

Na-Rich Interfacial Compound Impacted by Large Coherent Interfacial Strains in Na-doped p-type PbTe-PbS Thermoelectrics Investigated by S/TEM

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The rocksalt-structured, narrow-band-gap, lead chalcogenide family of semiconductors (PbX, X=Te, S and Se) and their alloys continue to attract considerable scientific interest because of potential applications in thermoelectric energy conversion [1]. These lead chalcogenides semiconductors can be turned p-type by adding alkali metals as dopants. Particularly Na, and sometimes K, has been extensively used for this purpose. Accordingly, a precise characterization and analysis of microstructure and chemical composition particularly those associated with the distribution of Na, as they relate to thermo-electrical transport, are vitally important for the fundamental understanding of thermoelectric materials.

Na dopant was conventionally considered to be homogeneously distributed in the material through forming solid solutions. Recent transmission electron microscopy (TEM) and atom probe study has shown, however, that Na and K may form nanostructures in PbTe [2]. However, because of the extremely small size of these nanostructures it was not yet possible to determine their structure explicitly before. Here, we present our transmission electron microscopy study on Na doped PbTe-PbS, which is an intrinsically immiscible system with multitude of precipitates and interfaces [3]. The distribution of Na associated with the PbTe-PbS interfaces are examined with analytical S/TEM.

Transmission electron microscopy results show the formation of Na-rich precipitates at the PbTe-PbS interfaces (Fig. 1). EDS measurements clearly show an abundance of Na in the interfacial compound, which is composed primarily of Na and S. The crystal structure of these Na-precipitates was thoroughly determined through a series of tilting experiments in TEM. (Fig. 2). The recorded set of diffraction patterns enables us to reconstruct the reciprocal lattice and to determine the lattice type and parameters. It turns out the Na-rich compound forms a long period superstructure.

Quantitative EDS analysis of the Na-rich Precipitate yields a composition approximately corresponding to $\text{Na}_3\text{S}_{2-x}\text{Te}_x$. However, it is also noted that accurate EDS quantitative analysis may need more dedicated processing of the EDS spectrum by taking into the absorption of Na-generated x-ray by S. The unusual structure of the new Na-rich phase is associated with large coherent interfacial stress and strains. An attempt of crystal reconstruction of the superlattice cell based on a subcell of defect anti-fluorite structure, whose lattice constants are close to the rock-salt PbS, was performed.

The presentation will cover S/TEM microscopy and microanalysis strategy, and quantitative x-ray analysis by considering the absorption effect, with an emphasis on unraveling the microstructural influence on thermoelectric properties and associated phenomena.

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References

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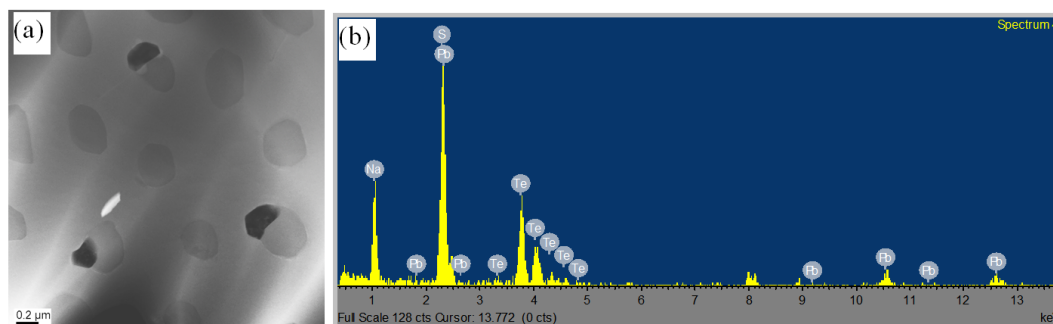


Figure 1. (a) Low magnification Z-contrast STEM image showing the structure of PbTe-PbS30%-Na2%, a composition located in the spinodal decomposition regime in phase diagram. (b) EDS spectrum taken from the dark interfacial compound under STEM mode clearly showing the Na-rich nature.

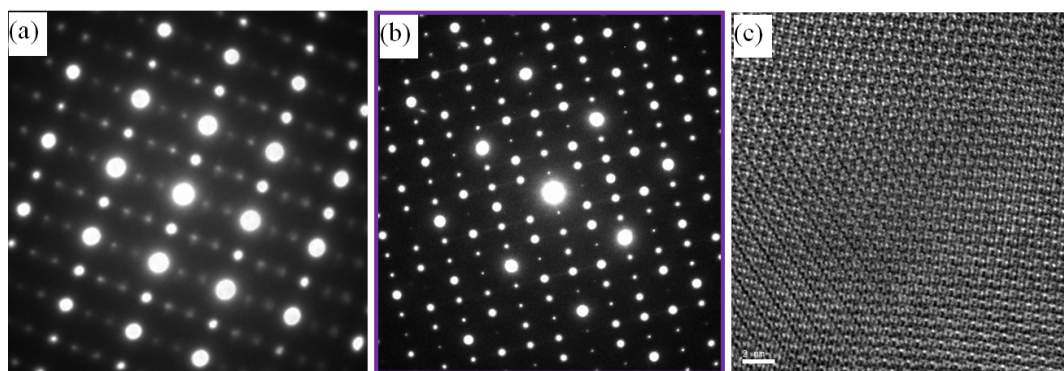


Figure 2. SAED patterns of the Na-rich compound observed in (a) [100], and (b) [001] directions. (c) HRTEM image showing clearly the modulated superstructure along <110> direction. The modulated structure has a subcell that matches perfectly with the PbS rock-salt unit cell.