Coherent and incoherent phase stabilities of thermoelectric rocksalt IV-VI semiconductor alloys

Jeff W. Doak and C. Wolverton
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, USA 60208
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Nanostructures formed by phase separation improve the thermoelectric figure of merit in lead chalcogenide semiconductor alloys, with coherent nanostructures giving larger improvements than incoherent nanostructures. However, large coherency strains in these alloys drastically alter the thermodynamics of phase stability. Incoherent phase stability can be easily inferred from an equilibrium phase diagram, but coherent phase stability is more difficult to assess experimentally. Therefore, we use density functional theory calculations to investigate the coherent and incoherent phase stability of the IVVI rocksalt semiconductor alloy systems Pb(S,Te), Pb(Te,Se), Pb(Se,S), (Pb,Sn)Te, (Sn,Ge)Te, and (Ge,Pb)Te. Here we use the term coherent to indicate that there is a common and unbroken lattice between the phases under consideration, and we use the term incoherent to indicate that the lattices of coexisting phases are unconstrained and allowed to take on equilibrium volumes. We find that the thermodynamic ground state of all of the IVVI pseudobinary systems studied is incoherent phase separation. We also find that the coherency strain energy, previously neglected in studies of these IVVI alloys, is lowest along [111] (in contrast to most fcc metals) and is a large fraction of the thermodynamic driving force for incoherent phase separation in all systems. The driving force for coherent phase separation is significantly reduced, and we find that coherent nanostructures can only form at low temperatures where kinetics may prohibit their precipitation. Furthermore, by calculating the energies of ordered structures for these systems we find that the coherent phase stability of most IVVI systems favors ordering over spinodal decomposition. Our results suggest that experimental reports of spinodal decomposition in the IVVI rocksalt alloys should be re-examined.

We provide here the density functional theory (DFT) calculations of mixing and coherency strain energies for six pseudo-binary semiconductor alloys: GeTe-PbTe, PbS-PbTe, PbSe-PbS, PbTe-PbSe, PbTe-SnTe, SnTe-GeTe. For each system, we have (i) special quasirandom structure (SQS) energies, (ii) small ordered structure $L1_1$, V_2, and Z_2 energies, and (iii) coherency strain energies along [100], [110], and [111].

The calculations are organized in the following manner. The calculations for each pseudo-binary system are contained in the top-level directories. Within each pseudo-binary system directory, there are sub-directories for (i) end-member rocksalt compounds, (ii) small ordered structures, (iii) SQS calculations, and (iv) coherency strain energy calculations. The SQS sub-directory contains calculations of SQS's with compositions of $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$. The coherency strain energy calculations were performed using the Alloy Theoretical Automated Toolkit (ATAT) [1], and contains a sub-directory structure as described within the ATAT manual. Each lowest-level directory contains a DFT calculation performed with the Vienna *Ab initio* Simulation Package (VASP) [2, 3], with most input and output files listed, including POSCAR, INCAR, KPOINTS, and OUTCAR files.

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[2] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
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