



Offre de thèse en CHIMIE

Titre de la thèse : Lead substitution in halogenated perovskites // Substitution du plomb dans les pérovskites halogénés

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Financement : Allocation doctorale, financement acquis

Sujet de Thèse :

For half a decade, 3D Halogenated Perovskites (HPs) $(A)(Pb)(X_{1-x}X'_x)_3$ ($A = CH_3NH_3^+$, $CH(NH_2)_2^+$ (and Cs^+); $X, X' = I^-, Br^-, Cl^-$) have revolutionized photovoltaics and more generally the domain of soft electronics. This family of HPs is known since the beginning of the 80's, with many results in the period 1992-2008 essentially on 2D HPs whose child structures are related to the 3D mother one. Their recent breakthrough has started in 2009 with the first report on MAPI ($A=CH_3NH_3$; $X=X'=I$) as sensitized material in a solar cell device. Since then, the development of organic-inorganic perovskite-based solar cells (PSCs) has increased unprecedentedly, the PCE (Photoelectric Conversion Efficiency) of the PSCs reaching more than 22%. Due to their exceptional luminescent properties, a domain of PeLEDs has also emerged (PeLEDs= perovskite light emitting devices). The success of MAPI and related 3D materials in electronics is due to the easy fabrication of thin films from solutions at room temperature, as in the case of organic electronics, and their intrinsic electronic properties. However, the main disadvantages of the 3D HPs are their instability to moisture, and the toxicity of Pb.

In this project, we propose to partially or fully substitute Pb^{2+} cations by non toxic cations (organic or inorganic) in halogenated perovskite materials for PSCs or PeLEDs applications. Recently, we have discovered a new family of hybrid perovskites, dubbed d-HPs, which are promising for the above mentioned issues (materials for PSCs or PeLEDs, more stable and with a reduced lead content). A d-HPs phase is lead and halide deficient compared to $(CH_3NH_3)PbX_3$, a $(PbX)^+$ unit being substituted by an organic monocation, while keeping a 3D architecture. By using two kinds of organic cations, MA^+ and the hydroxy-ethyl ammonium (HEA^+), a series of d-HPs compounds whose general formulation is $(A,A')_{1+x}[Pb_{1-x}I_{3-x}]$ ($0 < x < 0.20$) has been obtained.^[1] These HPs offer increased flexibility of their chemical composition with potential substitutions on the A, A', Pb and X sites.

A first direction of this work will be the preparation of such materials with different substitutions (PSCs and PeLEDs applications), such as: $A=MA^+ \rightarrow FA^+/Cs^+$; $A'=HEA^+ \rightarrow$ guanidinium/

$Y(\text{CH}_2)_2\text{NH}_3^+$ ($Y = \text{SH}, \text{F}, \text{Cl}, \text{Br}, \text{CN}$); $\text{Pb} \rightarrow \text{Sn}^{2+}/\text{Bi}^{3+}$; $\text{X} = \text{I} \rightarrow \text{Br}$. Moreover it is expected that stability will be improved by substituting MA^+ by FA^+ and/or Cs^+ . Priority will also be given to organic cations A' that will enhance stability to moisture. Lead content can also be tuned, either by increasing x or by substituting Pb^{2+} by Sn^{2+} . Finally, by using MA^+ or FA^+ and a functional A' cation such as $Y(\text{CH}_2)_3\text{NH}_3^+$ ($Y = \text{OH}, \text{SH}, \dots$), other types of d-HPs could be also discovered.

A second direction will be the exploration of system based on iodobismuthate or iodoantimonate inorganic anions (lead-free materials – PSCs application). Hybrid compounds based on such anions are known to be stable (unlike $\text{Pb}(\text{II})/\text{I}$ or $\text{Sn}(\text{II})/\text{I}$ materials), easily prepared as thin films, and often colored. However, due to the +3 charge of the Bi or Sb ion, there is yet no Bi(Sb)/I 3D HP, while 2D networks are rare: one Bi/I HP network $\text{Bi}_{2/3}\text{I}_4^-$ (deficient $n=1 <1\ 0\ 0>$ monolayer perovskite network) has been reported a long time ago, while recently the M_2X_9 ($\text{M} = \text{Bi}^{3+}, \text{Sb}^{3+}$; $\text{X} = \text{I}, \text{Br}$) perovskite network ($m=2 <1\ 1\ 1>$ bilayer) has been stabilized. Nevertheless, the use of such materials in PSCs has led to small PCE (<2%), which can be in part explained by the cluster type nature (0D) of the inorganic anions. We propose to prepare iodobismuthate hybrids based on trans-connected octahedra network, which will favor enhanced electronic dimensionality, as for instance the 2D $\text{Bi}_{2/3}\text{I}_4^-$ perovskite network by selecting organic cations able to self-assemble through weak interactions.

The synthesis of materials and their characterization (thermal analysis, optical properties), thin film preparation, X-ray characterization (single crystal, powder) and first attempts of PSCs devices will be carried out at MOLTECH-Anjou, while PSCs optimizations and PeLEDs fabrication will be carried out at IRCP/Paris (collaboration with T. Pauporté) and at Milano (collaboration with C. Botta), respectively.

[1] Lead and iodide deficient $(\text{CH}_3\text{NH}_3)\text{PbI}_3$, *d*-MAPI: the bridge between 2D and 3D hybrid perovskites Antonin Leblanc, Nicolas Mercier,* Magali Allain, Jens Dittmer, Vincent Fernandez, Thierry Pauporté* **Angew. Chemie, Int. Ed.** **2017**, 56, 16067-16072

Compétences souhaitées :

- Synthèse chimique par chimie douce et préparation de films minces
- Cristallographie et techniques de caractérisation par diffraction des rayons X, diffraction sur monocristal (de l'enregistrement jusqu'à la résolution de la structure cristalline) et diffraction par les poudres (thermodiffraction, recherche de maille)
- Des compétences en conception de cellules solaires ou diodes électroluminescentes seraient également les bienvenues.

Candidature : Toute candidature sera à effectuer par le site de l'Université Bretagne Loire (UBL) : <https://theses.u-bretagne Loire.fr/3m/>