High photocatalytic activity of hydroxyapatite biodegradable semiconductor for solar panels and environment protection

Activité photocatalytique élevée des semi-conducteurs biodégradables à base d'hydroxyapatite aux services des panneaux solaires et la protection de l'environnement

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ABSTRACT. Incorporating metal ions into a calcium hydroxyapatite structure is a successful pathway to increase their physical, chemical and biological properties. The calcium hydroxyapatite was obtained by solid state method at high temperature, using $CaCO_3$ and $(NH_4)_2HPO_4$ as sources of calcium and phosphorus. Metal ion ($M^{2+} = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}) incorporation was carried out by dint of grinding and high temperature effect for remove all impurity. Hydroxyapatite (HAP) powders doped with metal ions were characterized by uv-visible spectroscopy analysis to evaluate the photocatalytic activity of all samples of hydroxyapatite. The result shows the high photocatalytic activity of all HAP powders.

RÉSUMÉ. L'incorporation des ions métalliques dans la structure d'hydroxyapatite de calcium est une voie efficace pour augmenter leurs propriétés physiques, chimiques et biologiques. L'hydroxyapatite de calcium a été obtenue par une voie solide à haute température, en utilisant du $CaCO_3$ et du $(NH_4)_2HPO_4$ comme sources de calcium et de phosphore. L'incorporation des ions métalliques ($M^{2+} = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}) a été réalisée par force de broyage et sous l'effet de la température élevée pour éliminer toute impureté. Les poudres d'hydroxyapatite (HAP) dopées avec des ions métalliques ont été caractérisées par la spectroscopie Uv-visible pour évaluer l'activité photocatalytique de tous les échantillons de nos poudres d'HAP. Les résultats obtenus montrent une activité photocatalytique élevée dans toutes les poudres HAP.

KEYWORDS. Hydroxyapatite, Cobalt, Solar panel, Solid state, Urbach energy, Gap energy, Metal ion.

MOTS-CLÉS. Hydroxyapatite, Cobalt, Panneau solaire, Etat solide, Energie d'Urbach, Energie de gap, Ion Métallique.

1. Introduction

Solar energy is radiant light and heat from the Sun that is harnessed using a range of ever-evolving technologies such as solar heating, photovoltaics, solar thermal energy, solar architecture, molten salt power plants and artificial photosynthesis. It is an important source of renewable energy and its technologies are broadly characterized as either passive solar or active solar depending on how they capture and distribute solar energy or convert it into solar power. Active solar techniques include the use of photovoltaic systems, concentrated solar power and solar water heating to harness the energy. Passive solar techniques include orienting a building to the Sun, selecting materials with favorable thermal mass or light-dispersing properties, and designing spaces that naturally circulate air.

A solar cell, or photovoltaic cell, is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon. It is a form of photoelectric cell, defined as a device whose electrical characteristics, such as current, voltage, or resistance, vary when exposed to light. Individual solar cell devices can be combined to form modules, otherwise known as solar panels. In basic terms a single junction silicon solar cell can produce a maximum open-circuit voltage of approximately 0.5 to 0.6 volts.

The hydroxyapatite (HAP) with general formula $Ca_{10}(PO_4)_6(OH)_2$ is a phosphorus apatite which crystallizes natural state in the hexagonal system [GUO 09 , BAH 09]. It is the main constituent of bones and teeth, it has excellent affinity with bone tissue. So its advantage is to create strong chemical bond with the bone [SOP 07]. The hydroxyapatite can be used also for the purification of aqueous media [ZHO 07, RUS 05] and the immobilization of uranium in nuclear waste[ARE 98]. Also HAP can be used for energy storage, and energy production by conversion of ligh energy to electrical energy following its high photovoltaic activity after doping by metals transition elements.

2. Materials and methods

Crystalline powders of HAP with general chemical formula $Ca_{10}(PO_4)_6(OH)_2$ is prepared by solid state method were all reagents are in the solid state. We mix and grind directly and manually with mortar and pestle a 1.5773 g of ammonium phosphate $(NH_4)_2HPO_4$ and 1.9927 g of calcium carbonate $CaCO_3$, then we put it in the oven at 200°C and we raise the temperature by 200°C and achieve the inter grinding after each 24 hours duration. Until we reach 1000°C.

Hydroxyapatite- metal-doped HAP-M, with chemical formula $Ca_{9.5}M_{0.5}(PO_4)_6(OH)_2$ where (M= Mn, Co, Ni, Cu) is also prepared by solid state method, and all reagents precursors are in the solid state with well determined masses for each sample. We mix and grind directly and manually with mortar and pestle an ammonium phosphate $(NH_4)_2HPO_4$ and calcium carbonate $CaCO_3$ and precursor that contains metal for each sample as follows:

Nickelapyrroline C_4H_6Ni for Hydroxyapatite- Nickel (HAP-Ni) : $Ca_{9.5}Ni_{0.5}(PO_4)_6(OH)_2$

Copper (II) Chloride Dihydrate $CuCl_2.2H_2O$ for Hydroxyapatite- Copper (HAP-Cu) : $Ca_{9.5}Cu_{0.5}(PO_4)_6(OH)_2$

Cobalt (II) nitrate hexahydrate $CoN_2O_6.6H_2O$ for Hydroxyapatite- Cobalt (HAP-Co) : $Ca_{9.5}Co_{0.5}(PO_4)_6(OH)_2$

Manganese (II) carbonate $CMnO_3$ for Hydroxyapatite- Manganese (HAP-Mn) : $Ca_{9.5}Mn_{0.5}(PO_4)_6(OH)_2$

Each sample was prepared independently. And we follow same thermic treatment than the HAP in the oven from 200°C to 1000°C and we raise the temperature by 200°C realizing an inter grinding every 24 hours duration.

3. Results and discussions

3.1. *Optical properties*

The optical properties of the pure HAP and HAP-M were determined from the transmittance measurement in the range of wavelength 200-850 nm as shown in Figure 1.The transmittance spectra of our samples are very significatif. As for solid samples, are not the same absorption bands. For the pure HAP, the absorption band is not found, However , the absorption bands have been found in the case of the substituted HAP-M, these bands are related to charge transfer phenomena between metals ions transition element Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Ca^{2+} ion of HAP Figure 2. In the case of copper Cu^{2+} ion there are two bands centered on 450 and 750 nm, cobalt Co^{2+} ion found three bands around 750, 550 and 610 nm. High intensity and width are observed may explain the probability of transition [MOR 86].

The UV–visible absorption of the HAP-Co is greatly enhanced compared with that of HAP. This remarkable absorption of HAP-Co is attributed to Co in different coordination environments which is caused by substitution of Co for Ca in HAP crystal .Meanwhile, these doped Co ions can introduce an energy level into the electronic band structures of HAP-Co, which leads to the photocatalytic activity under visible light [MOH 17].

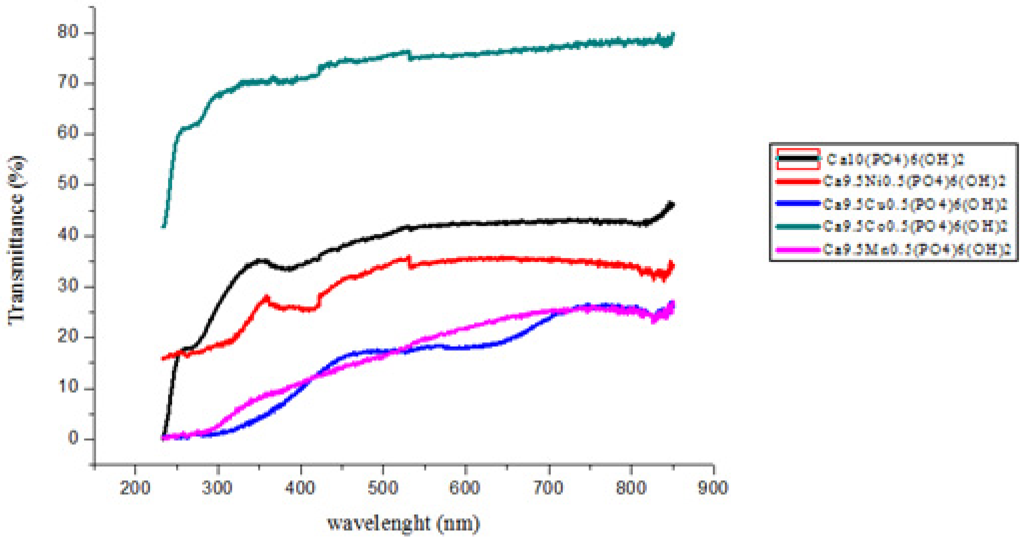

Figure 1. *The Transmission spectra of HAP and HAP-M (M=Ni, Cu, Co, Mn).*

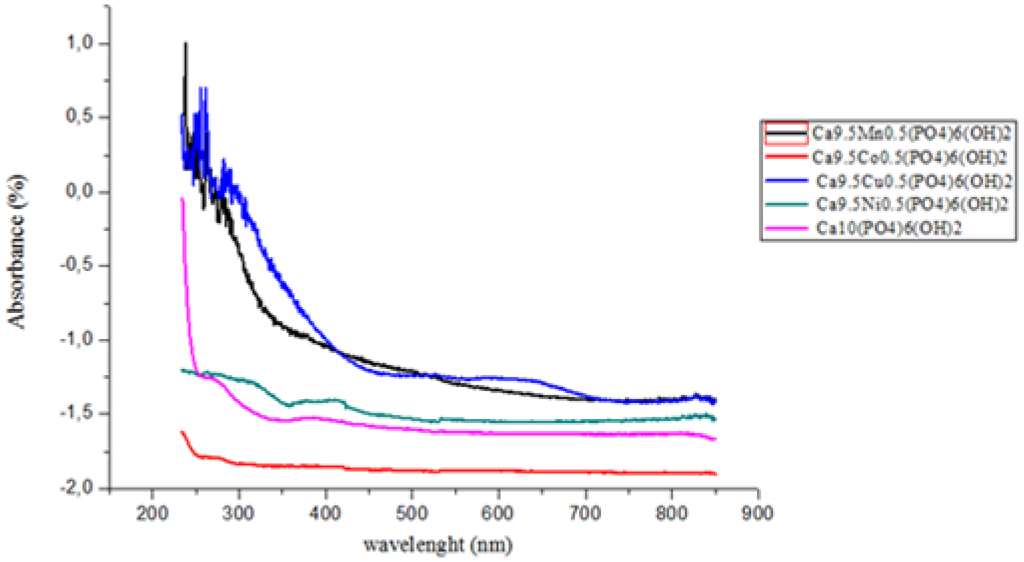

Figure 2. *The absorption spectra of HAP and HAP-M (M=Ni, Cu, Co, Mn).*

3.2. *Gap energy*

The optical gap for all our samples has been deduced by transmittance spectra using the Tauc's relationship [MOH 08]:

$$\alpha h\nu=\alpha_0(h\nu-Eg)^n \qquad [1]$$

α: absorption coefficient, h: Planck constant, α_0: constant; Eg: gap energy; n = 2 in the case of a direct gap. We plot $(\alpha h\nu)^2$ function hν, the value of the gap energy is obtained by the extrapolation of the linear part of the curve on the abscissa axis (hν). All spectrum of dependence of $(\alpha h\nu)^2$ On energy (eV) of HAP and HAP-M as shown in Figure 3.

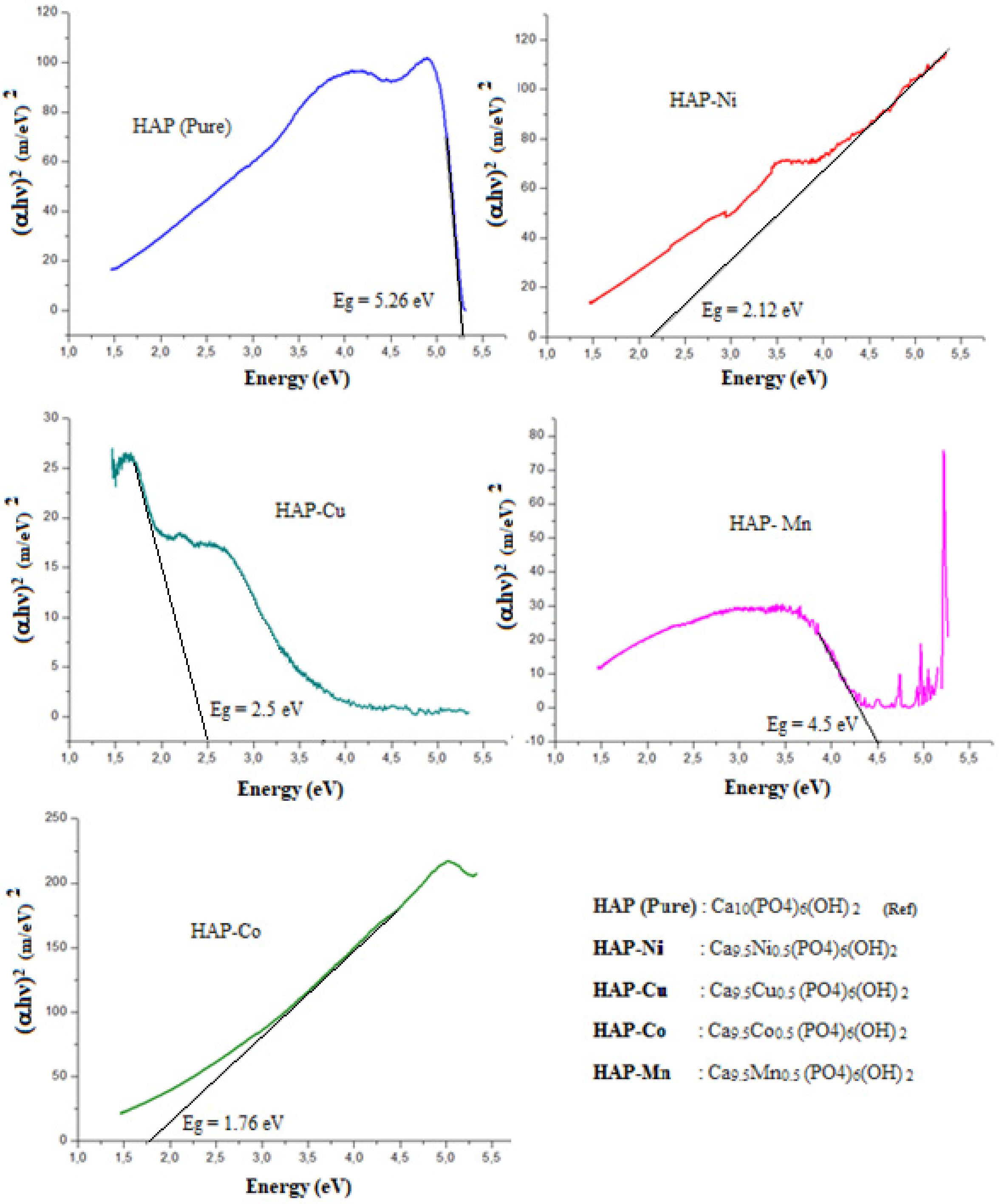

Figure 3. *The dependence of $(ahv)^2$ on energy (eV) of HAP and HAP-M (M=Ni, Cu, Co, Mn).*

3.3. *Urbach Energy (disorder)*

The Urbach energy (Eu) reflects the disorder state of the material [WAS 01]; it is related to the absorption coefficient by the following relationship [URB 53]:

$$\alpha=\alpha_0 e^{(h\nu/Eu)} \qquad [2]$$

Where (α) absorption coefficient and photon energy (hν) and Eu is energy of Urbach. We plot Ln(α) function energy (hν). The Urbach energy (Eu) was deduced by calculate the inverse slope of linear part extrapolation of spectra for each sample. All results as showns in figure 4.

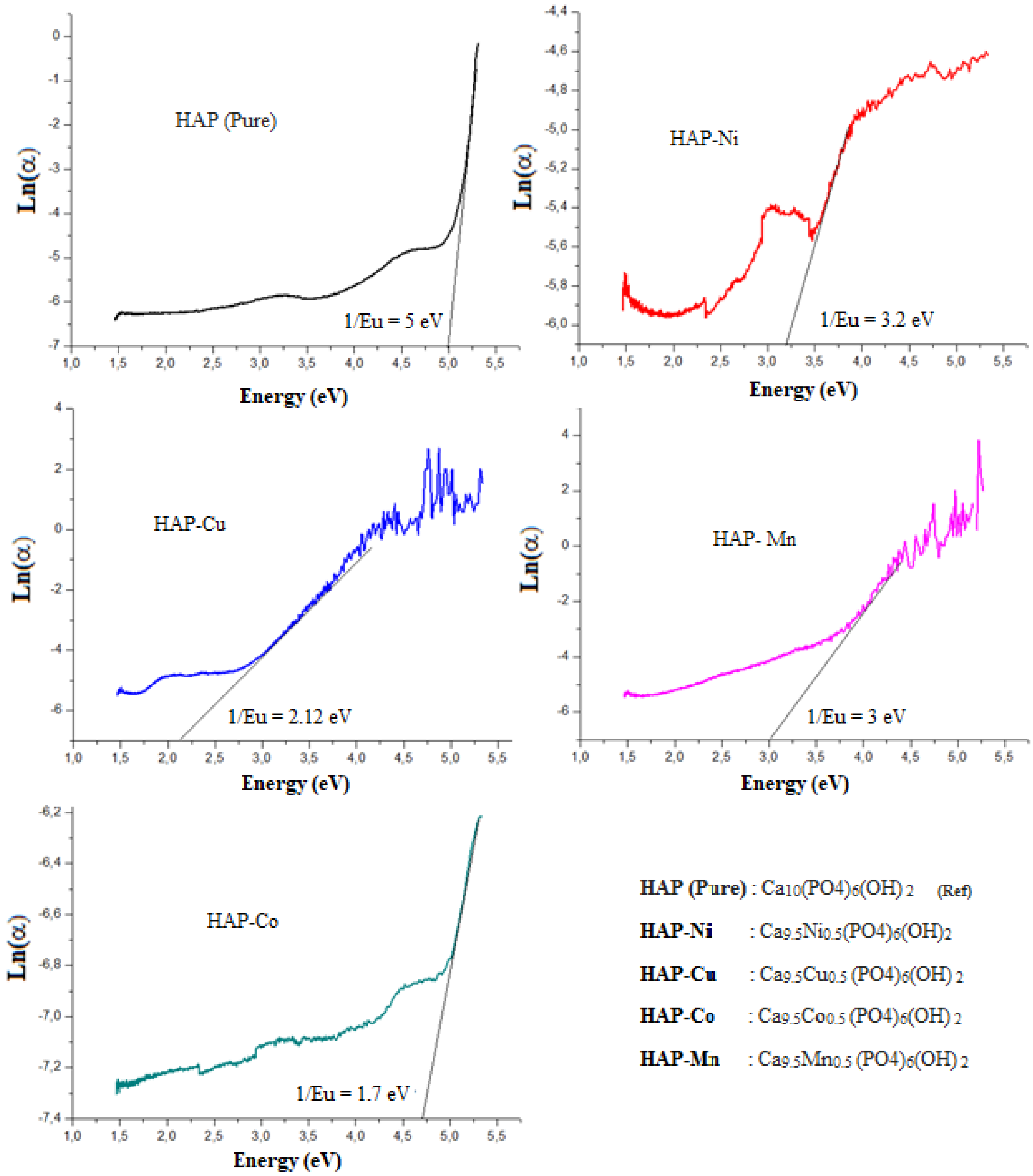

Figure 4. *Determination of the Urbach energy of HAP and HAP-M (M=Ni, Cu, Co, Mn).*

In the case of crystalline materials, the energy separating the valence band from the conduction band is perfectly defined by Ev and Ec. The energy Ec - Ev corresponds to the energy of the forbidden band [CAR 13]. The shape of the distribution functions of the energy states is a parabola [STR 67]. See Figure 5.

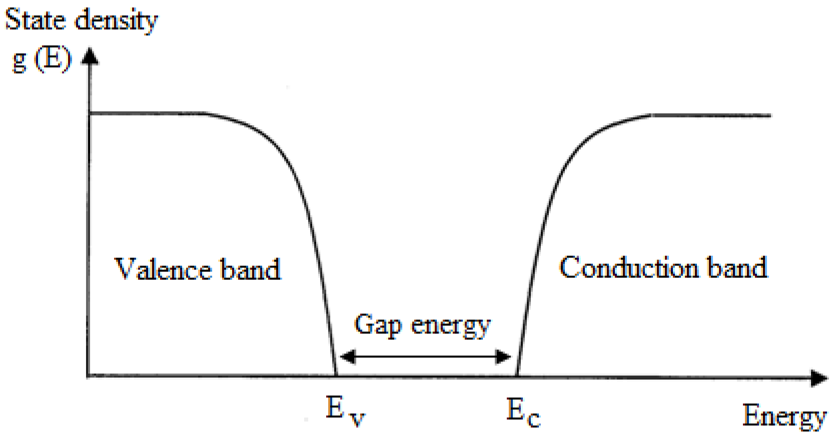

Figure 5. *The State density function as energy for Hydroxyapatite pure Before incorporing Metals*

When in a material occur variations of interatomic distances, lengths or angles of connection, there appears what is called a "disorder". In this case, the band edges described in the case of crystal lattices and delimited by Ev and Ec may disappear. We observe what are called localized states formed at strip tails at the boundaries of the forbidden band in the valence and conduction band [FAN 04]. For energies higher than Ec and lower than Ev, are the extended states (Figure 6).

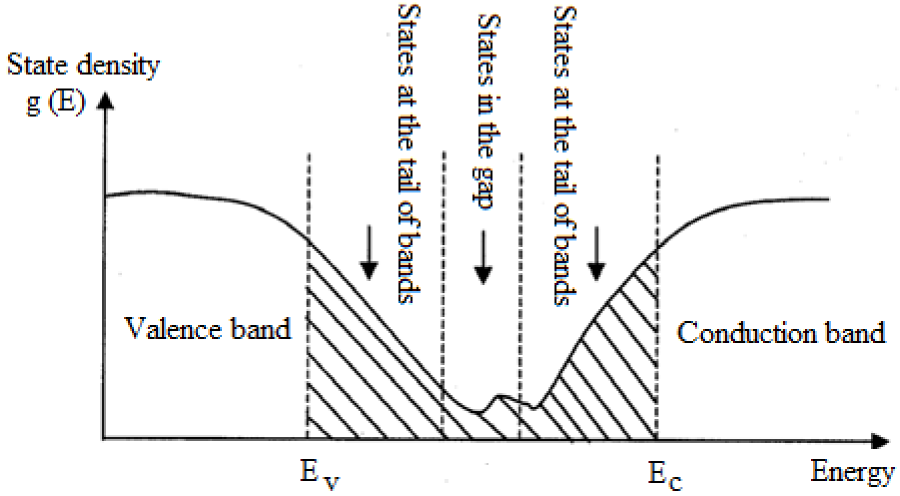

Figure 6. *The State density function as energy for Hydroxyapatite After incorporing Metals ions*

When the disorder becomes too important (for example with the appearance of links dangling or impurities in the material), the tails may become entangled. Caused by Urbach parameter (Eu) which corresponds to transitions between the extended states of the valence band and the localized states of the conduction band. The decrease or increase of the energy of Urbach is translated successively by the decrease or increase of the structural disorder and the improvement of the stoichiometry [BHA 12], which is due in this case to the incorporation of the metal ion in the structure of hydroxyapatite. Urbach energies as showns in table 1 presents the disorder of the material.

	HAP	HAP-Ni	HAP-Cu	HAP-Co
Optical Gap energy (eV)	5.26	2.12	2.5	1.76
Urbach energy (eV)	0.20	0.25	0.47	0.57

Table 1. *Value of the gap energy and Urbach energy for HAP*

It is found that the Urbach energy has increased after the incorporation of the metal ions in the hydroxyapatite matrix, because these metal ions are considered as impurities in the hydroxyapatites and present more structure disorder of the initial cell of hydroxyapatie. See figure 7.

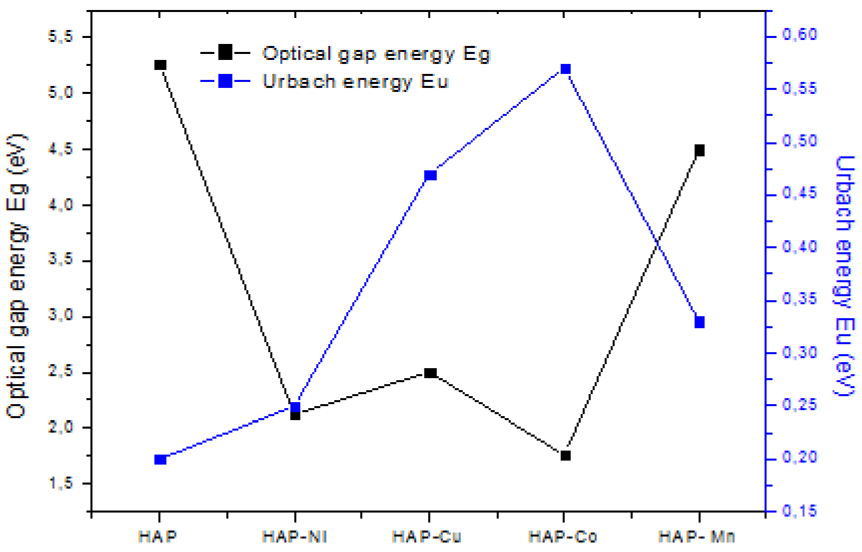

Figure 7. *Optical gap energy and Urbach energy of HAP and HAP-M (M=Ni, Cu, Co, Mn).*

4. Conclusion

The incorporation of Co, Ni, Cu and Mn metal ions in hydroxyapatites (HAP) gave us four biomaterials to be used in solar panels with improuved mechanical and electronic performance and less risk of environment pollution due to its biodegradable properties. The decrease of the electrical gap energy of all our samples HAP-M (with M is a metal material where M = Co, Ni, Cu, Mn) compared to the pure HAP, gives the possibility the new semiconductor materials with high photovoltaic activity. Moreover, the low Urbach energy value of all our HAP-M (M = Co, Ni, Cu, Mn) exhibit a high stcuctural stability wich result a long lifespan of our powder and solar panels.

We may suggest that samples of hydroxyapatites HAP-M (M = Co, Ni, Cu, Mn) are sparsely colored and their colors can be exploited for esthetic reason, solar panels with various colors and other potential applications.

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