Negative-Pressure Polymorphs via Heterostructural Alloying

Scientific Achievement

For some heterostructural alloys, a metastable low-density polymorph can be the preferred structure for non-phase-separated intermediate compositions (top panel). For the MnSe-MnTe system, where this effect was predicted theoretically (middle panel), the low-density metastable wurtzite (WZ) phase was successfully synthesized using non-equilibrium thin-film growth (bottom panel).

Significance and Impact

Although high pressure can often be used to synthesize high-density phases not stable at ambient pressure, the analogous low-density (negative-pressure) phases are not readily synthesizable. Here, we have shown that heterostructural alloying is a viable synthesis method to realize such materials. This opens a new design space for targeting functional materials such as piezoelectric WZ-Mn(Se,Te).

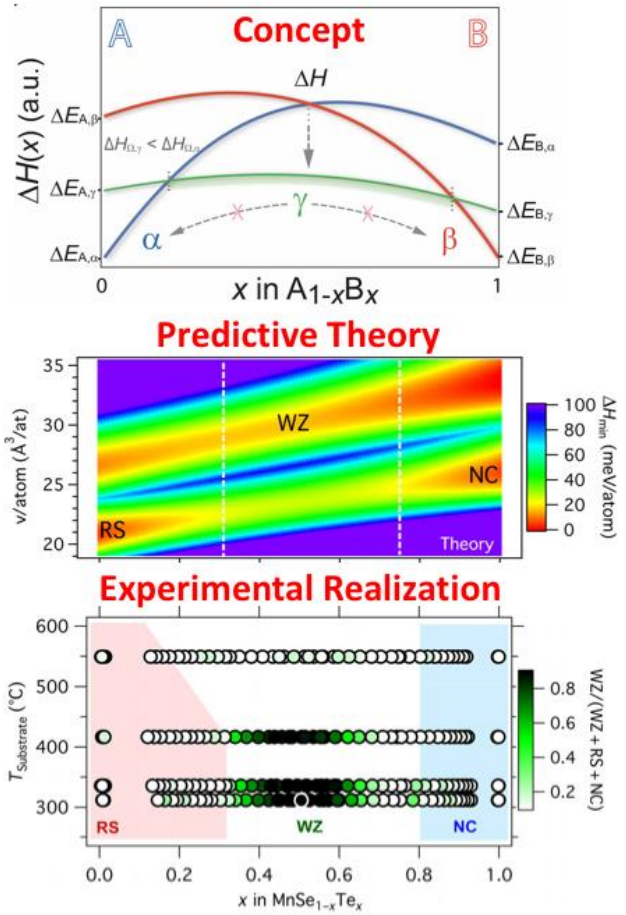
Research Details

Theory: For $MnSe_{1-x}Te_x$ alloys, the mixing enthalpy for the low-density WZ structure has smaller bowing than for high-density nickeline (NC) and rock salt (RS) structure (middle panel).

Experiment: Mixing high-density forms of RS-MnSe and NC-MnTe at low temperature using non-equilibrium synthesis stabilizes a $MnSe_{1-x}Te_x$ alloy with a low-density WZ structure (bottom panel).

S. Siol, A. Holder, J. Steffes, L.T. Schelhas, K.H. Stone, L. Garten, J.D. Perkins, P.A. Parilla, M.F. Toney, B.D. Huey, W. Tumas, S. Lany, A. Zakutayev, "Negative-pressure polymorphs made by heterostructural alloying," *Sci. Adv.* **4**, eaaq1442 (2018).

Low-Density WZ $MnSe_{1-x}Te_x$ Polymorph



Top: *Concept to access lower-density γ phase via heterostructural alloying.* ***Middle:*** *Quantitative predictive theory shows wurtzite (WZ) single-phase structure at intermediate compositions.* ***Bottom:*** *Experimental realization via thin-film synthesis.*

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