Negative-pressure Polymorphs Made by Heterostructural Alloying

Polymorphism is a fascinating natural phenomenon across many areas of materials science – from small molecules in chemistry, to minerals in geology, to drugs in pharmaceutical industry, to solid-state materials in electronics. High-density polymorphs with unique properties, such as a transparent insulating form of sodium (*1*) are routinely synthesized under compressive strain at very high pressure. In contrast, applying large negative pressure is very difficult, because large tensile strain usually causes materials to rupture. This logically leads to a question: *how could negative pressure polymorphs be synthesized and what functional properties would such unusual materials have?*

Researchers from NREL and SSRL have recently reported on "Novel phase diagram behavior and materials design in heterostructural alloys."(*2*). This approach utilizes non-equilibrium thin-film synthesis techniques to access a broad range of chemical compositions, which provides new routes to designing functional materials. Building upon that work, shown here is how such heterostructural alloying (mixing two materials with different crystal structures) can be used to discover new polymorphs that are otherwise stable only under negative pressure (i.e. large tensile strain). The resulting new understanding of how to synthesize such "negative pressure polymorphs" should be broadly applicable to discovery of many previously inaccessible materials.

In this work, the research team demonstrated how to synthesize low-density negative pressure polymorphs, by mixing two compounds with different high-density crystal structures. Theoretical calculations suggest that such low-density polymorphs tend to have lower alloy mixing enthalpy in heterostructural alloy due to less competition for space between the atoms (higher atomic volume and hence lower atomic interactions). As a proof of concept, the researchers showed by both computations and experiments that MnSe-MnTe alloys adopt a low-density wurtzite (WZ) structure – a negative pressure polymorph compared to the parent compounds with the high-density rocksalt (RS - MnSe) and nickeline (NC - MnTe) structures (Figure 1, left).

To synthesize the MnSe-MnTe alloys, high throughput combinatorial thin film co-sputtering was used.(*3*) This approach allowed the researchers to produce libraries of samples with varying composition and deposition temperature. Using x-ray diffraction, Vegard's law, and the disappearing phase method (*4*) they determined that the WZ-$Mn(Se_{1-x}Te_x)$ structure is present for compositions of $0.31 < x < 0.75$. This deposition method produces oriented samples that result in missing x-ray diffraction peaks when characterized using small area detectors. By measuring the full two-dimensional scattering pattern at SSRL Beam Line 11-3 (Figure 1, top right) the researchers were able to observe all the characteristic peaks of the WZ structure and confirm that the predicted low density polymorph is stabilized at the $MnSe_{0.5}Te_{0.5}$ composition.

The Figure's bottom right panel summarizes depositions done at different substrate temperatures. Higher temperatures (500°C) resulted in only the end member phases being present; while the lower temperature (300 – 400°C) depositions produced WZ rich regions. Using *in-situ* annealing capabilities at Beam Line 11-3 the research team heated a sample deposited at 320°C to 400°C for 90 minutes in a helium atmosphere and observed binodal decomposition of the alloy into its end members: RS – MnSe and NC – MnTe. This observation suggests that the WZ alloy is kinetically trapped during synthesis at lower temperatures.

Interestingly the heterostructural alloying of MnSe and MnTe lead to the emergence of a piezoelectric response, and to non-monotonic change in optoelectronic properties (band

gap, effective masses) showing the potential for this approach to produce new functional materials. The researchers believe heterostructural alloying could be used to access other II-VI and III-V alloys, which is further predicted to be a potentially rich space for this type of alloying approach. By utilizing publically available high-throughput computational databases such as the NRELMatDB (https://materials.nrel.gov/) and the Materials Project (https://materialsproject.org/) the search for promising candidate materials can be accelerated and provides a promising route to new materials discovery. The experimental data associated with this paper can be found at the High Throughput Experimental Materials (HTEM) database (https://htem.nrel.gov/) that was recently released by NREL. (*5*)

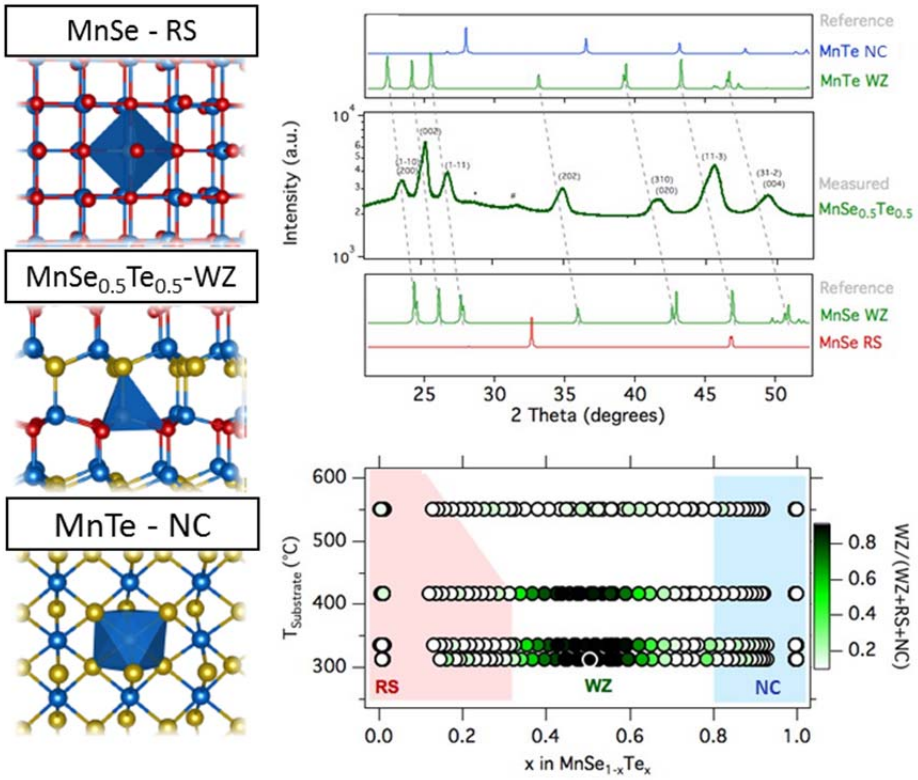

Figure: *(Left)* MnSe, rock salt (RS), $MnSe_{0.5}Te_{0.5}$, wurtzite (WZ), and MnTe, nickeline (NC) crystal structures. *(Top right)* Synchrotron XRD measurements of $MnSe_{0.5}Te_{0.5}$ thin films grown on glass at 320°C substrate temperature *(white circle in bottom right)* confirm the stabilization of the high-enthalpy, low-density WZ polymorph. Trace amounts of MnTe NC (*) and MnSe RS (#) could be present in the film. The top and the bottom panels show the simulated XRD patterns of MnSe and MnTe in WZ and other structures, and the dashed lines are extrapolations of the WZ peaks. *(Bottom right)* Color scale map of the WZ phase fraction for the sputter deposited $MnSe_{1-x}Te_x$ thin films on glass. For intermediate compositions and lower deposition temperatures, the $MnSe_{1-x}Te_x$ films crystallize predominantly in WZ structure with some RS-type and NC-type impurities. Shaded areas represent single-phase regions of RS-MnSe and NC-MnTe determined by the disappearing phase methods.

References

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