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Fei Ren^a, Jane Y. Howe^a, Larry R. Walker^a, Eldon D. Case^b & Edgar Lara-Curzio^a

^a Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^b Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA

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An *in situ* SEM experimental study of the thermal stability of a LAST thermoelectric material

Fei Ren^{a*}, Jane Y. Howe^a, Larry R. Walker^a,
Eldon D. Case^b and Edgar Lara-Curzio^a

^aMaterials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA; ^bDepartment of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA

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Thermal stability is a requirement for the deployment of thermoelectric (TE) materials in the application of power generation. Lead–antimony–silver–tellurium (LAST) is an emerging material with promising TE properties. This study focuses on the thermal stability of a LAST sample with composition $\text{Ag}_{0.86}\text{Pb}_{19}\text{SbTe}_{20}$ fabricated from a cast ingot. Using a customized heating stage, the morphology of the LAST particles was studied via scanning electron microscopy (SEM) *in situ*, between room temperature and 848 K. The material was found to be stable below 823 K. The inclusion phase, which was antimony-rich, had a lower thermal stability than the PbTe-rich matrix. SEM findings were consistent with the results of a thermogravimetric analysis. The results from an *in situ* heating study suggest that protective environments should be used during the processing and application of LAST materials.

Keywords: thermoelectric; thermal stability; microstructure change; SEM

1. Introduction

There is an increasing interest in developing power generators using thermoelectric (TE) materials [1], which can convert waste heat into useful electrical energy. In addition to possessing high ZT (dimensionless figure of merit) values, TE materials need to be thermally stable within the desired service temperature range in order to be good candidates for TE power generation.

One of the emerging TE systems is lead–antimony–silver–tellurium (LAST), a family of quaternary compounds with a ZT value as high as 1.7 at 700 K [2]. Although many researchers have investigated the temperature-dependent TE and thermomechanical properties [3], there is limited information on the thermal stability of LAST. Using synchrotron X-ray diffraction, Cook et al. [4] found nanostructures in $\text{Ag}_{0.86}\text{Pb}_{19}\text{SbTe}_{20}$ were stable to at least 800 K in an argon atmosphere. However, direct observation of these nanostructures at high temperature using transmission electron microscopy was obscured by thermally induced defects [4].

*Corresponding author. Email: renf@ornl.gov

Powder processing has become a popular technique for fabricating LAST materials that are stronger than those made by the ingot casting approach [5,6]. However, hot-pressed LAST usually bloat (owing to the development of porosity) after being reheated [7], which may be related to the thermal stability of the powder particles. Here we report on an *in situ* study of the thermal stability of LAST TE material using a scanning electron microscope (SEM) equipped with a heating system and find that the powder is stable at approximately 823 K, when Sb and Pb began to evaporate.

2. Materials and methods

The LAST sample used in this study was cast from high-purity elemental materials. The nominal composition of the cast ingot was $\text{Ag}_{0.86}\text{Pb}_{19}\text{SbTe}_{20}$. Details of ingot casting are given elsewhere [8].

The SEM (Model S-3400, Hitachi, Japan) used in this study was equipped with an energy-dispersive X-ray spectroscope (EDAX, Mahwah, NJ) and a heating system (Aduro™ *In Situ* System, Protochips, Inc. Raleigh, NC) capable of reaching 1200°C. A fraction of a gram of the LAST material was crushed into sub-millimeter particles and spread onto a heating chip outside of the SEM using a cotton-tipped applicator. The heating chip with the powder specimen in place was mounted on the heating stage, which was then inserted into the SEM chamber (Figure 1).

The temperature on the chip was controlled by varying the current applied to the heating stage according to the calibration curve provided by the vendor. An SEM study was performed at room temperature, and at 25 K intervals between 423 and 848 K. According to the vendor specifications, the temperature of the heating chip can reach equilibrium within 0.5 s. However, since the temperature of the sample surfaces was not measured directly, a 10-minute isothermal hold was used to achieve thermal equilibrium before performing the SEM examination at each given temperature.

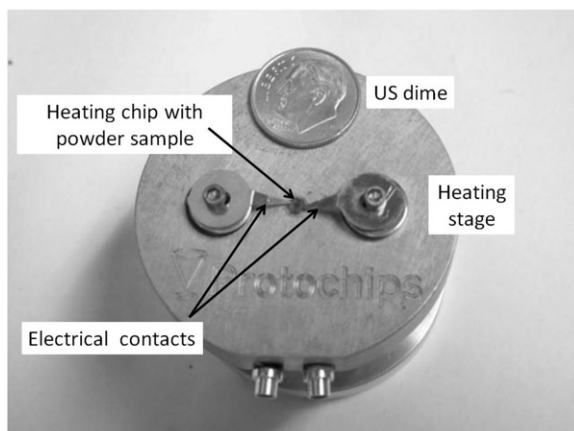


Figure 1. The heating chip and stage used in this study.

In addition, a thermogravimetric analysis (TGA) was performed at Netzsch Applications Laboratories (Selb/Bavaria, Germany) using a commercial unit (STA 409 CD[®], Netzsch Instruments, Burlington, MA). Approximately, 150 mg of crushed LAST powder was heated from room temperature to 973 K at a heating rate of 10 K/min. The TGA experiment was conducted in argon atmosphere at a flow rate of 70 mL/min.

3. Results and discussion

In this study, five LAST particles were selected as representatives, which are labeled as particles 1–5 in Figure 2a. Particle 1 appeared darker in the backscattered-electron imaging mode than the other four particles (Figure 2a). EDS analysis revealed that particle 1 had a very high concentration of Sb (Figure 2b), in contrast to the other four particles which consisted of mostly Pb and Te (Figure 2c). Stoichiometric LAST materials are solid solutions between PbTe and AgSbTe₂ [9]. While the Ag_{0.86}Pb₁₉SbTe₂₀ composition included in this study represents a slight deviation from stoichiometry, these materials possess compositional inhomogeneities on the nanoscale [2,10].

There is also evidence of macro-scale inhomogeneities in LAST materials. For example, using a scanning Seebeck microprobe, Chen et al. [11] observed macro-scale variations of the Seebeck coefficient on the surface of slowly solidified LAST samples. In previous work by the authors on the same LAST composition as that included in this study, inclusions rich in Ag and Sb were observed in a PbTe-rich matrix [12]. Thus, particle 1 in this study is likely an Sb-rich inclusion that broke off from the PbTe-rich matrix (particles 2–5).

When the sample was heated in the SEM, no significant morphology changes occurred below 823 K. At 823 K, particle 1 (which was initially about 30 µm long and 10 µm wide) became smaller in size with increasing holding time. Within several minutes, the initially monolithic particle with sharp edges gradually changed into a collection of many particles (mostly sub-micrometer in size) with smooth surfaces (Figure 2d). An EDS spectrum of particle 1 taken at 823 K (Figure 2e) indicated that the Sb concentration in the particle decreased, likely due to sublimation of Sb which in turn implies the Sb-rich inclusion was less thermally stable than the PbTe-rich matrix.

The morphology of particle 5 also started to change at 823 K. The particle not only shrank in size, but also developed ridge-like features on the surface (Figure 3a). An EDS elemental mapping showed a uniform distribution of Te on the particle (Figure 3b) along with inhomogeneous distributions of Pb (Figure 3c) and Ag (Figure 3d). The Ag-rich areas (Figure 3d) corresponded to those areas deficient in Pb (Figure 3c), which indicated that Pb likely evaporated preferentially from the surface while Ag remained.

After being heated to 848 K, particle 5 became kidney-shaped (Figure 4a). It consists mostly of Te (Figure 4b) and Ag (Figure 4c) and is nearly devoid of Pb (Figure 4d). In addition, at 848 K the shape of particle 3 dramatically changed from a 40-µm polygonal particle (Figure 2a) to multiple smaller rounded particles (Figure 4a) rich in Te (Figure 4b) and Ag (Figure 4c). Meanwhile, starting at a

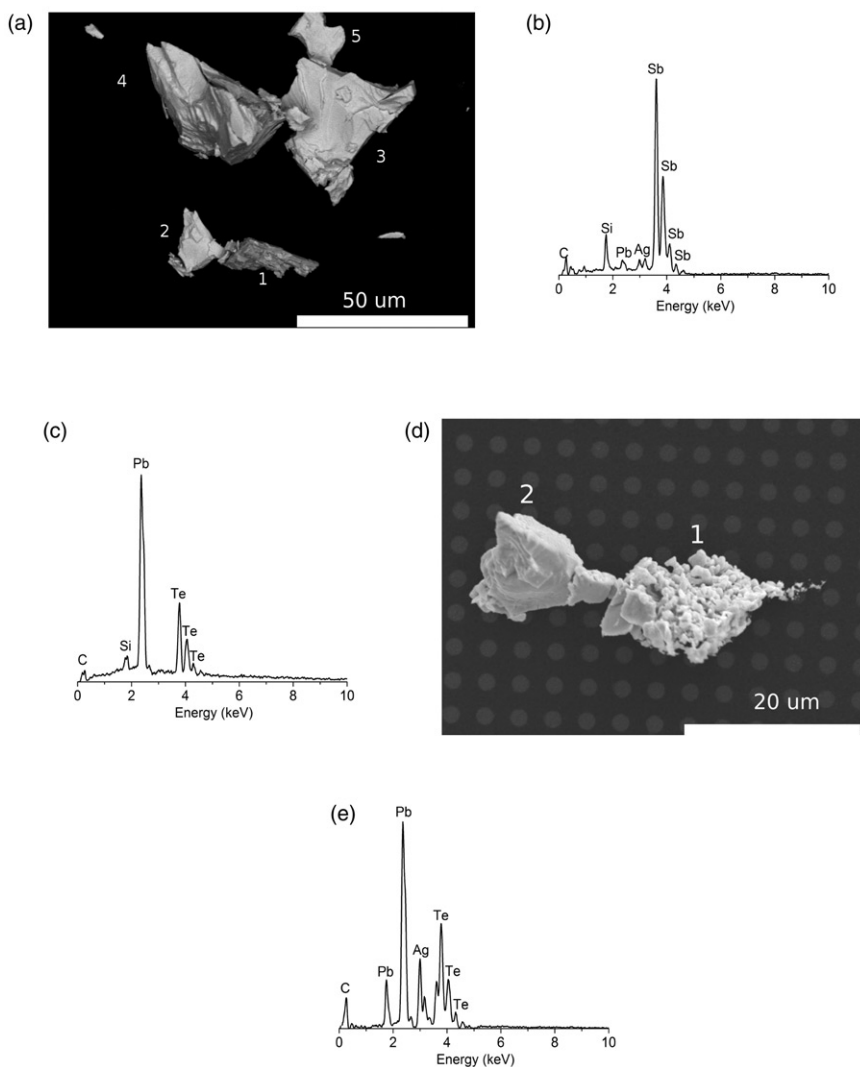


Figure 2. (a) Backscattered electron image at room temperature showing LAST ($\text{Ag}_{0.86}\text{Pb}_{19}\text{SbTe}_{20}$) particles labeled as 1–5. EDS spectra of (b) particle 1 and (c) particle 3 at room temperature. (d) An SEM image showing the morphology of particles 1 and 2 at 823 K, and (e) the corresponding EDS spectrum of particle 1.

temperature of 848 K, ridge features evolved on the surface of particle 4 (Figure 4a) that were similar to the ridges observed on the surface of particle 5 at 823 K (Figure 3a). The delay in morphological changes for particle 4 compared to particles 3 and 5 was likely due to particle height differences that led to different temperatures. (Note that heat flows from the particle-heating chip contact at the bottom of the particle to its top.) Particle 3 was significantly larger than particle 5 at room temperature (Figure 2a). However, particles 3 and 5 showed comparable size after

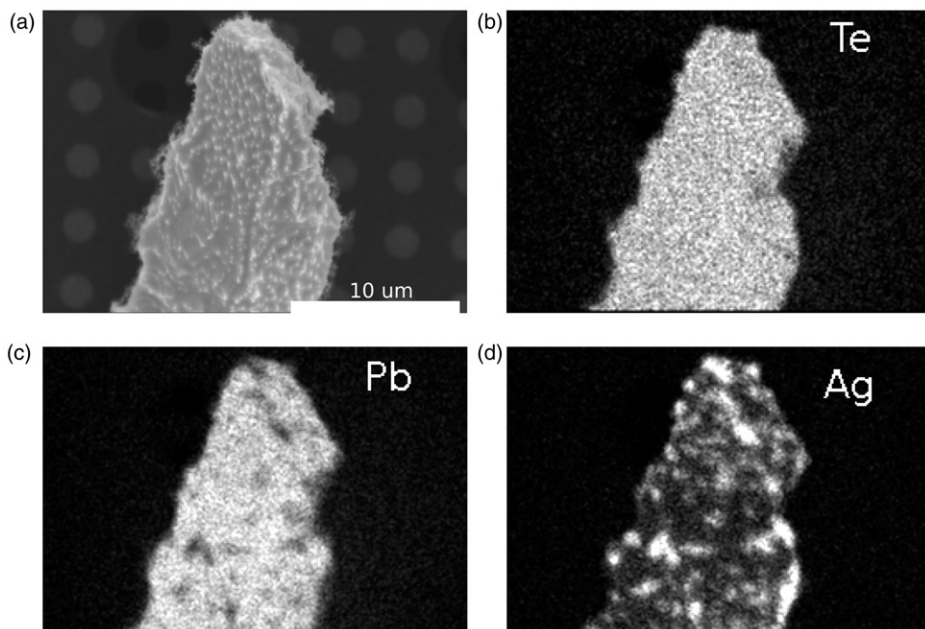


Figure 3. (a) An SEM image showing the morphology of particle 5 at 823 K, and the corresponding EDS elemental mapping of (b) Te, (c) Pb, and (d) Ag.

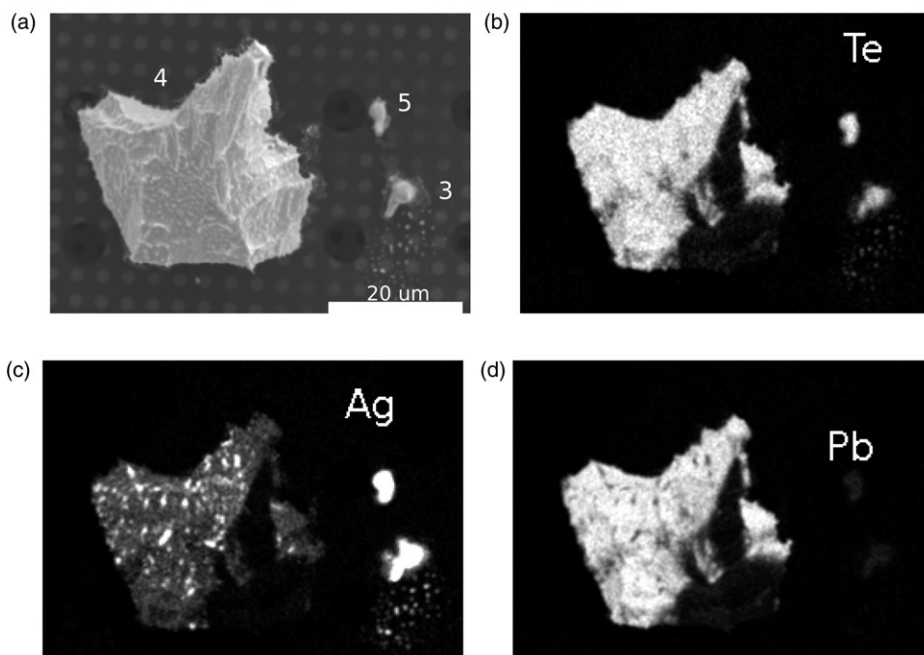


Figure 4. (a) An SEM image showing the morphology of particles 3–5 at 848 K, and the corresponding EDS elemental mapping of (b) Te, (c) Ag, and (d) Pb.

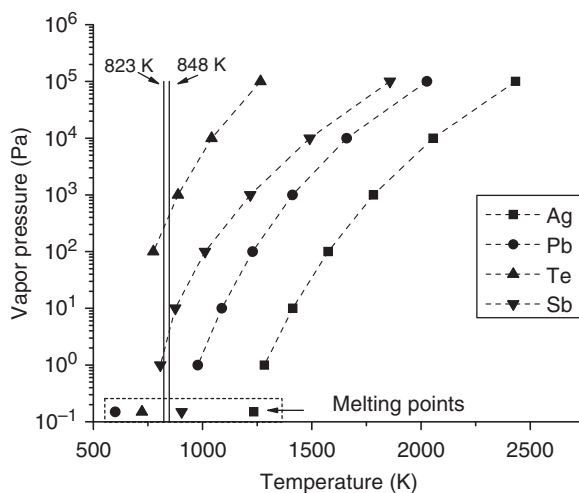


Figure 5. Vapor pressures and melting points of the four elements in LAST materials: Pb, Sb, Ag, and Te.

being heated to 848 K (Figure 4a). The relatively large size change observed in particle 3 was likely due to its higher content of volatile species than that in particle 5, which also demonstrates the compositional inhomogeneity in this material.

It is important to point out that electron beam heating in electron microscopy experiment can induce substantial temperature increases if the samples have low thermal conductivities [13], such as ceramics [14]. LAST materials are designed to possess low thermal conductivities [2], which could be prone to local beam heating. Thus identifying and separating the potential effects due to electron beam heating are important issues to address for *in situ* SEM studies of the thermal stabilities of TE materials.

Vapor pressure, which depends on temperature, also plays an important role in determining the thermal stability of a substance. The vapor pressures and melting points of the four elements of LAST [15] are illustrated in Figure 5. Both Pb and Te remained stable at 823 K, although the melting points of Pb and Te are both lower than 823 K, and Te has a relatively high vapor pressure at 823 K (approximately 300 Pa) (Figure 5). This is likely because Pb and Te form Pb–Te bonding in LAST materials, resulting in better thermal stability (the melting point of PbTe is 1197 K [15]).

Figure 5 shows that Sb has the highest vapor pressure apart for Te. In fact, Sb was found to be the first element to evaporate in this study. Ag has the lowest vapor pressure and the highest melting point among the four elements comprising LAST (Figure 5), and it seemed to be the most stable element in this experiment.

Following Sb, Pb was the second element to evaporate, which implied the onset of decomposition of PbTe. It was possible that Te also evaporated along with Pb, since Te has a higher vapor pressure than Pb (Figure 5). However, Te and Ag also form Ag_2Te , which could be the major composition of the remains of particles 3 and 5 (Figure 4).

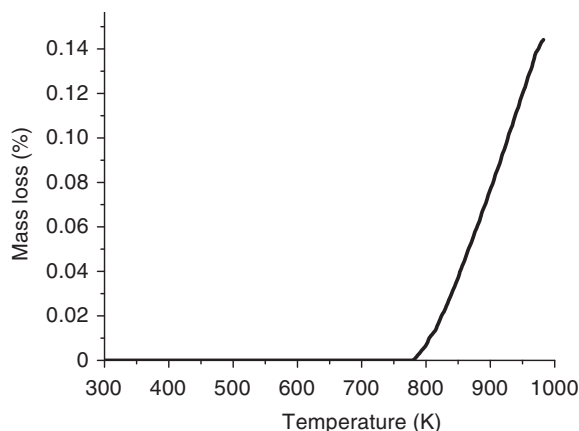


Figure 6. Mass loss between room temperature and 973 K as measured by TGA.

From the SEM observations, the LAST material included in this study started to decompose at approximately 823 K, which agrees with the result of TGA (Figure 6). The mass loss as a function of temperature indicated that the decomposition of the LAST sample began in the temperature range between 773 and 823 K. However, the mass loss in the TGA experiment appears to be only a small fraction (e.g. 0.03% at 848 K) of that observed in the SEM experiment (the entire Pb composition was absent).

There are several factors that can affect the thermal stability of LAST materials, including the heating environment, the heating rate, and the powder particle size. The different heating environment may explain the different mass loss revealed by SEM and TGA; the SEM observations were performed in a vacuum chamber ($\sim 6.7 \times 10^{-3}$ Pa) while the TGA experiments were undertaken in an alumina crucible under 70 mL/min flowing argon. Because the evaporation rate is proportional to the difference of the equilibrium vapor pressure and the ambient hydrostatic pressure acting on the evaporant on the solid phase, greater rates of evaporation are expected to occur inside the SEM compared to the TGA at the same temperature. The heating rates used in the TGA and the SEM were also different, in that the TGA sample was continuously heated at a rate of 10 K/min while the sample studied in SEM was held isothermally after the heating chip reached the pre-selected temperature via a very fast heating rate (< 0.5 s per 25 K temperature increment).

The powder samples used in TGA and SEM might contain similar particle sizes since they were both crushed manually. However, the particles were spread out on the SEM heating chip while they were packed in an alumina crucible in the TGA experiment. Thus, the free surface area of the powder particles exposed to the ambient environment was likely to be higher for the SEM sample than the TGA sample, which might also contribute to the greater mass loss observed in the SEM experiment.

The SEM and TGA results suggest that, due to thermal instability, LAST materials may not be suitable for applications or processing well above 773 K in vacuum environments. However, using a protective atmosphere (such as the

flowing argon used in the TGA experiment) and/or encapsulation may reduce the evaporation rate of LAST materials. Since the evaporation rate is proportional to the difference between the equilibrium vapor pressure and the hydrostatic pressure acting on the surface of the solid phase, the pressure of the protective environment should be at least equal, and preferably greater than the vapor pressure of the material. Another implication of this study is that densification of LAST materials by techniques such as hot pressing or pulsed electric current sintering (PECS) should be performed below 773 K in an inert atmosphere rather than in vacuum.

4. Conclusions

Using *in situ* SEM technique, we found that slow-cooled LAST material $\text{Ag}_{0.86}\text{Pb}_{19}\text{SbTe}_{20}$ was stable below 823 K. Inclusions rich in Sb were observed, which were thermally less stable than the PbTe-rich matrix by approximately 25 K. Decomposition of the matrix material began via evaporation of the Pb, leaving the specimens enriched in Te and Ag. In contrast to the SEM study, a TGA experiment performed in flowing argon showed a much smaller mass loss. This study suggests that powder processing of LAST materials should be performed in protective atmospheres. Also, if TE devices that utilize LAST are operated at temperatures above about 773 K, a protective environment such as an inert atmosphere with appropriate pressure should be provided to diminish the thermal degradation of LAST and hence extend the useful lifetime of the device.

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