THERMODYNAMICS OF COMPOSITIONALLY COMPLEX ("HIGH-ENTROPY") OXIDES

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In the current scientific literature, the "high-entropy oxide" (HEO) term is often applied rather loosely to oxides containing five or more metal cations within one sublattice, typically in equimolar proportions. In theory, if an assumption of random mixing holds true, such an oxide phase possesses a configurational entropy $\Delta S_{conf} \geq R\ln(5)$ per formula unit. This additional contribution to the total entropy of a HEO may boost its thermodynamic stability and is believed to play a significant, if not dominant, role in stabilizing some HEOs, especially those that are metastable at low temperatures. Consequently, HEO phases may comprise cations in atypical for them crystal structures – for instance, Zn and Cu in the rock-salt structure of (Co,Cu,Mg,Ni,Zn)O – possessing interesting properties that are not merely averages of the properties of simple oxide constituents. This possibility is what makes HEOs increasingly attractive research objects.

However, the great expectations for the enhanced stability and exceptional performance of high-entropy materials are not always met. Even in the field of high-entropy alloys, which have been investigated for nearly twice as long as HEOs, relatively few truly single-phase solid solutions have been identified, and their properties are often determined by the average of the properties of the constituting elements. Likewise, not always do the functional properties of HEOs exceed those of the "low-entropy" oxides. Therefore, while it is not known a priori what exact combination of elements will make up a HEO with outstanding characteristics, it is clear that arbitrary element selection is insufficient. The same applies to stability: one cannot expect to obtain a more stable material simply by adding more cations to an oxide sublattice. As of now, the stability issues of all HEOs, those with unique and mediocre properties alike, remain severely underinvestigated. Moreover, while valuable for rapid screening of the broad composition space in search of new HEOs, the statistical, empirical and purely computational approaches cannot yet be used for the deep analysis of stability and chemical compatibility of particular materials.

It is clear that enthalpy and all kinds of entropy (configurational, vibrational, electronic and magnetic) do contribute to formation and stability thermodynamics of compounds. The extent of these contributions remains to be ascertained with experimental thermodynamic methods. The results of such studies will be discussed in this talk.

This work was financially supported by the Russian Science Foundation (grant № 24-23-00478).