doi: 10.1017/S1431927609094379
Microsc Microanal 15(Suppl 2), 2009
Copyright 2009 Microscopy Society of America

Structural Analysis of Nanoparticles in Thermoelectric $AgPb_{18}SbTe_{20}$ Single Crystal

Lijun Wu*, Juan Zhou*, Jin-Cheng Zheng**, Qing Jie*, Qiang Li*, Jihui Yang*** and Yimei Zhu*

* Brookhaven National Laboratory, Upton, New York, 11973
** Department of Physics, Xiamen University, Xiamen 361005, P.R. China
*** General Motors R&D Center, Warren, MI 48090-9055

Chalcogenide lead-based compounds, $AgPb_{18}SbTe_{20}$ (LAST-18), is one of the most promising bulk thermoelectric materials. The ZT value of LAST-18 was reported to be ~2.1 at 800K, which outperforms the other bulk thermoelectric materials [1]. The LAST-18 compounds possess an average NaCl structure with Ag, Sb and Pb randomly occupying at Cl sites and Te at Na site. Recent studies using x-ray diffraction and high resolution transmission electron microscopy (HRTEM) reveal that LAST-18 is inhomogeneous with nanoparticles coherently embedded in the matrix [2]. The enhanced thermoelectric properties of LAST-18 were attributed to the presence of the nanoparticles [1-2]. However, information about the nanoparticles, e.g. atomic arrangements of Pb and Ag-Sb, defects inside the nanoparticle and strain field induced by the nanoparticles, are still lacking. Here, we report our extensive studies about nanoparticles using HRTEM, nano-electron diffraction, energy dispersive spectrum (EDS) and electron energy-loss spectrum (EELS).

An overall observation indicates that the sample consists of NaCl-type matrix and Ag-Sb rich nanoparticles. We observed a range of nanoparticles with different size (from less than 1 nm to more than 10 nm), shape (sphere, ellipse, square, etc.) and lattice parameters. Fig. 1a is a high-resolution image, showing an elliptical-like nanoparticle coherently embedded in the matrix. Comparing to the matrix which has fcc lattice, the nanoparticle has a primitive tetragonal lattice with Pb and Pb/Ag/Sb ordering along c direction. The nanoparticle is Ag-Sb rich and its lattice parameter is measured to be c=0.64 nm, slightly smaller than that of the matrix. Nanoparticles with large lattice parameter difference (up to 6%) are also observed (Fig. 1b). Fig. 1c shows a square-shape nanoparticle with tetragonal structure. Three twin variants with their ***c*** direction pointing to $\boldsymbol{c_1}$, $\boldsymbol{c_2}$ and $\boldsymbol{c_3}$ exist in the nanoparticle. Careful observations reveal that there are tiny plate-like nanoprecipitates, as indicated by the arrows in Fig. 1b. Their dimension is only 0.64 nm (two atomic layers) in one dimension and varies from 1.22 nm to 3.86nm in the other two dimensions.

Strain contrast around the nanoparticles is observed for most of the nanoparticles. An example is given in Fig. 2. We use geometric phase analysis (GPA) to retrieve the distribution of the strain field from HRTEM image. Fig. 2b and 2c show the strain map ε_{xx} and ε_{yy}, retrieved from Fig. 2a with $\boldsymbol{g_1}$=200 and $\boldsymbol{g_2}$=002, and x- and y-axis pointing to the [100] and [001] direction. The ε_{xx} map basically shows negative strain in both matrix and nanoparticle. The ε_{yy} map shows positive and negative strain in the nanoparticle area, indicating a phase separation in this nanoparticle. The strain in the matrix, however, is quite different from that generated by an isotropic misfitting spherical inclusion in an infinite isotropic matrix. First, the strain amplitude does not decrease with the increase of the distance from the nanoparticle at least in the range of the measurement (~20nm). The bright-field image (inset in Fig. 2a) shows that the strain contrast extends to the area about 55 nm away from the nanoparticle. Second, the ε_{yy} strain around nanoparticle is not symmetric, e.g. ε_{yy} at bottom-left is larger than that at top-right. Near the nanoparticle, there is a small region showing

https://doi.org/10.1017/S1431927609094379 Published online by Cambridge University Press

positive ε_{yy}. We consider that the strain-field around the nanoparticle is not only caused by the misfit between the nanoparticle and the matrix, but also by the local fluctuation in the composition.

References

[1] K.F. Hsu, S. Loo, F. Gao, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, and M. Kanatzidis, Science 303 (2004) 8181.
[2] Eric Quarez, Kuei-Fang Hsu, Robert Pcionek, N. Frangis, E.K. Polychroniadis and M.G. Kanatzidis, J. Am. CHEM. SOC. 127 (2005) 9177.
[3] The work is support by the U.S. DOE, under contract No.DE-AC02-98CH10886.

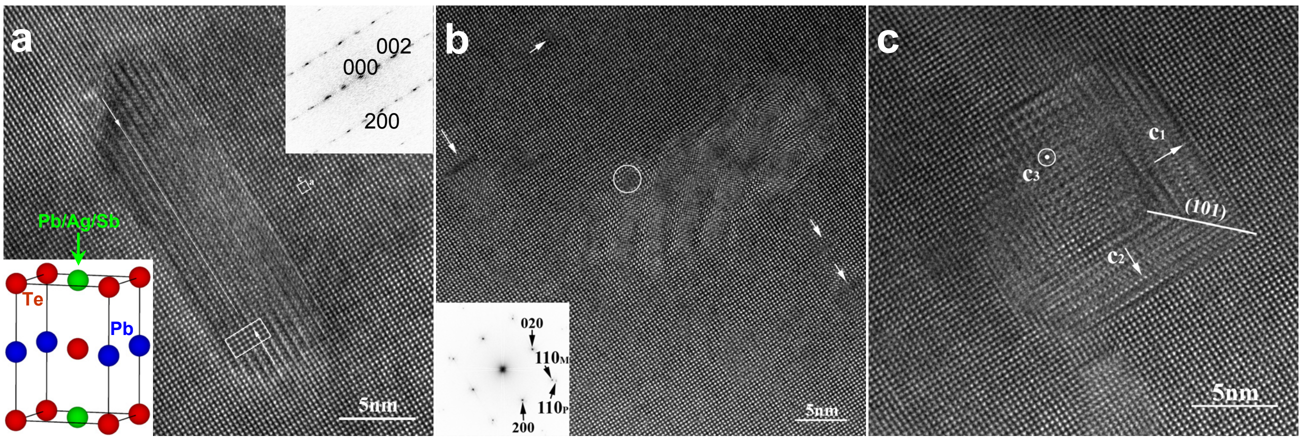

Fig. 1. (a) HRTEM image of LAST-18 single crystal sample, showing a nanoparticle coherently embedded in the matrix. The insets at top-right and bottom-left are the diffractogram and the structure model of the nanoparticle, respectively. A calculated HRTEM image is also included (rectangular region). (b) HRTEM image of $AgSbTe_2$ nanoparticle in PbTe matrix. The inset is the diffractogram of the whole image, showing that the reflections of the matrix and nanoparticle are well separated. Morié pattern presents due to the overlap of the nanoparticle and the matrix in the projection. Interfacial dislocations and plate-like nanoprecipitates with two atomic layers thickness are also present as indicated by the circle and arrows, respectively. (c) Twinning in square shape nanoparticle.

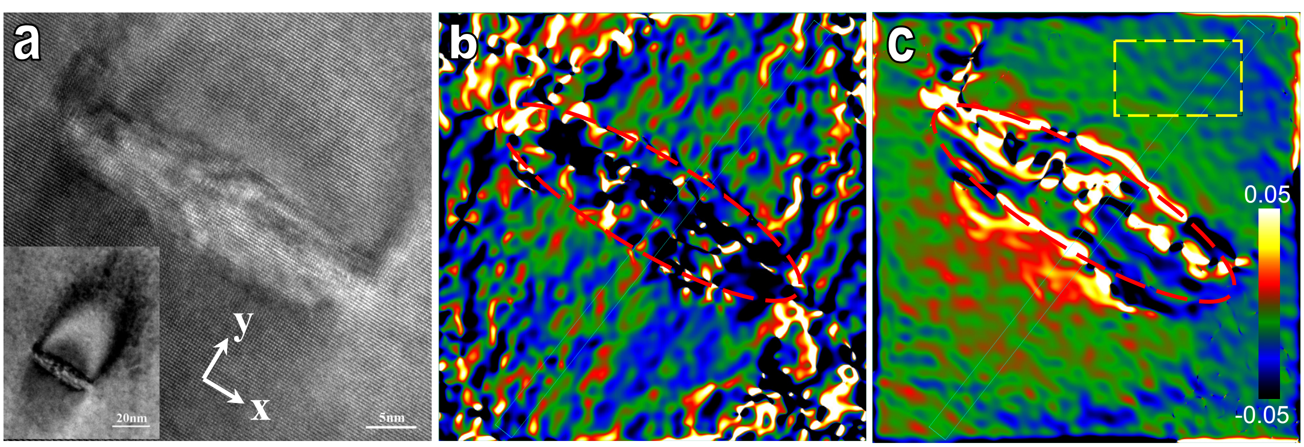

Fig. 2. (a) HRTEM image of an elliptical nanoparticle. The inset is the low-magnification bright field image, showing strain field contrast. (b-c) Strain-map of (b) ε_{xx} and (c) ε_{yy} calculated from (a). The ellipses in the figures outline the nanoparticles.

https://doi.org/10.1017/S1431927609094379 Published online by Cambridge University Press