PhD Project: New high entropy oxides for H2 production by photo(electro)catalysis

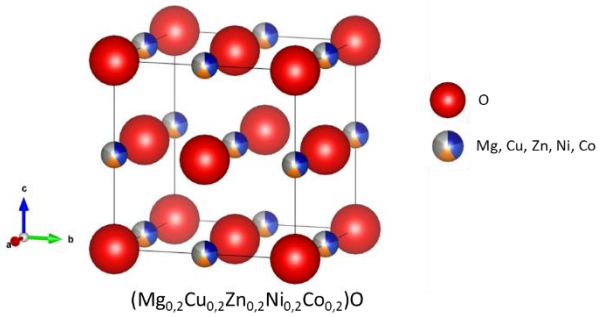
1. ***Scientific context of the study***

Entropy is usually associated with disorder but can sometimes be used as a driving force to create new structurally simple materials. In multi-element systems and at high temperatures, the entropy term TΔS can become the dominant part of the total Gibbs energy ahead of the binding energy. In this case, the entropy is maximal for a statistical distribution of atoms among the available sites and will control the outcome of the reaction, leading to new structures. In that case, the system crystallizes in an entropy-stabilized phase, usually of high symmetry, even for compounds that usually do not form solid solutions. This metastable phase can be kinetically frozen at room temperature leading to compounds with unexpected structures and properties. This approach has been used since 2004 for metallic alloys and recently for oxides, sulfides, carbides, etc.
The particularities of using entropy for materials synthesis are, first, that it is possible to obtain new structures and compositions because the reaction is not determined by interatomic interactions. These new structures can "force" atoms into unusual states (coordination, oxidation state, ...) generating new properties. Secondly, there is a huge diversity of compositions that can be considered, which enables a fine optimization of properties.

These compounds are therefore not only new materials, but they represent a transformative change in the design of new functional materials, a significant change in materials science that encompasses several other fields. It is not just a new method of synthesis "but an extremely broad philosophy on how to combine elements".

Our team at ICMMO was the first to study the doping and properties of new high entropy oxides of the parent compound (Mg,Co,Ni,Cu,Zn)O. We found that, for some compositions, they exhibit very high dielectric constant values or high ionic conductivities of Li+ ions, which makes them promising for battery or supercapacitor applications. We also found the existence of an unexpected long-range magnetic order with a transition temperature that can be controlled by the composition.

Since the first publication in 2015 the number of new structures and compositions published in the literature has practically exploded but the study of the physicochemical properties of these compounds for applications is still low. One of the promising applications for these systems is catalysis because the synthesis method can "impose" particular geometries for cations and the quasi-continuous variation of compositions allows to refine their properties and in particular the bandgap.



$(Mg_{0,2}Cu_{0,2}Zn_{0,2}Ni_{0,2}Co_{0,2})O$

The main objective of this PhD project is to synthesize new compositions of high entropy oxides and to study their physico-chemical properties for applications, in particular for the (electro)photocatalytic reaction of water-splitting.

Some papers of the team:

1. N. Dragoe, *"Entropy driven synthesis of new materials",* Material Lab **1**, 220001 (2022).
2. W. Mnasri, D. Berardan, S. Tusseau-Nenez, T. Gacoin, I. Maurin, N. Dragoe, "*Synthesis of (MgCoNiCuZn)O entropy-stabilized oxides using solution-based routes: influence of composition on phase stability and functional properties",* Journal of Materials Chemistry C **9**, 15121 (2021).
3. Vayer, F; Decorse, C; Berardan, D; Dragoe, N, "*New entropy-stabilized oxide with pyrochlore structure: Dy2(Ti0.2Zr0.2Hf0.2Ge0.2Sn0.2)(2)O7*", Journal of Alloys and Compounds 883, 160773 (2021).
4. N. Dragoe, D. Berardan, "*Order emerging from disorder*", Science **366**, 573 (2019).
5. N. Osenciat, D. Berardan, D. Dragoe, B. Leridon, S. Holé, A.K. Meena, S. Franger, N. Dragoe*, "Charge compensation mechanisms in Li-substituted high-entropy oxides and influence on Li superionic conductivity",* Journal of the American Ceramic Society **102**, 6156 (2019).
6. M.P. Jimenez-Segura, T. Takayama, D. Berardan, A. Hoser, M. Reehuis, H. Takagi, N. Dragoe*, "Long-range magnetic ordering in rocksalt-type high-entropy oxides",* Applied Physics Letters **114**, 122401 (2019).
7. D. Berardan, A.K. Meena, S. Franger, C. Herrero, N. Dragoe*, "Controlled Jahn-Teller distortion in (MgCoNiCuZn)O-based high entropy oxides",* Journal of Alloys and Compounds **704**, 693 (2017).
8. D. Berardan, S. Franger, A.K. Meena, N. Dragoe*, "Room temperature lithium superionic conductivity in high entropy oxides",* Journal of Materials Chemistry A **4**, 9536 (2016).
9. D. Berardan, S. Franger, D. Dragoe, A.K. Meena, N. Dragoe*, "Colossal dielectric constant in high entropy oxides",* Physica Status Solidi RRL **10**, 328 (2016).

2. ***PhD project***

a. Objectives

Although the field is still in its infancy, the properties and possible applications of these new materials are diverse, for example: in electrochemical applications, dielectrics, magnetic properties, thermal barrier coatings, thermoelectric materials, water splitting and especially in catalysis. Entropic effects have also been observed at low temperatures in perovskite hybrid solar cells.

Some new compositions have started to be reported for more complex crystal structures with several cations. In these structures, the properties are no longer only controlled by the chemical nature of the cations present on one or the other site, but by the interaction between cations of the two sites, which may lead to the possibility to develop multifunctional materials, or exotic physical properties.
The systems chosen for this project are complex oxides, with d^0 electronic configurations that can be doped to make them semiconducting. Starting materials will belong to tungstates, fluorites and pyrochlore families. For these structures several starting compositions have already been synthesized and have shown promising properties. The scientific activity of the thesis will be divided into an exploratory stage in order to identify the compositions stabilized by configuration entropy and to determine the suitable dopants to control their absorption spectra. In a second step, for the compositions that seem interesting, catalytic activity studies will be performed.

b. Methodology

The research work will include:
-the synthesis of materials in polycrystalline form, mainly by solid phase synthesis under controlled atmosphere
-the synthesis of nanoparticles of these materials
-structural and microstructural characterizations (XRD, SEM, TEM, XPS, EDX…)
-their preparation for applications in catalysis, for example in the form of nanocrystalline powders, or of thin films
-the study of their physical properties (electrical conductivity, optical properties,..)

The project may also involve the use of large instruments, in particular for the study by X-ray absorption (XANES, EXAFS).

c. Supervision and organization

This research project will be mainly carried out at the Institute of Molecular and Materials Chemistry of Orsay (ICMMO), Univ. Paris Saclay, in the team Synthesis, Properties and Modeling of Materials (SP2M). It is based on a collaborative project funded by ANR (PEPR-H2, HYDRO project, 2023-2027) between ICMMO (Orsay), IC2MP (Poitiers), IJL (Nancy), ICPEES (Strasbourg) and LISE (Paris). Other projects related to high entropy synthesis are ongoing in our team, and a postdoctoral researcher and three other theses are in progress in our team on related topics. All the equipment necessary for the success of this project is available within our team or through collaborations.

Within the SP2M team, the supervision of the project will be carried out by a group of three researchers: Pr Nita DRAGOE, Dr. David BERARDAN and Dr. Adrien MOLL.

Nita Dragoe and David Bérardan are among the pioneers of entropy-stabilized oxides, co-authors of several important publications in the field, particularly in the study of their physical properties, which they were the first to study. Adrien MOLL has recently joined our group as assistant professor and starts his research activity in this field.

3. ***Candidate profile and contacts, general informations***

- Master degree in materials science
- Experience in materials solid-state synthesis, as well as structural and microstructural characterization
- Strong skills in oral and written communication
- Motivated, curious, autonomous

The Institute of Molecular and Materials Chemistry of Orsay (ICMMO), Univ. Paris Saclay, is located in the south of Paris, France.
The position is open, the PhD project should begin before December 1st 2023 for 3 years. The net salary, including social security, is about 1700€ per month.

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