Structure prediction in the Zn-Al-O phase diagram

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In a world that is using ever more transparent conducting oxides (TCO), the ideal Sn_2O_3:In (ITO) is becoming more and more expensive. A commercially available alternative is ZnO:Al(2 wt%), which is, however, far from optimal. As part of a larger project, our goal is to search and evaluate alternative TCO's.

Since the Zn-Al-O system already delivered a TCO, one could wonder whether more is to be found in this ternary system. This phase diagram has only 3 known binary structures (ZnO, ZnO_2, Al_2O_3) and 1 known ternary ($ZnAl_2O_4$, gahnite) [1]. A machine learning method [2] returned a few metastable aluminium-oxides and 1 metastable ternary structure on top of the experimentally known ones. Several low-density ZnO-polymorphs have been predicted ([3], [4]), which should be stable at slight negative pressures. This suggests that metastable ternary Al-Zn-O alloys are not unfeasible.

By making total energy DFT calculations, using VASP [5], for a set of crystal structures that appear experimentally in chemically similar ternary systems, we identified 16 new Al-Zn-O alloys. They form a line in the Al-Zn-O composition triangle, connecting ZnO and Al_2O_3. Every composition on this line has the common property that the weighted sum of oxidation states of the elements amounts to zero (O(Zn)=+II, O(Al)=+III, O(O)= -II). None of these 16 structures is stable against decomposition into ZnO, Al_2O_3 and/or $ZnAl_2O_4$. Their excess formation enthalpy is sufficiently low, however, to expect that they could be stabilized e.g. as epitaxial thin films.

We plan to use an evolutionary search as a tool to identify crystal structures for Al-Zn-O stoichiometries along this line of interest, for which no analogies in chemically similar ternary systems are known.

References

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