Bi–Se–Te, Bi–Sb–Te, and Bi–Sb–Se–Te alloys were synthesized through selected coprecipitation, metal–organo complex, and hydrogen reduction techniques developed in our laboratory. Identification of the alloys was based on total elemental analysis supported by XRPD data. These techniques offer the advantages of (1) precursor synthesis in aqueous solution from commonly available chemicals, (2) alloy synthesis at a temperature 300–400 °C lower than that commonly used in melt processing, and (3) alloys in fine-powder form, thus eliminating the crushing and sieving required after melt processing.

Further work will be necessary to resolve possible compositional control problems with the antimony-containing alloys.

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