UV-VISIBLE ABSORPTION STUDY OF SOME PEROVSKITE LAYER COMPOUNDS

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ABSTRACT

Perovskite Layer compounds with the general formula $(C_nH_{2n+1}NH_3)_2MX_4$ (C_nMX_4 for short) or $[NH_3\text{-}(CH_2)_n\text{-}NH_3] MX_4$ (Short notation $2C_nMX_4$) where M is a divalent metal atom and X an halogen (M = Cu, Mn, Zn, Co, Cd…) (X = Cl, Br…) are lamellar type structures and typical "Sandwich" system because of the regular alternation of inorganic and hydrocarbon regions that consist of long chain alkylammonium groups ionically bonded to an inorganic support. Perovskite Layer compounds are Phase Change Material which have solid-solid transitions and thermal properties good for Thermal Energy Storage. UV-Visible absorption measurements was taken for six samples synthesized in our lab, from the spectrums we defined a charge transfer transitions and try to find the influence of the organic chain and the nature of metal on these transitions. Intra-atomic d-d transition was expected for cupric compounds.

Keywords: Perovskite layer, UV-Vis, Charge transfer transitions, D-d transition

1. INTRODUCTION

The organic–inorganic perovskites are one of the most extensively studied crystalline families of nanaohybrids which offers an important opportunity to combine useful properties from two chemical realms, organic and inorganic compounds, within a single molecular scale composite (Elmebrouki *et al.*, 2011). Among these compounds, the perovskite layers organometalics with the general formula [NH$_3$-(CH$_2$)$_n$-NH$_3$] MX$_4$ (Short notation 2C$_n$MX$_4$) where M is a divalent metal atom and X an halogen (M = Cu, Mn, Zn, Co, Cd…) (X = Cl, Br…). These compounds are lamellar type structures in which the sheets of corner-shared MX$_6$octahedra are sandwiched between a pair of layer of n-alkylammonium chains. The cavities between the octahedra are occupied by the NH$_3$ groups which are attracted to the MX$_6$ by hydrogen bonds N-H….X. So, the Perovskite Layers are typical "Sandwich" system because of the regular alternation of inorganic and hydrocarbon regions that consist of long chain alkylammonium groups ionically bonded to an inorganic support (Tamsamani *et al.*, 2011).

These compounds are the origin of a number of useful and peculiar properties due to the organic layer or to the inorganic one or to the organic inorganic hybrids (Elmebrouki *et al.*, 2011). In fact the studies have shown that these Perovskite Layers are among the Phase Change Material (PCM) good for Thermal Energy Storage (TES) because of the solid-solid transition (Tamsamani *et al.*, 2011). In addition, these materials have a distinct set of advantages, including good electric mobility, tunable band gap property, magnetic property, but only few studies have been done to the electrical behaviour and the magnetic properties for this kind of perovskite layers when the same studies were already known for layer compounds (Balamurugan *et al.*, 2009);(Wei Ning *et al.*, 2009a);(Wei Ning *et al.*, 2009b).

We have synthesized several compounds with two different organic chains and some different metals where the halogen was always Chlorine. In this work, by means of UV-Visible absorption spectrum, we try to study transitions in these compounds and their origin and the influence of the organic chain or the metal on these transitions.

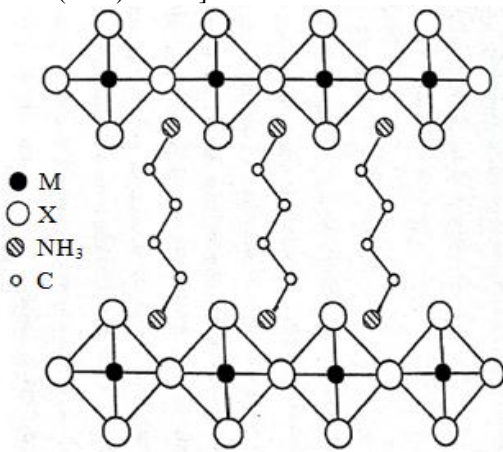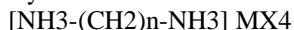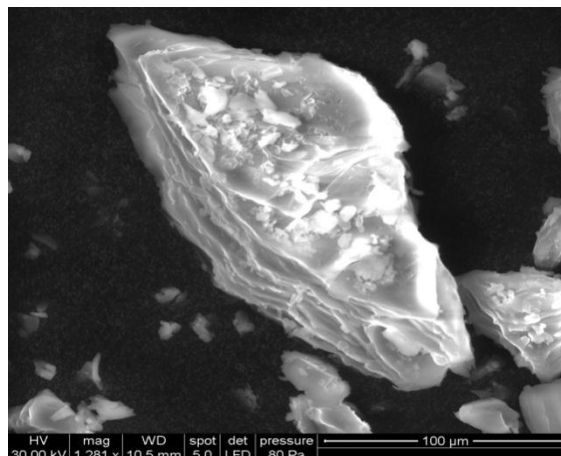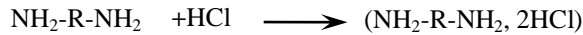**Fig.1.** Organic inorganic layers in a Perovskite layer
[NH3-(CH2)n-NH3] MX4

Fig.2. Lamellar structure of a Perovskite Layer 2C10MnCl4 by MEB

1.1. Synthesis of the Compounds

In our synthesis, we used two organic chains (C_8 and C_{10}) and four Metals (M: Cu, Mn, Ni and Zn)

The first step in the synthesis is adding gazeaosHCl to the organic chain

$$NH_2\text{-}R\text{-}NH_2 \quad +HCl \quad \longrightarrow \quad (NH_2\text{-}R\text{-}NH_2, 2HCl)$$

(gaseous HCl is obtained by adding drop by drop H_2SO_4 acid to solid NaCl)

Next, we complete the synthesis of the complexes by mixing stoechiometric quantities of the products of the first reaction and aqueous solution of MCl_2.

$$(NH_2\text{-}R\text{-}NH_2, 2HCl) \quad + \quad MCl_2 \quad \longrightarrow \quad [NH_3\text{-}R\text{-}NH_3]MCl_4$$
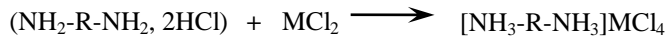
The acquired solution is clear, homogeneous and uncolored. It is left in dark at room temperature several days to obtain single crystals (Elmebrouki *et al.*, 2011), (Emebrouki *et al.*, 2013).

We have studied the UV-Visible absorption spectrums of some of synthesized complexes in order to determine the transitions and the influence of organic chain and nature of metals on it. The studied complexes are: $2C_8CuCl_4$, $2C_8ZnCl_4$, $2C_8MnCl_4$, $2C_{10}CuCl_4$, $2C_{10}ZnCl_4$, $2C_{10}NiCl_4$.
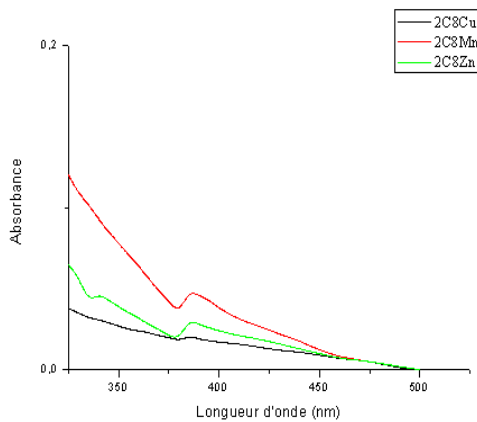
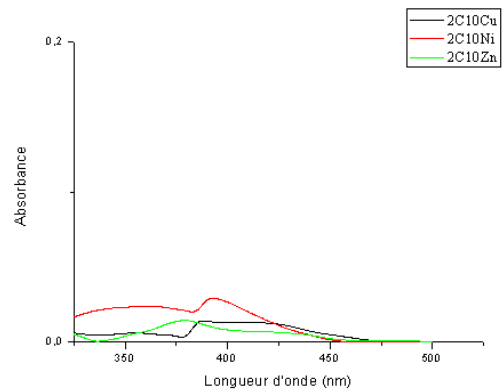## 1.2. Absorption UV-Vis
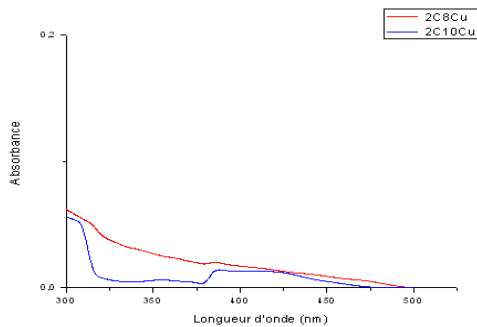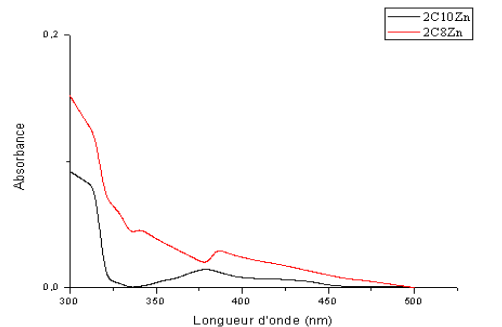
Fig 3

Fig 4

Fig 5

Fig 6

UV-Visible absorption measurements were taken in the range of 200 – 500 nm for the six samples. All spectra shows o peak at 385nm with different intensities of absorption. This absorption band is known to correspond to charge-transfer transitions (Edward, 2006),(Anne, 2006), (Mokhtaria Rosa, 2012).

1.3. Charge-transfer Transitions

Indeed, at still higher energy (UV-Vis), electrons are exited from the filled ligand-centred orbitals to the half-occupied d orbital, producing ligand to metal charge transfer transitions (Edward, 2006). As said before, organic and inorganic groups are attracted by hydrogen bonds N-H....Cl. This bonding is reducing the electronic density around the chlorine ion and cause the charge transfer metal-to-ligand Cu---Cl.

The charge transfer transitions are key to understanding the nature of ligand-metal bonds because high covalency is associated with low energy (Edward, 2006). The intensities of these transitions are proportional to the overlap of the donor and acceptor orbitals involved in the charge transfer process (Edward, 2006).

We have grouped the spectrums in a way to determine the influence of the metal ion and the organic chain on the charge transfer process and the covalency of the hydrogen bonds.

Fig 3 and 4 shows the absorption spectra of three different metal ions for a same organic chain. The intensity of absorption for compounds with Zinc ion is higher than compounds with copper ion.

Fig 5 and 6 shows the absorption spectra of two different organic chains with a same metal ion. For both, we see taht more the length of the organic chain is higher, more the intensity of absorption is lower; and so the contribution in the charge transfer process is lower, and more the hydrogen bond is weaker.

1.4. Intra-atomic d-d Transition

On the other hand, other transition is expected for some of these compounds. For exemple, on the $2C_8CuCl_4$, $2C_{10}CuCl_4$ compounds, cupric ion is placed in an octahedral ligand field, the five d orbitals split into t_{2g} and e_g sets. Placing nine electrons into these ligand field split orbitals gives one in the e_g set and thus unstable to Jahn-Teller distortion. This splitting allows a d-d transition.

Those samples was active to ESR and their spectrum have been studied in another work, so, we expect an absorption band between λ=750nm and λ=1800nm relative to intra-atomic d-d transition (Anne, 2006); (Mokhtaria Rosa, 2012).

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