

Entropy Driven Synthesis of New Materials

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Abstract

The use of entropy in obtaining new materials has been known for some years for alloys but recent developments were made for a variety of ceramics. An outstanding compositional space is thus open by statistical distribution of components in a given structure. In this Perspective the author provides a description of entropy stabilized compounds and outlines directions for applications.

Key words: entropy-stabilized ceramics; metastable materials

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Main text

There is a misconception in the general public that "*Diamonds are forever*". Actually, diamond is not the thermodynamic stable form of carbon. Thermodynamic stability is governed by the Gibbs law and some metastable materials, like diamond, can be kinetically stabilized. In other words, thermodynamics "tells" the direction of a chemical reaction while kinetics decide how fast to reach the reaction products. The Gibbs law, bearing the name of Josiah Willard Gibbs who incidentally was the first PhD in engineering in the US, at Yale in 1863, states that the outcome of a chemical reaction is governed by the free enthalpy which is the difference between the enthalpy of reaction and the entropic term $\Delta G = \Delta H - T\Delta S$.

Entropy is commonly associated with disorder but sometimes can be used as a driving force for creating new and structurally simple materials.^[1,2] In systems with several elements and at high temperatures, the entropic term $T\Delta S$ may become the dominant part of the total Gibbs energy. In this case, the entropy is maximal for statistical distribution of atoms among available sites and will control the outcome of the reaction, leading to new and generally simple structures.

Considering only the entropy of configuration and for a single crystallographic site: $S = -R\sum x_i \ln(x_i)$ with x_i the molar fraction of component i , the entropy increases with the number of components and is maximum for equimolar composition. For example, for a five-element equimolar system the configuration entropy S is equal to $1.61R$; at typical ceramics reaction temperatures the term $T\Delta S$ amounts to 15–25 kJ mol⁻¹. This entropic stabilization energy is of the same order of magnitude as some enthalpies of reactions in solids. Thus, instead of forming phases driven by the interactions between the atoms (enthalpy controlled), the system crystallizes in an entropy stabilized phase at high temperature. This phase can be "frozen" at room temperature by quenching, obtaining a remnant metastable phase.^[3] This is an entropy driven synthesis

and can provide a wealth of new compounds with potentially unusual structures and interesting properties.

This approach was initially proposed by Yeh et al^[4] and independently by Cantor et al^[5] for alloys, these are known as high entropy alloys and are in full development today.^[6] To date, there are several classifications of high entropy materials, as either materials with an entropy larger than 1.5 R or 1.61R, or materials with at least 5 elements in equimolar or close concentration.^[7] By taking into account this last definition, any compound with at least five different cations in close concentration is a "high entropy" material. However, some of these compounds are not entropy-stabilized, for instance when ΔH is negative, which means the entropy is not playing a major role in their formation, **Figure 1**. The structure and properties of these materials are close to classical solid solutions although some interesting features in their phase stability might appear.^[8]

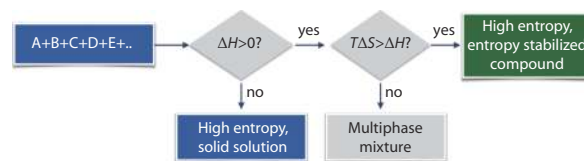


Fig. 1 Distinction between "high entropy" and "entropy stabilized" systems

Oppositely, for a positive reaction enthalpy, a critical temperature for which $\Delta H = T\Delta S$ exists and corresponds to a transition temperature from a low temperature, enthalpy-controlled phase (or mixture) to a high temperature and entropy controlled phase that can be quenched to room temperature in a metastable state. The properties of this metastable compound are not necessarily just a mixture of the starting materials, they can present a non-linear answer coming from the novel structures or combinations of elements.^[1,2] An example of non-linear effects in properties is the superconductivity observed for a high-entropy alloy

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Ta₃₄Nb₃₃Hf₈Zr₁₄Ti₁₁^[9] or, among many others, outstanding mechanical properties.^[10]

By using the principle originally developed for alloys^[4,5], the first entropy stabilized oxide (Mg,Co,Ni,Cu,Zn)O, was reported in 2015, in a seminal paper by Rost et al.^[11] This new material contains five different cations in equimolar ratio, presents a reversible phase transition at about 1150 K and has a simple rock-salt structure at high temperature. When quenched to room temperature this phase retains the structure with the five cations equally distributed on the cationic sites. We note that some constituting binary oxides do not crystallize in a rock-salt structure and they do not form solid solutions: this material is a *metastable* solid solution. Heating the obtained compound at a temperature where $T\Delta S < \Delta H$, for this case below 1150 K, leads to the separation into several constituents, [Figure 2](#).

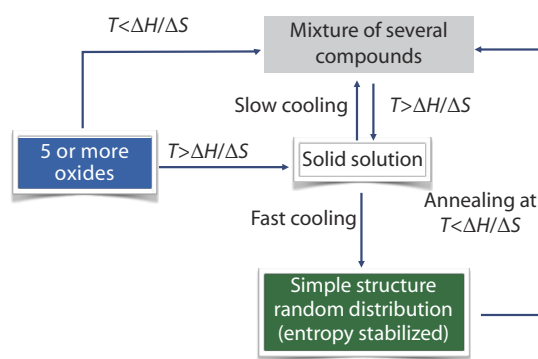


Fig. 2 Evolution of a five-component oxide and entropy driven synthesis.

Entropy governs the formation of this structure, and all five cations are randomly distributed to octahedral sites. We can infer that, to obtain a material with a specific cation in an octahedral site we can use this approach, for this structure, as long as the enthalpy "cost" of inserting this specific cation in an octahedral site will be smaller than the entropic stabilization energy, at an attainable temperature of synthesis.

The particularities of using entropy for the synthesis of new materials are, first that we can obtain new structures and compositions as the reaction is not determined by interatomic interactions. These new structures may force atoms in unusual states generating new properties. Second, there is a tremendous diversity of compositions that can be envisioned. To illustrate this last point, let's consider "mixing" five metals, out of 26 found in alloys, and vary their compositions within 1%: the number of combinations obtained, for a single structure type, is 2 822 599 802 880. For six elements the number of possible compositions, again for a single structure, is 902 943 619 878 430.^[12] By considering a more restrictive definition for high entropy alloys, that the concentration of components is from 5% to 35%^[7] these numbers are reduced to about a third, they are still very large and even if only a small fraction of these would be stable, still an impressive number of new compounds could be obtained. For this staggering number of compositions theoretical calculations are inefficient but some descriptors were already proposed and found to be quite effective in predicting the stability of materials.^[13]

For oxides the situation is even more complex than that of alloys because several cationic and anionic sites can be available. If we take the example of perovskite ABO₃ several compounds with random occupancies on A site, on B site or even on both A and B sites can be obtained. We can add other configurations on the anionic sites. With over 9000 structure prototypes^[14], the number of combinations for oxides is difficult to estimate. As an example, for just a single structure and only for the anionic site, a recent work indicates a number of 237 258 possible compositions, and among these 143 744 are of high-entropy.^[15] Notwithstanding, just a handful of entropy stabilized oxides systems are known today.^[16]

The interest in finding new systems is related to the fact that entropy stabilized oxides have structures and properties difficult to predict as they are not classical solid solutions. They are not only new materials, but represent a transformative change in the design of new functional materials, a significant change in material science which encompasses several other fields. This is not merely a new synthesis method "but an extremely broad philosophy on how to combine elements".^[17]

While the field is still in its infancy, the properties and possible applications for these new materials are diverse^[16], besides mechanical properties in electrochemical applications^[18–22], dielectrics^[23,24], magnetic properties^[25–27], thermal barrier coatings^[28], thermoelectric materials^[29,30], water splitting^[31] and particularly in catalysis.^[32–37] Entropic effects were also observed at low temperature in hybrid perovskite solar cells.^[38]

These unexpected and, most importantly, tailorable properties^[8] led to an effervescence in the field of new materials by using this approach of synthesis^[16,39–42], it represents a paradigm shift in materials' synthesis, and it is expected that this new method of synthesis will bring about new materials and hopefully new properties.

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Conflict of interest

The authors declare no conflict of interest.

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Biography



After a master degree in inorganic chemistry in University of Bucharest, Nita Dragoë obtained a PhD from Université Paris-Sud and University of Bucharest in materials science in 1996. He then joined University of Tokyo as JST-CREST postdoctoral fellow from 1997 to 2000 and then as a Lecturer in the Department of Applied Chemistry of University of Tokyo until 2001. From 2001 to 2004 he was Associate Professor in Université Paris-Sud and from 2004 he is a Professor at Université Paris-Sud (which later became Université Paris-Saclay). He had several visiting scientist or professor positions in Japan and China. His interests are related to synthesis and functional properties of advanced materials.