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Interfacial reactions between PbTe-based thermoelectric materials and Cu and Ag bonding materials

C. C. Li,^{ab} F. Drymiotis,^{†c} L. L. Liao,^d H. T. Hung,^b J. H. Ke,^e C. K. Liu,^d C. R. Kao^{*b} and G. J. Snyder^{*a}

The development of reliable bonding materials for PbTe-based thermoelectric modules that can undergo long-term operations at high temperature is carried out. Two cost-effective materials, Cu and Ag, are isothermally hot-pressed to PbTe-based thermoelectric materials at 550 °C for 3 h under a pressure of 40 MPa by the rapid hot-pressing method. Scanning electron microscopy, electron probe micro-analysis, and X-ray diffraction analysis are employed to identify intermetallic compounds, chemical reactions, and microstructure evolution after the initial assembly and subsequent isothermal aging at 400 °C and 550 °C. We find that Cu diffuses faster than Ag in PbTe. Neither Cu nor Ag is a good bonding material because they both react vigorously with Pb_{0.6}Sn_{0.4}Te. In order to be able to use Cu electrodes, it would be necessary to insert a diffusion barrier to prevent Cu diffusion into PbTe.

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Introduction

In recent years, the issues of sustainable energy and global warming have attracted attention worldwide. Reducing both energy consumption and our carbon footprint is a necessary step to prevent a future energy crisis.¹ To this end, thermoelectric (TE) materials have begun to gain attention due to their capability of transforming waste heat into useful electrical energy. For example, in the 1950s, NASA used TE materials to generate electricity from radioisotope heat for space exploration.^{2–4} Other examples of industrial applications include the development of a 10 kW thermoelectric generator system that operates by converting the radiant heat (under 250 °C) released from hot steels in a steel production plant into electricity.⁵ Further, many research teams have successfully embedded thermoelectric generators in vehicles, which recycle the waste heat generated by the heat exchanger.^{6,7} However, the low

conversion efficiency of current thermoelectric power generation systems, coupled with the high cost of modules, has limited their applications. If these shortcomings are addressed, TE modules could see greater use and lead to a significant reduction in waste energy in the form of heat.⁸

High-efficiency bulk thermoelectric materials have seen extensive development over the past decade.⁹ For some of these materials, the dimensionless thermoelectric figure of merit (zT) could reach a value of 2, which corresponds to an efficiency value of 20% when incorporated into a device.^{10,11} Despite this progress, the development of thermoelectric modules to accommodate these materials has not been as rapid. So far, only low-temperature thermoelectric materials have been constructed successfully and incorporated into commercial devices with any real success.^{12–14} However, for power generation applications, the temperature region of interest is above 300 °C, and the best thermoelectric material in terms of conversion efficiency for intermediate temperature applications (300–500 °C) is n- and p-type PbTe. Unfortunately, high temperatures make it difficult to establish low electrical and thermal resistance contacts, due to chemical reactions between the electrodes (or metallization layers) and PbTe. For example, in the case of metallization of PbTe with Ni, it was observed that both Ni-Te intermetallics and voids can form near the bonding interface.¹⁵ This can lead to high electrical- and thermal-resistance contacts, rapid deterioration of the joint, and subsequent module failure. It is also difficult to obtain a metallurgical high-strength joint with Fe and Mo foils.^{16,17} These issues are not limited to PbTe but are present in other TE materials as well, such as CoSb₃-based

^a Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA. E-mail: jsnyder@caltech.edu; Tel: +1-626-502-6126

^b Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan. E-mail: crkao@ntu.edu.tw; Tel: +886-2-33663745

^c Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA, USA

^d Electronic and Optoelectronics Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan

^e Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI, USA

[†] Current address: Thermal Energy Conversion Technologies Group, NASA Jet Propulsion Laboratory, Pasadena, CA 91109, USA.

materials.^{18,19} Severe diffusion and the brittleness of the chemical reaction products will undoubtedly lead to degradation of thermoelectric performance, which causes reliability problems during high-temperature operation. Consequently, appropriate bonding materials and fabrication methods should be developed for PbTe thermoelectric modules to allow for reliable long-term operation.

In our previous study, we showed that Ag is an efficient and stable bonding layer for PbTe when the temperature of operation is less than 400 °C.²⁰ Therefore, Pb_{0.6}Sn_{0.4}Te fabricated by using Ag as the bonding material is also examined in this work, and it appears that Cu and Ag may yield similar results. In addition, the coefficient of thermal expansion (CTE) of Cu is $17.5 \times 10^{-6} \text{ K}^{-1}$, which is very close to those of PbTe ($20.4 \times 10^{-6} \text{ K}^{-1}$) and Pb_{1-x}Sn_xTe ($20 \times 10^{-6} \text{ K}^{-1}$).²¹⁻²³ This small difference mitigates the potential reliability issues induced by a CTE mismatch. Hence, Cu was selected as a bonding material for both PbTe and Pb_{0.6}Sn_{0.4}Te in this study due to its CTE as well as its well-known electrode properties. However, Cu could react with PbTe to form Cu₂Te, and based on the vertical section of the CuPbTe ternary phase diagram, it may have low solubility in the PbTe matrix at the temperature of interest.²⁴ Cu serves as a donor impurity in PbTe systems,^{25,26} presumably by forming interstitial Cu. The conductivity and power factor in bulk p-type Cu_{2-x}Te were found to increase significantly as *x* decreases,²⁷⁻²⁹ and a high *zT* value of 2.1 was reported in the Cu₂Te mosaic crystals.³⁰ Issues related to the identification of intermetallic compounds, chemical reactions and microstructure evolution during mid-temperature operation will also be discussed here.

Experimental

The bulk stoichiometric PbTe and Pb_{0.6}Sn_{0.4}Te ingots were prepared by melting Pb (99.999%, Alfa Aesar), Te (99.999%, Alfa Aesar), and Sn (99.9999%, Alfa Aesar) powders in a vacuum encapsulated quartz tube at 1000 °C for 6 h, followed by annealing at 700 °C for 48 h to ensure homogeneity. Both the resulting PbTe and Pb_{0.6}Sn_{0.4}Te ingots were ball milled into micro-scale powders under an Ar atmosphere for 1 h. Powder X-ray diffraction patterns show that both are single phase with a NaCl crystal structure. Ag (99.9%, Alfa Aesar) and Cu foils (99.9%, Alfa Aesar) with a thickness of 127 μm and 500 μm, respectively, were polished using 800 grit SiC sandpaper and then cleaned with acetone in an ultrasonic bath. PbTe or Pb_{0.6}Sn_{0.4}Te powders ($4 \pm 0.001 \text{ g}$) were placed between two polished Ag foils or Cu foils inside a graphite die. The resulting Ag/Pb_{0.6}Sn_{0.4}Te/Ag, Cu/PbTe/Cu, and Cu/Pb_{0.6}Sn_{0.4}Te/Cu structure was subsequently placed in a rapid hot-press furnace, in which it was heated by induction and isothermally sintered for 3 h under an Ar flow. The bonding pressure and temperature were set at 40 MPa and 550 °C, respectively. The pressure was then removed and the samples were allowed to cool to 60 °C (the detail configuration and design of the rapid hot-pressing equipment have been characterized elsewhere³¹). The samples

were then retrieved and sealed in quartz under vacuum to prevent oxidation and evaporation of Pb or Te during the following high-temperature storage. Finally, the as-bonded samples sealed in quartz were isothermally annealed at 400 °C for periods up to 1000 h and at 500 °C for 50 h. The chosen aging temperatures reflect that the module will be operating in the intermediate temperature range. For each specific aging time, the samples were mounted in epoxy resin and polished using a series of SiC paper from 240 to 800 grit, and were then polished with Al₂O₃ powder suspensions (1 and 0.05 μm). In addition to conventional mechanical polishing, ion milling polishing (E-3500; HITACHI) was used for final polishing to prevent artifacts from mechanical polishing. The metallographic observations were characterized using a scanning electron microscope (SEM) (S-3000N; HITACHI) equipped with a backscattered electron (BSE) detector. Chemical compositions were analyzed using both an energy dispersive spectrometer (EDS, Oxford 6587) and an electron probe micro-analyzer (JEOL, JXA-8200). X-ray diffraction experiments were carried out using a powder X-ray diffractometer (Rigaku, TTRAX III) over a range of 20–70° (2θ). The X-ray diffraction patterns were further cross-referenced with the Joint Committee on Powder Diffraction Standards (JCPDS).

Results and discussion

Microstructure evolution of the Cu/PbTe/Cu structures after aging at 400 °C is shown in Fig. 1. Fig. 1(a) reveals the smooth interface between Cu and PbTe after bonding; the interface is uniform and free of cracks, which suggests a high-quality bond. As the aging time increases, the interface remains stable even after 1000 h of aging, at which time additional black particles ($\leq 2 \text{ μm}$) precipitated within the PbTe matrix, as shown in Fig. 1(b)–(d). A zoom-in view of these black particles is shown in Fig. 1(e), and according to EDS analysis they are identified as Cu₂Te. Some isolated Cu₂Te can be detected at the interface when aging up to 500 h, but these did not accumulate into a dense layer. Interestingly, two different color contrasts could be distinguished within some Cu₂Te precipitates, suggesting that local PbTe gradually transforms into the Cu₂Te phase. Since the phase is uniformly distributed, quantitative metallographic measurements were conducted to determine its volume fraction. This technique estimates the volume fraction of a certain phase by measuring the area fraction occupied by this phase in a two-dimensional cross-sectional image.³² Multiple cross-section samples were imaged at five random locations. For aging times of 200, 500, and 1000 h, the Cu₂Te volume fraction was statistically estimated to be $1.5 \pm 0.12\%$, $2.0 \pm 0.16\%$, and $2.2 \pm 0.20\%$, respectively. The Cu₂Te volume fraction is plotted *versus* the square root of aging time in Fig. 1(f). It can be seen that the amount of Cu₂Te increases by following parabolic kinetics, which suggests that the formation of this phase is a diffusion-limited process. Unlike in the previous study, the growth rate of Cu₂Te in Cu/PbTe/Cu is higher than that of Ag₂Te in Ag/PbTe/Ag under the same heat treatment. The kinetic study should provide a useful guide for estimating the

Fig. 1 Interfaces of Cu/PbTe/Cu after aging at 400 °C for (a) 0, (b) 200, (c) 500 and (d) 1000 h. (e) Zoom-in view of the PbTe matrix of (d). (f) Volume fraction of X₂Te (X = Cu or Ag) as a function of square root of the aging time. (g) and (h) are the zoom-in views of (a) and (d), respectively.

time required for n-type doping of PbTe or for exhausting the Cu layer. Fig. 2 shows the SEM image and EDS element mappings in the red region of Cu, Te, and Pb for a large Cu₂Te formation. The pure Cu phase appears on the edge of Cu₂Te and PbTe. It is currently unclear why pure Cu precipitates within the PbTe matrix and how this large Cu₂Te volume disappears for subsequent aging periods, but these behaviors might occur as Cu_{2-x}Te loses Cu upon cooling. Nevertheless, the volume fraction of Cu₂Te in as-bonded samples is small and increases rapidly with annealing.

Although the Cu/PbTe/Cu makes a strong bond at 400 °C for a very long soaking time, this behavior is weaker at higher temperatures. Fig. 3 shows the micrographs of Cu/PbTe/Cu after aging at 550 °C for 50 h. Analogous to the case of Ag/PbTe/Ag, the Cu foils reacted vigorously with PbTe to form Cu₂Te, according to the following balanced reaction:

The interface region in Fig. 3(a) experiences a severe adverse reaction during this process, which leads to void formation and crack propagation. Therefore, the adhesion of Cu to PbTe should be poor. Voids also show the tendency to appear at the grain boundaries, which may induce intergranular fractures. The mechanism of void formation due to the presence of

Fig. 2 EDS element mappings for selected large Cu₂Te found in the matrix of the Cu/PbTe/Cu sample after bonding.

liquid Pb has been proposed in a former study. It should be noted that 550 °C is higher than the melting temperature of pure Pb (327.5 °C). Hence, Pb is in the liquid phase during annealing and can easily flow through the PbTe matrix, causing the formation of large voids.²⁰ Fig. 3(b) shows a close-up view of the interface, which shows the presence of Cu, Cu₂Te, and voids. As previously noted, pure Cu can also be observed near the Cu/PbTe interface. Large amounts of Cu and Cu₂Te phase material precipitated within 100 μm from the interface. Fig. 3(c) indicates that Cu atoms could diffuse into the inner part of PbTe to form Cu₂Te.

Many studies have reported that Pb_{1-x}Sn_xTe compounds serve as promising p-type thermoelectric materials.³³⁻³⁵ For Pn_{0.6}Sn_{0.4}Te in particular, higher Z values were observed when the temperature was above 400 °C.³⁶ As a result, the reactions of Pb_{0.6}Sn_{0.4}Te with Cu were also inspected. Fig. 4 shows microstructure details of the Cu/Pb_{0.6}Sn_{0.4}Te/Cu structures after bonding, where a reaction depth of 1.7 mm is observed from the outer Cu side to inner Pb_{0.6}Sn_{0.4}Te. Both the upper and the lower 500 μm Cu foils were nearly exhausted. The diffusion depth of Cu atoms could reach more than 1.4 mm along the grain boundaries of Pb_{0.6}Sn_{0.4}Te. Four zones have been

Fig. 3 (a) Micrograph of Cu/PbTe/Cu after aging at 550 °C for 50 h. (b) Interface observation showing reaction products and voids. (c) Micrograph of occasional distribution of the Cu_2Te phase within the PbTe matrix.

tentatively defined in this reacted bulk material. Zone 1 is shown in Fig. 4(b) encircled by a yellow dashed line. Three phases in this region could be easily differentiated by color contrasts, which were identified to be PbTe (white), Cu_2Te (grey), and Cu (black). The Cu solubility was detected in the PbTe phase (about 20–50 at%), but the adjacent Cu phase may contribute to this composition variation due to the small size of the PbTe phase. One should know that there is no Pb–Te–Cu ternary compound reported; however based on X-ray inspection in Fig. 6, the crystal structure of Pb–Te–Cu is present as a NaCl prototype, which further indicated that it was a PbTe phase with solubility of Cu. Fig. 4(c) shows the typical microstructure in zone 2. The Cu concentration in PbTe phase gradually decreased across a gradient from 28 to 8 at% from zone 1 toward zone 3. The grey-contrast phase was identified to be Cu_2Te . The phase with a discerning black color contrast within Cu_2Te shows the composition of Cu and Sn. The Sn

Fig. 4 (a) Series electron overlay images of Cu/ $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ /Cu across from Cu toward inner $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ after bonding. Zoom-in views of the region of (b) zone 1 and zone 2, (c) zone 2 and (d) zone 3.

concentration in this phase ranges from 17 to 25 at%. Based on the X-ray patterns in Fig. 6, the crystal structure of this black phase was identified to be Cu_3Sn , which is consistent with composition variation according to the Cu–Sn phase diagram.³⁷ Fig. 4(d) shows that the $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ was surrounded with PbTe, Cu_2Te and Cu_3Sn in zone 3. The $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ phase contained about 7 ± 2 at% Cu, and the PbTe phase contained about 6 at% Cu. $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ was transformed into PbTe due to the formation of Cu_3Sn and Cu_2Te , as summarized by the following balanced reaction:

The growth of Cu_3Sn and Cu_2Te at grain boundaries may result in depletion of Sn and Te from $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ adjacent to the boundaries, causing $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ to transform into the PbTe phase. Zone 4 was unaffected and remained as normal unreacted $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$.

Fig. 5 shows the microstructures of zone 2 and zone 3. It is evident that the Cu atoms diffuse and react to form PbTe, Cu_2Te and Cu_3Sn along the grain boundaries of $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$, as observed in the lower half of Fig. 5(a); the grain boundary precipitation is known as a heterogeneous nucleation behavior of the second phase. Fig. 5(b) shows a close-up view of the red squared region of Fig. 5(a), where a large amount of needle-like phases precipitate and intersect each other within the $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ grain. This result suggests that zone 3 will gradually turn into zone 2 on extending the bonding time if a sufficient number of Cu atoms are present. These needle-like phases can be considered to be Widmanstätten

Fig. 5 (a) Electron micrograph of zone 3 of Cu/Pb_{0.6}Sn_{0.4}Te/Cu after bonding. Some grain boundaries of Pb_{0.6}Sn_{0.4}Te are outlined with a yellow dashed line. (b) Zoom-in view of the square region in (a) showing the Widmanstätten structure. (c) Electron micrograph of zone 4.

structures, which grow in an aligned manner along specific crystal planes or directions of the matrix crystals. The width of these needle-like phases is less than 1 μm , but the length can reach more than 10 μm . Such phenomena have also been observed in pseudobinary PbTe–Sb₂Te₃ systems³⁸ and in Se-doped p-type AgSbTe₂.³⁹ Further studies of this phase are planned, and will be performed by transmission electron microscopy (TEM). Fig. 5(c) shows that the first phase that precipitates along the grain boundaries in zone 4 is Cu₃Sn. X-ray diffraction techniques were used to identify the exact phases that appear in as-bonded Cu/Pb_{0.6}Sn_{0.4}Te/Cu; from the provided pattern shown in Fig. 6, the peaks of PbTe and Cu₃Sn can be easily identified. The 2θ angles of (200), (220), (222), (420) and (400) from (Pb, Sn)Te were slightly higher than those observed for PbTe ranging from 0.2 to 0.589 (JCPDS file no. 65-0134 for PbTe, no. 65-4470 for (Pb, Sn)Te, no. 65-4653 for Cu₃Sn, and no. 10-421 for Cu₂Te). The

Fig. 6 X-ray diffraction patterns of as-bonded Cu/Pb_{0.6}Sn_{0.4}Te/Cu. The inset is the zoom-in view of those peaks between 35 and 70 degree.

pattern is consistent with the microstructure shown in Fig. 4. The precipitation along the boundaries of grains and powders indicates that grain boundary diffusion of Cu plays an important role in the observed microstructure; Cu atoms can diffuse quickly into the Pb_{0.6}Sn_{0.4}Te through the grain boundaries during hot-pressing, and react fiercely to form Cu₂Te and Cu₃Sn. PbTe then appears due to the depletion of Sn in Pb_{0.6}Sn_{0.4}Te. Unfortunately, such a diffusion coefficient of Cu along Pb_{0.6}Sn_{0.4}Te grain boundaries is not available in the literature to our knowledge, so this present study focused on the microstructure characterization and addresses the serious issue. The rigorous and quantitative analyses of diffusion are left for future directions of studies.

The microstructure of Cu/Pb_{0.6}Sn_{0.4}Te/Cu structures, which were isothermally annealed at 400 $^{\circ}\text{C}$ for 1000 h, is shown in Fig. 7. Fig. 7(a) shows that the depth of Cu diffusion into Pb_{0.6}Sn_{0.4}Te can reach more than 1.7 mm after heat treatment. Therefore, the unreacted Pb_{0.6}Sn_{0.4}Te (zone 4) no longer exists, and only three zones can be outlined in this bulk material. Three evident color contrasts in zone 1 have been identified: PbTe (white), Cu₂Te (grey), and Cu₃Sn (black) (Fig. 7(b)). The PbTe phase contains 7 ± 2 at% Cu. As mentioned, the formation of PbTe phase originates from the depletion of Sn in Pb_{0.6}Sn_{0.4}Te. In contrast to zone 1 in the as-bonded sample, not only has the pure Cu phase disappeared and transformed into the stable Cu₃Sn phase, but the solubility of Cu in PbTe was reduced due to the long-term aging treatment. Typical bonding processes include heating, isothermal aging, and cooling. After the cooling process, the phases that form are usually under non-equilibrium states and oversaturated solid solution forms, due to the insufficient time for precipitate nucleation. Therefore, the unstable phase will most likely be eliminated and transformed into a stable phase after subsequent long-term aging. Fig. 7(c) shows the typical microstructure in zone 2, where the Cu concentration in the PbTe phase has decreased to 6 at%. The grey contrast phase was identified to be Cu₂Te, while the black color contrast phase within Cu₂Te is Cu₃Sn. The phases present in zone 3 are the same as the

Fig. 7 (a) Series electron overlay images of Cu/Pb_{0.6}Sn_{0.4}Te/Cu across from Cu toward inner Pb_{0.6}Sn_{0.4}Te after aging at 400 °C for 1000 h. Zoom-in views of (b) the interface showing co-existence of reactants and products, (c) zone 2, and (d) zone 3.

phases present in zones 1 and 2, as shown in Fig. 4(d). However, in moving from zone 1 to zone 3, Cu₂Te and Cu₃Sn gradually coarsen and the Cu amount in PbTe reduces to about 4 at%. Imaging analysis shows that the occupied area ratios of (Cu₂Te + Cu₃Sn) and (PbTe + Pb_{0.6}Sn_{0.4}Te) moving from zone 1 to zone 3 are 1.22, 0.77, and 0.65. This indicates that the amount of Cu-based products gradually decreases, which is consistent with the gradient of Cu concentration established from the Cu side and towards the inner Pb_{0.6}Sn_{0.4}Te. Compared to the as-bonded sample, more Pb_{0.6}Sn_{0.4}Te was depleted and transformed into PbTe, exhausting the unreacted zone 4 in the as-bonded sample.

In our previous study, we demonstrated that Ag can be an effective bonding layer for PbTe based modules that are designed to operate at $T \leq 400$ °C.²⁰ The interface remained mechanically sound and without cracks even after extended aging. Although formation of Ag₂Te precipitates occurred at 400 °C within the PbTe matrix, the Ag₂Te showed no inclination to aggregate at the interface and further inhibit the brittle fractured-interface. Furthermore, the coefficient of thermal expansion of Ag ($18.9 \times 10^{-6} \text{ K}^{-1}$) is very close to that of Pb_{1-x}Sn_xTe ($20 \times 10^{-6} \text{ K}^{-1}$),²³ which will greatly decrease the stress present at the interface. Therefore, Pb_{0.6}Sn_{0.4}Te bonded with the same material, Ag, was also evaluated in this study. Fig. 8 shows the electron micrographs of as-bonded Ag/Pb_{0.6}Sn_{0.4}Te/Ag structures. Both the upper and the lower 127 μm Ag foils are totally consumed, and reacted along the grain boundaries of Pb_{0.6}Sn_{0.4}Te, more than 500 μm into the matrix. The region above the yellow dashed curve in Fig. 8(a) experiences the most severe reaction, while the region below is denoted as unreacted bulk Pb_{0.6}Sn_{0.4}Te. Fig. 8(b) shows a

Fig. 8 Electron micrographs of the as-bonded Ag/Pb_{0.6}Sn_{0.4}Te/Ag sample. (a) Low magnification view showing that the Ag foil was totally consumed. (b) Zoom-in view showing the reaction zone above the yellow curve outlined in (a).

close-up view of the upper region, where Pb_{0.6}Sn_{0.4}Te is surrounded by PbTe (white), Ag₂Te (grey), and Ag₄Sn (black), similar to the case of Cu/Pb_{0.6}Sn_{0.4}Te/Cu, while the Pb_{0.6}Sn_{0.4}Te grains contain about 6 at% Ag. The reaction of Ag foils with Pb_{0.6}Sn_{0.4}Te to form Ag₂Te and Ag₄Sn could be given by eqn (3) as

However, in the region below the yellow dashed curve, no Ag solubility is detected for the unreacted bulk Pb_{0.6}Sn_{0.4}Te. In sum, both Cu and Ag bonding layers face the same difficulty in maintaining a stable interface with Pb_{0.6}Sn_{0.4}Te, due to the severe Cu-Sn and Ag-Sn reactions. Thus, one should choose an appropriate bonding layer, such as Al, which would not vigorously react with Sn, to reach the goal of long-term high-temperature operation. On the other hand, Cu and Ag kept the stable structures with PbTe not only during assembly but also during subsequent aging below 400 °C. Based on this study, Cu is found to be a fast diffusing species in PbTe, even faster than Ag. Therefore, if Cu electrodes are to be used, then the insertion of a diffusion barrier layer is recommended in order to prevent Cu diffusion into PbTe, even at low temperatures.

Conclusion

The interface between Cu and PbTe remains uniform and crack-free even after prolonged aging below 400 °C. The compound Cu₂Te precipitates within the PbTe matrix, but Cu₂Te shows no

tendency to aggregate at the interface. In addition, Cu atoms diffuse faster than Ag in PbTe. Therefore, if Cu electrodes are to be used, the insertion of a diffusion barrier layer is recommended in order to prevent excessive Cu diffusion into the PbTe. On the other hand, both Cu and Ag are not compatible with $\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$ due to the massive diffusion and severe reactions during assembly, which is attributed to the high reactivity of Sn. To avoid this, an alternative material, which will not react with Sn, has to be used.

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References

- 1 International Energy Agency, Paris, France, "Energy Technology Perspectives: Scenarios and Strategies to 2050", 2010.
- 2 R. W. Fritts, in *Thermoelectric Materials and Devices*, ed. I. B. Cadoff and E. Miller, Reinhold Pub. Corp., New York, 1960, pp. 143–162.
- 3 R. R. Heikes, R. C. Miller and R. W. Ure, in *Thermoelectricity: Science and Engineering*, ed. R. R. Heikes and R. W. Ure, Interscience Publishers, New York, 1961, pp. 405–442.
- 4 Y. I. Ravich, B. A. Efimova and I. A. Smirnov, *Semiconducting Lead Chalcogenides*, Plenum Press, New York, 1970.
- 5 T. Kuroki, K. Kabeya, K. Makino, T. Kajihara, H. Kaibe, H. Hachiuma, H. Matsuno and A. Fujibayashi, *J. Electron. Mater.*, 2014, **43**, 2405–2410.
- 6 E. F. Thacher, B. T. Helenbrook, M. A. Karri and C. J. Richter, *Proc. Inst. Mech. Eng., Part D*, 2007, **221**, 95–107.
- 7 X. Liu, C. G. Yu, S. Chen, Y. P. Wang and C. Q. Su, *J. Electron. Mater.*, 2014, **43**, 2218–2223.
- 8 L. E. Bell, *Science*, 2008, **321**, 1457.
- 9 G. J. Snyder and E. S. Toberer, *Nat. Mater.*, 2008, **7**, 105.
- 10 K. Biswas, J. He, I. D. Blum, C. I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid and M. G. Kanatzidis, *Nature*, 2012, **489**, 414.
- 11 Y. Pei, H. Wang and G. J. Snyder, *Adv. Mater.*, 2012, **24**, 6125.
- 12 S. Karabetoglu, A. Sisman, Z. F. Ozturk and T. Sahin, *Energy Convers. Manage.*, 2012, **62**, 47.
- 13 C. C. Li, Z. X. Zhu, L. L. Liao, M. J. Dai, C. K. Liu and C. Robert Kao, *Sci. Technol. Weld. Joining*, 2013, **18**, 421.
- 14 Y. Zhang, J. Fang, C. He, H. Yan, Z. Wei and Y. Li, *J. Phys. Chem. C*, 2013, **117**, 24685.
- 15 H. Xia, F. Drymiotis, C. L. Chen, A. Wu and G. J. Snyder, *J. Mater. Sci.*, 2014, **49**, 1716.
- 16 H. Xia, F. Drymiotis, C. L. Chen, A. Wu, Y. Y. Chen and G. J. Snyder, *J. Mater. Sci.*, 2015, **50**, 2700–2708.
- 17 M. Weinstein and A. I. Mlavsky, *Rev. Sci. Instrum.*, 1962, **33**, 1119.
- 18 K. T. Wojciechowski, R. Zybala and R. Mania, *Microelectron. Reliab.*, 2011, **51**, 1198.
- 19 D. Zhao and H. Geng, *Int. J. Appl. Ceram. Technol.*, 2012, **9**, 733.
- 20 C. C. Li, F. Drymiotis, L. L. Liao, M. J. Dai, C. K. Liu, C. L. Chen, Y. Y. Chen, C. R. Kao and G. J. Snyder, *Energy Convers. Manage.*, 2015, **98**, 134–137.
- 21 D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Florida, 84th edn, 2003.
- 22 B. Houston, R. E. Strakna and H. S. Belson, *J. Appl. Phys.*, 2003, **39**, 3913.
- 23 G. Bauer, F. Kuchar and H. Heinrich, *Two-Dimensional Systems, Heterostructures, and Superlattices*, Springer, Berlin, Heidelberg, 1984.
- 24 H. Gravemann and H. J. Wallbaum, *Z. Metallkd.*, 1956, **47**, 433–441.
- 25 A. J. Strauss, *J. Electron. Mater.*, 1973, **2**, 533–569.
- 26 R. F. Brebrick and E. Gubner, *J. Chem. Phys.*, 1962, **36**, 1283–1289.
- 27 B. Mansour, F. Mukhtar and G. G. Barakati, *Phys. Status Solidi A*, 1986, **95**, 703.
- 28 K. Sridhar and K. Chattopadhyay, *J. Alloys Compd.*, 1998, **264**, 293–298.
- 29 C. Nethravathi, C. R. Rajamathi, M. Rajamathi, R. Maki, T. Mori, D. Golberg and Y. Bando, *J. Mater. Chem. A*, 2014, **2**, 985–990.
- 30 Y. He, P. Lu, X. Shi, F. Xu, T. Zhang, G. J. Snyder, C. Uher and L. Chen, *Adv. Mater.*, 2015, **27**, 3639–3644.
- 31 A. D. LaLonde, T. Ikeda and G. J. Snyder, *Rev. Sci. Instrum.*, 2011, **82**, 025104.
- 32 G. F. V. Voort, *ASM Handbook: Metallography and Microstructures*, ASM International, Materials Park, OH, 1985.
- 33 A. D. Lalonde and P. D. Moran, *J. Electron. Mater.*, 2010, **39**, 8.
- 34 K. Qiu and A. C. S. Hayden, *J. Power Sources*, 2008, **180**, 884–889.
- 35 J. Androulakis, K. F. Hsu, R. Pcionek, H. Kong, C. Uher, J. J. D'Angelo, A. Downey, T. Hogan and M. G. Kanatzidis, *Adv. Mater.*, 2006, **18**, 1170.
- 36 J. L. Cui, X. Qian and X. B. Zhao, *J. Alloys Compd.*, 2003, **358**, 228–234.
- 37 J. Miettinen, *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, 2008, **32**, 500–505.
- 38 T. Ikeda, V. A. Ravi and G. J. Snyder, *Acta Mater.*, 2009, **57**, 666–672.
- 39 B. Du, H. Li, J. Xu, X. Tang and C. Uher, *Chem. Mater.*, 2010, **22**, 5521.