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# Preparation and characterization of the semiconductor CuMnO<sub>2</sub> by sol-gel route

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## ABSTRACT

Nano crystallites of the crednerite CuMnO<sub>2</sub> are prepared by sol gel method with two step annealing process. The powder heated at 450 °C under air flow shows a mixture of CuO, Mn<sub>2</sub>O<sub>3</sub> and Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub>. However, when calcined at 900 °C under N<sub>2</sub> atmosphere, the crednerite CuMnO<sub>2</sub> with a monoclinic structure (space group: *C2/m*) is obtained. The Raman spectrum shows a single peak at 679 cm<sup>-1</sup> as signed to A<sub>1g</sub> mode whereas the infrared analysis confirms the linearity of CuO<sub>2</sub><sup>3-</sup> units. The optical transition at 1.70 eV, determined from the diffuse reflectance is attributed to the inter band *d-d* transition of Cu<sup>+</sup> ion. The oxide exhibits semiconducting properties with an activation energy of 0.21 eV. The photo electrochemical measurement shows *p* type conduction due to O<sup>2-</sup> insertion in the two dimensional lattice. The flat band potential (+0.12 V<sub>SCE</sub>), indicates a cationic character of both valence and conduction bands deriving from Cu<sup>+</sup>: 3*d* orbital.

## 1. Introduction

The 3*d* metals based oxides A Mn O (A=La, Ag, Cu....) possess interesting physical properties because of the presence of the Jahn Teller (J T) ion Mn<sup>3+</sup> [1-4]. Among the candidates, CuMnO<sub>2</sub> has two different structures depending on the temperature of the heat treatment: namely the hexagonal variety at high temperature [5] and the monoclinic form crednerite at room temperature [6]. The crednerite CuMnO<sub>2</sub> involves magnetic Mn<sub>2</sub>O<sub>3</sub> sheets and excitonic Cu<sub>2</sub>O semiconducting layers and can be applied as hydrogen catalyst under illumination owing to the high energy of the conduction band [7]. It has also been used for the removal of toxic gases like carbon monoxide and nitrous oxides [8].

The synthesis by sol gel route permitted the formation of many oxides in various configurations (monolithic, thin films, fibers, powders). This great diversity is attractive in various technological fields like optic, electronic, biomaterials, photocatalysis etc.... In the sol gel method, the oxides are treated at temperatures lower than those of conventional synthetic routes and offer the ability to combine organic and inorganic species to form new families of hybrid compounds with specific properties. The principle of the sol gel process is based on a succession of hydrolysis condensation reactions at moderate temperatures [9], to prepare oxides networks.

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The process consists of a conversion process of metal alkoxides, such as silicon alkoxides, zirconium, aluminum, titanium ... The soluble metal species may also contain organic components which may be adjusted according to specific applications.

To our knowledge, only few works on the synthesis of the crednerite CuMnO<sub>2</sub> are reported in the literature. CuMnO<sub>2</sub> is usually prepared by solid state reaction [6] or ionic exchange reaction [10]. More recently, Toufiq et al. have used hydrothermal synthesis to prepare Cu<sub>0.45</sub>Mn<sub>0.55</sub>O<sub>2</sub> [11], while Chen et al. have reported Cu<sub>1.1</sub>Mn<sub>0.9</sub>O<sub>2</sub> thin films onto quartz substrates by spin coating [12]. On the other hand, CuMnO<sub>2</sub> is an attractive photo catalyst due to its layered lattice which can intercalate oxygen species [13]. The J T ion Mn<sup>3+</sup> is photoelectrochemically active since it can generate polarization domains that favor the charge separation [7]. Since the X ray diffraction with temperature has not been reported on powder, the present work is devoted to the preparation of CuMnO<sub>2</sub> by sol gel method in an air free atmosphere along with the structural, optical and photo electro chemical characterizations.

## 2. Experimental

CuMnO<sub>2</sub> was prepared by sol gel route according to the following protocol: Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O (> 99%, Merck) was mixed to a solution of Mn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (> 98%, Alpha Aesar) with a molar ratio (0.025/0.025) in ethylene glycol (60 mL, 99% BDH) and

maintained under magnetic agitation (350 rpm) for 2 h. The mixture was heated at 70 °C (6 h) at reflux; and the viscous solution was dried at 120 °C during four days. The gelation occurred on a hot plate till a brown color appeared. Then, the amorphous powder was heated at 450 °C in air (2.5 °C/min) for the total denitrification and elimination of organic residues. Thermo gravimetric analysis (TGA) of the powder (20 mg) was performed up to 900 °C (2.5 °C/min) under nitrogen flow (99.9995%) using a Setaram TAG 1750 apparatus to follow the course of the reaction. The powder was calcined at 900 °C in an alumina crucible (8 h) under nitrogen flow. The end product exhibits a black brown coloration. The X ray diffraction (XRD) was recorded in the 2θ range (15–100°) using X ray diffractometer (Bruker D4 Endeavor) with Cu Kα radiation ( $\lambda=0.154178$  nm) up to 900 °C, the patterns were compared with the JCPDS cards using Eva Program. The particle size was determined from a particle size analyzer (Mastersizer 3000, Malvern Instruments); CuMnO<sub>2</sub> powder was suspended in distilled water using an ultrasonic bath for 15 min. The surface morphology was examined with a scanning electron microscope (SEM, Microscope Jeol 6510LV) operating at 20 kV.

CuMnO<sub>2</sub> was dissolved in acid and the chemical analysis was carried out by inductively coupled plasma (ICP, Varian Vista Pro CCD, and Simultaneous ICP OES). The concentration was determined by interpolation from a calibration plot. The FTIR spectrum was recorded with a Nicolet spectrometer 6700; the powder (~15%) was pressed into disks using dried spectroscopic KBr. The Raman spectrum was measured on the CuMnO<sub>2</sub> powder over the range (300–1200 nm) using a Jobin Yvon T64000 spectrometer; 514.5 nm lines Ar<sup>+</sup> laser excitation was provided from a Spectra Physics Krypton ion laser (4 W) and the beam was concentrated on the sample. The diffuse reflectance was measured with a double beam spectrophotometer (Specord 200 Plus). The powder was pressed into pellets ( $\varnothing=13$  mm) under a pressure of 200 MPa and fired at 1000 °C under N<sub>2</sub> blanket. The dimensions and weight of the pellets were used to evaluate the density of CuMnO<sub>2</sub> (73%); conductive silver paint was used for the electric contact. The conductivity was measured by the two probe method under argon atmosphere using an Agilent LCR meter 4363B. The working electrode (CuMnO<sub>2</sub>, 1.32 cm<sup>2</sup>) was encapsulated in a glass holder with epoxy resin. A conventional cell with Pt electrode (Tacussel) and a saturated calomel electrode (SCE), were used for the plot of the intensity potential J(V) curves. The working electrode was illuminated with a tungsten lamp (200 W, Phillips) through an optical window, positioned below the cell. The potential was controlled with a PGZ 301 potentiostat (Radiometer analytical) with a scan rate of 10 mV s<sup>-1</sup>. The electrolytic KOH solution (0.5 M) prepared in distilled water was continuously bubbled with pure nitrogen and all tests were carried out at ambient temperature.

### 3. Results and discussion

Heating the powder at 450 °C in air permits the elimination of water, nitrates and ethylene glycol. The XRD analysis is illustrated in Fig. 1, the spectrum shows only the peaks of the tenorite CuO (JCPDS card No 48.1548), bixbyite Mn<sub>2</sub>O<sub>3</sub> (JCPDS card No 41.1442) and spinel Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub> (JCPDS card No 074.1921). The TG plot of the powder heated under N<sub>2</sub> atmosphere (Fig. 3a) shows a weight loss at ~200 °C ascribed to water vaporization, while the loss in the range (700–750 °C) is due to the reduction of CuO to Cu<sub>2</sub>O, according to the stability diagram of CuO where the transition CuO/Cu<sub>2</sub>O occurs at 723 °C [14], this value is close to the reduction temperature of our TGA curve, which requires a residual pressure of  $1.68 \times 10^{-4}$  atm for CuO. In this work, under very high N<sub>2</sub> flow, one can estimate p(O<sub>2</sub>) less than that in nitrogen bottle (with P

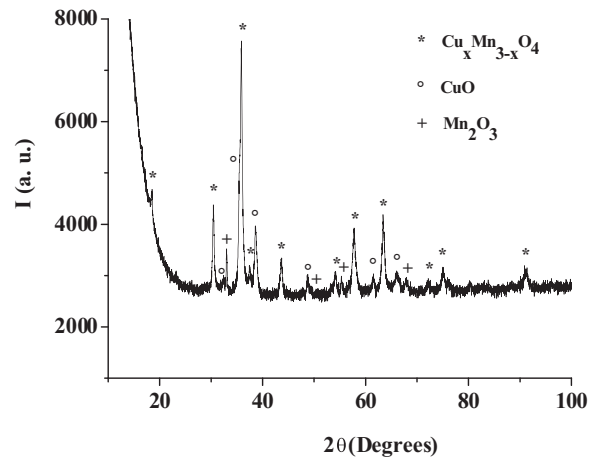
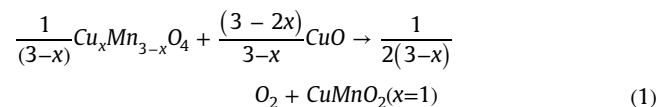


Fig. 1. XRD pattern of powder heated after heating to 450 °C in air.

(O<sub>2</sub>) = 10<sup>-6</sup> atm). Indeed, Chen et al. [12] have deposited films of Cu<sub>1.1</sub>Mn<sub>0.9</sub>O<sub>2</sub> onto quartz substrate using sol gel processing, they first treated the powder at 500 °C in air to stabilize the oxidation states Cu<sup>2+</sup> and Mn<sup>3+</sup>, Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub> and CuO were obtained. Then, they annealed the mixture in the temperature range (600–750 °C) in N<sub>2</sub> atmosphere. CuMnO<sub>2</sub> was formed above 600 °C, indicating a reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>. Besides that, Kurokawa et al. [15] have investigated a two step process both in air and under argon flow. They found that the sample annealed at 350 °C in air leads to the formation of CuMn<sub>2</sub>O<sub>4</sub> while the calcination in argon atmosphere between 750 and 950 °C leads to pure rednerite CuMnO<sub>2</sub>. So, we can deduce that the transition 2CuO → Cu<sub>2</sub>O +  $\frac{1}{2}$ O<sub>2</sub> starts at ~600 °C under inert atmosphere. Following our XRD results at 450 °C in air (Fig. 1), the spinel Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub> and single oxides CuO and Mn<sub>2</sub>O<sub>3</sub> are present with molar percentages of 42.7, 43.1 and 14.5 respectively according to the structural refinement. Hence, we can propose two different mechanisms for the formation of CuMnO<sub>2</sub>:

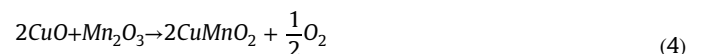
a) One step



b) Two step



The two equations give the final reaction:



On the other hand, Götzendörfer [16] reported that a thermal treatment of dip coated copper manganese oxide in air in the temperature range (400–700 °C) stabilizes the cubic spinel Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub>, which contain Cu<sup>2+</sup> ions and mixed valences of manganese (Mn<sup>3+</sup>/Mn<sup>4+</sup>). So, high temperatures favor small x values (< 1.5) i.e. low Mn(IV) content as evidenced by the existence of a small amount of CuO. Such result is also consistent with the XRD quantification which indicates x value of 1.33 for a molar ratio Cu/Mn = 1. Ping et al. have shown that both the temperature and cation ratio have a strong effect on the stoichiometry of Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub> [5].

It is worthwhile to mention that at 450 °C in air, the pattern (Fig. 2) shows only the peaks of CuO, Mn<sub>2</sub>O<sub>3</sub> and Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub>.

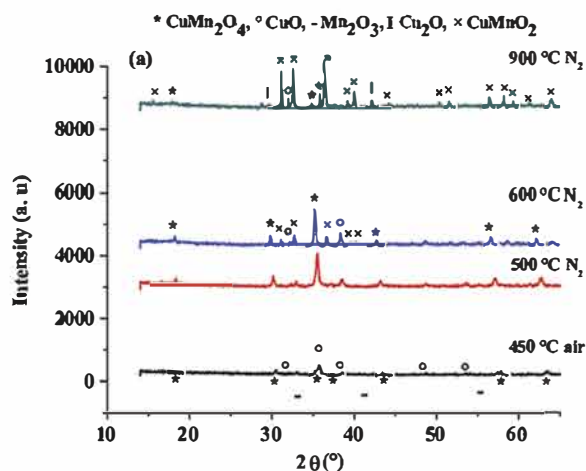


Fig. 2. Sol-gel copper manganese oxide annealed in air at 450 °C and post annealed under N<sub>2</sub> flow. The structural evolution is shown as function of temperature.

However, the peaks of the spinel decrease in intensity above 600 °C under N<sub>2</sub> flow while the characteristic peaks of the crednerite start to appear (2θ = 15.49°, 36.77°, 39.61°, 40.21°, 47, 13°).

The XRD analysis recorded after calcination at 900 °C under nitrogen flow shows the formation of the crednerite CuMnO<sub>2</sub> (Fig. 3b) in agreement with the literature data [6,17,18]. The XRD pattern, free from secondary phases, is indexed in a monoclinic unit cell with the space group C2/m according to the JCPDS card No 01.083.0034. The lattices parameters of CuMnO<sub>2</sub> refined in the C2/m space group by the Rietveld method are: a = 5.59585 Å; b = 2.8826(2) Å; c = 5.89075 Å and β = 104° (Fig. 3b). The phase CuMnO<sub>2</sub> synthesized by sol gel method as a particle size distribution in the range 200–400 nm determined from granulometry as shown in Fig. 4a and confirmed by XRD with the intercept at θ = 0 for the Williamson Hall in Fig. 4b plot being (71 ± 6 nm).

The atomic coordinates (xOz) of oxygen (position 4i of the space

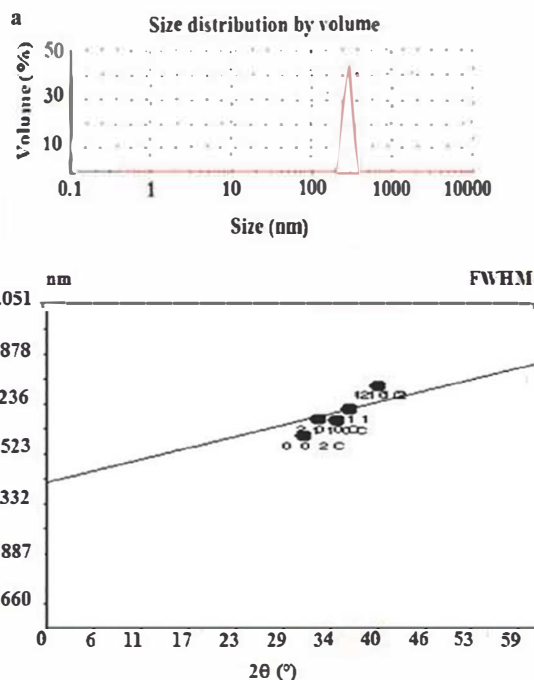


Fig. 4. Grain/particle size analysis of powdered CuMnO<sub>2</sub>: (a) Particle size distribution from granulometry (by volume). (b) A Williamson-Hall plot showing the average particle size from the intercept. The particle size is found to be 71.03 ± 5.49 nm (correlation coefficient 0.893).

group, unit axis b, cell choice 1) are x = 0.404(1) and z = 0.175(2). Mn<sup>3+</sup> and Cu<sup>+</sup> ions are located in particular positions 2a (0 0 0) and 2d (0 1/2 1/2) respectively. The pattern can be fitted with all recorded peaks and an excellent matching between the observed and fitted intensities is obtained.

The layers of MnO<sub>6</sub> octahedra joined by common edges are linked to each other by monovalent Cu<sup>+</sup> forming linear link O-Cu-O (Fig. 5). The manganese forms triangular sublattices stacked along the [001] direction in a three-sheet repeat unit ABCABC. The MnO<sub>6</sub> octahedron is elongated along the [001] direction, leading to an orbital ordering of occupied d<sub>z<sup>2</sup></sub>. The d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals are directed toward the four closer oxygen atoms in the (a, b) planes, while the d<sub>z<sup>2</sup></sub> orbital with an odd number of electrons gives rise to an antiferromagnetism with a Neel temperature of 42 K [19]. Accordingly, a monoclinic symmetry is obtained because of the lift of degeneracy of Mn<sup>3+</sup> ion where the Mn-O distances (Table 1) differ from those calculated from the sum of ionic radii (d(Mn<sup>3+</sup><sub>VI</sub>-O<sup>2-</sup><sub>IV</sub>) = 2.025 Å) [20]; the large c/a value is ascribed to Mn<sup>3+</sup> ion in high spin (HS) configuration (t<sub>2g</sub><sup>3</sup> d<sub>z<sup>2</sup></sub><sup>1</sup> d<sub>x<sup>2</sup>-y<sup>2</sup></sub><sup>0</sup>). The distortion of MnO<sub>6</sub> octahedron, agrees with two long apical Mn-O bonds at 2.260 Å and four short in the plane (a, b) at 1.929 Å, leading to an elongation of the MnO<sub>6</sub> octahedron (Mn-O<sub>||</sub>/Mn-O<sub>⊥</sub> = 1.17). The length Cu-O (1.86 Å) is in perfect agreement with that calculated from the sum of ionic radii of <sup>11</sup>Cu<sup>+</sup> (0.46 Å) and <sup>16</sup>O<sup>2-</sup> (1.38 Å) [20], thus confirming the ionicity and linearity of the [O-Cu-O]<sup>3-</sup> unit. The Cu-O-Cu bond adjoining two MnO<sub>6</sub> octahedra belonging to successive layers is slightly bent below the ideal value of 180°. Selected interatomic distances are reported in Table 1.

The thermal stability of CuMnO<sub>2</sub> was also investigated and the thermal analysis was plotted in air (Fig. 5a). The weight increases progressively and reaches a maximum at 560 °C, accounting for 6.53%; it corresponds to the spinel Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub> (x = 1.37) and is close to that reported by Ping et al. [21]. The weight loss at ~1000 °C corresponds to the reformation of the crednerite; such results agree with those of Bessekhouad et al. [10] and two reactions can be proposed:

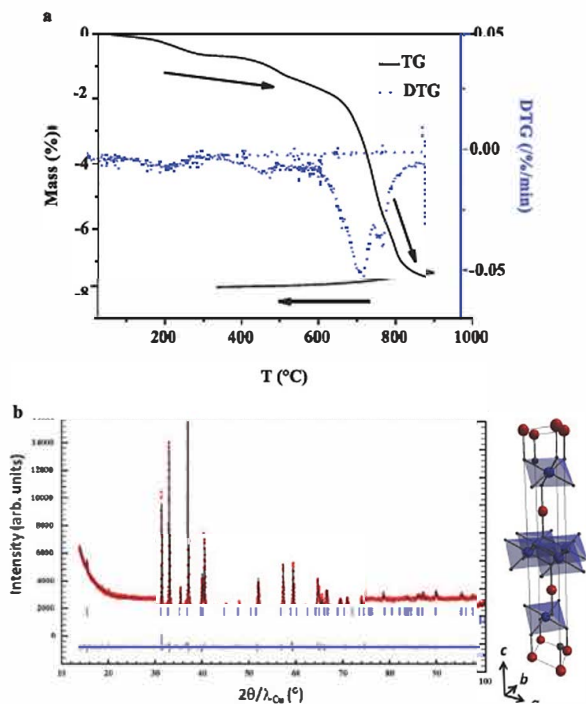


Fig. 3. (a) TGA and DTG plot under high purity N<sub>2</sub> (5 °C/min), of the powder prepared by heat treatment at 450 °C (1 h). (b) Rietveld refinement and structure of the crednerite CuMnO<sub>2</sub> synthesized by sol-gel method and annealed at 900 °C under N<sub>2</sub> flow.

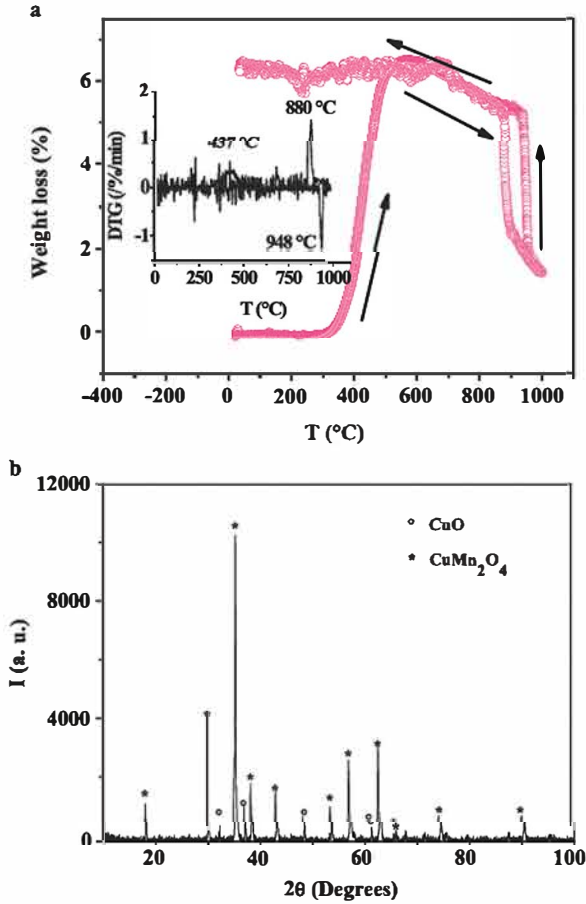
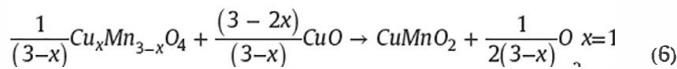
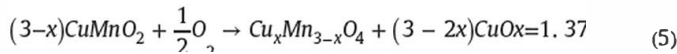


Fig. 5. (a) Analysis of a sample annealed at 1000 °C in air. (a) TGA and DTG (Inset) and (b) XRD pattern indicating a mixture of CuO and CuMn<sub>2</sub>O<sub>4</sub>.

**Table 1**  
Interatomic distances in CuMnO<sub>2</sub>.

Interatomic distances (Å)	
Mn-O <sub>1</sub>	2.28
Mn-O <sub>4</sub>	1.92
Cu-O	1.86
O <sub>1</sub> -O <sub>2</sub>	3.12
O <sub>1</sub> -O <sub>4</sub>	2.84
O <sub>2</sub> -O <sub>3</sub>	2.61
O <sub>3</sub> -O <sub>4</sub>	2.88



The peaks at 437 and 950 °C in the DTG plot (Fig. 5a, Inset) are attributed to the formation of Cu<sub>1.37</sub>Mn<sub>1.63</sub>O<sub>4</sub> and CuMnO<sub>2</sub> respectively. During the cooling, the peak at 880 °C is assigned to the oxidation of CuMnO<sub>2</sub> into spinel and tenorite, in agreement with the results reported by some of us [10]. The oxide heated at 1000 °C in air and slowly cooled indicates an oxidation to the cubic spinel (JCPDS Card No 01.071.1143) and CuO (JCPDS Card No 01.080.0076), as evidenced from the XRD analysis (Fig. 5b).

The Cu/Mn ratio of the crednerite CuMnO<sub>2</sub>, determined by inductively coupled plasma, is found to be equal to unity, a result consistent with the XRD analysis. Mn<sup>3+</sup> is more oxidant than Cu<sup>+</sup>

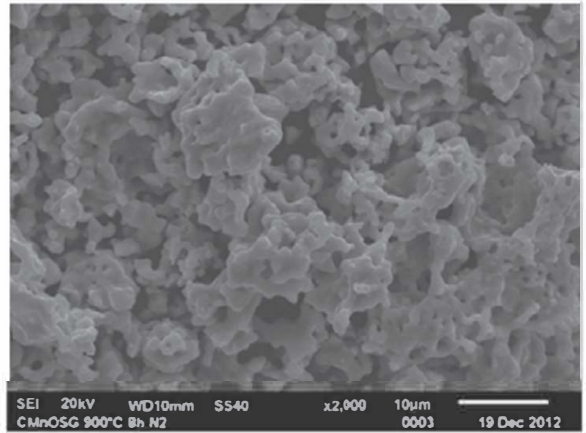
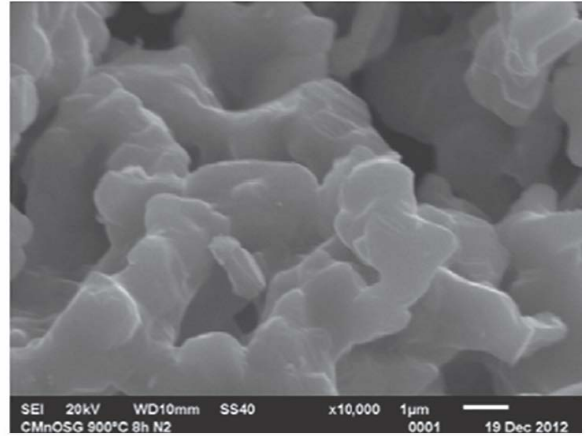


Fig. 6. SEM images at different magnifications of CuMnO<sub>2</sub> powder synthesized by sol-gel method and annealed at 900 °C under N<sub>2</sub> flow.

and the formulation (Cu<sup>+</sup>/Mn<sup>3+</sup>) in the crystal lattice is maintained by the lattice energy. However, in acid solution (pH~2) CuMnO<sub>2</sub> is dissolved and the reaction {CuMnO<sub>2(s)</sub> + 4H<sup>+</sup> → Cu<sup>2+</sup><sub>(aq)</sub> + Mn<sup>3+</sup><sub>(aq)</sub> + 2H<sub>2</sub>O} is shifted to the right side, thus permitting the determination of the average valence of copper by chemical titration [10]; the found value (1.03) is obtained which corresponds to an oxygen excess (δ) of 0.015 in CuMnO<sub>2+δ</sub>. It is quite logical to find a low value because the radius of Mn<sup>3+</sup> (r=0.645 Å) is smaller than the limit distance for the oxygen incorporation (r<sub>c</sub>=0.70 Å) in the crednerite lattice. Consequently, the phase transition to the spinel is favored in such a case [22].

The SEM image of CuMnO<sub>2</sub> (Fig. 6) shows a uniform morphology with dense particles of similar sizes and shapes; the particle size is 0.5–2 µm. The EDS analysis shows that the final oxide contains Mn, O, and Cu in stoichiometric ratios, suggesting that the synthesized nanostructures are made of pure crednerite CuMnO<sub>2</sub>. Indeed, the analysis (Table 2) agrees with the nominal composition and shows a homogeneous elemental distribution with a Mn/Cu molar ratio of 1.13 (the percentages are Mn=36.12% and Cu=41.03%, these being very close to the theoretical ones 36.50% and 42.22% respectively).

The crystallographic location of inorganic ions is corroborated

**Table 2**  
EDS obtained data of CuMnO<sub>2</sub>.

Elements	W <sub>theo</sub> (%)	W <sub>exp</sub> (%)	At (%)
Mn	36.50	36.12	24.07
Cu	42.22	41.03	23.64
O	10.62	22.85	52.29

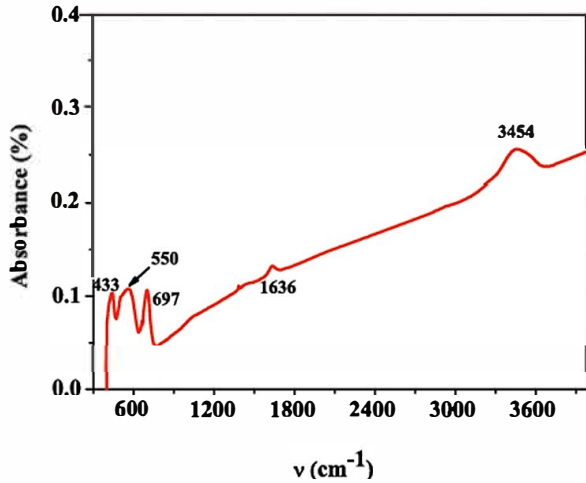


Fig. 7. FTIR spectrum of CuMnO<sub>2</sub> synthesized by sol-gel method and annealed at 900 °C under N<sub>2</sub> flow.

by the infrared spectroscopy [23]. The bands in the range (400 1000 cm<sup>-1</sup>) are assigned to active vibrations in mineral oxides. While, the bands at 1630 and 3440 cm<sup>-1</sup> are due to the bending and stretching modes of adsorbed water (Fig. 7). The spectra of manganese based oxides are divided into three domains (250 450 cm<sup>-1</sup>), (450 600 cm<sup>-1</sup>), and (600 750 cm<sup>-1</sup>), attributed respectively to the vibrations of stretching, bending and wagging in MnO<sub>n</sub> polyhedra [24]. The peaks in the range (700 400cm<sup>-1</sup>) are due to Mn O vibrations in Mn<sup>3+</sup> based compounds [25] while the peak at 550 cm<sup>-1</sup> corresponds to the vibration of monovalent copper linearly coordinated by O<sup>2-</sup> ions [26].

The delafossite structure has two Raman active modes; the mode A<sub>1g</sub> attributed to O Cu O vibration along the *c* axis and the mode E<sub>g</sub> derived from MO<sub>6</sub> octahedra along the *a* axis [27 29]. The active mode A<sub>1g</sub> is around ~700 cm<sup>-1</sup> for the delafossites CuMO<sub>2</sub> (M=Al, Cr, Fe) [27 29]. Our spectrum (Fig. 8) shows a single intense peak at 679 cm<sup>-1</sup> attributed to A<sub>1g</sub> mode [30]; such result is corroborated by Runka et al. which have assigned the peak at 675 cm<sup>-1</sup> to symmetric stretching vibrational modes of MnO<sub>6</sub> octahedra [31].

The fundamental optical transition in the reflectance diffuse spectrum is used to determine the forbidden band (E<sub>g</sub>) using the Tauc relation:

$$(\alpha h\nu)^{1/n} = \text{Cons} \tan t \times (h\nu - E_g) \quad (7)$$

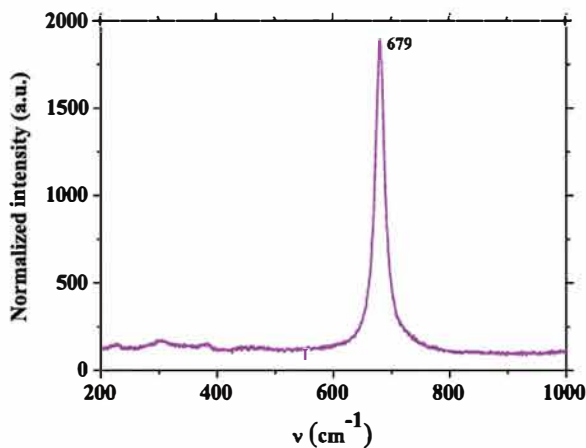


Fig. 8. The Raman spectrum of CuMnO<sub>2</sub> synthesized by sol-gel method and annealed at 900 °C under N<sub>2</sub> flow, recorded at room temperature.

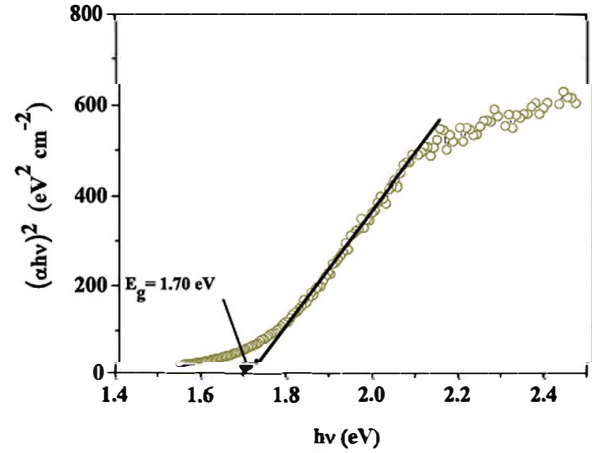


Fig. 9. The direct optical transition of CuMnO<sub>2</sub> synthesized by sol-gel method and annealed at 900 °C under N<sub>2</sub> flow.

where  $\alpha$  is the optical absorption coefficient and  $h\nu$  the energy of the incident photon. The exponent  $n$  is equal to 1/2, 2 and 3/2 respectively for direct, indirect and direct forbidden transitions. From the plot of  $(\alpha h\nu)^{1/n}$  versus  $h\nu$  (Fig. 9), a direct transition is obtained at 1.70 eV, due to interband transition *d d*, in conformity with the black brown color of CuMnO<sub>2</sub>, this transition is close to that obtained elsewhere [32].

The transport properties of CuMO<sub>2</sub> are strongly dependent on their chemical compositions and particularly on the deviation from stoichiometry. Metal oxides are non stoichiometric because of mixed valences of 3*d* elements. The increase of the electrical conductivity ( $\sigma$ ) with raising temperature indicates a semi conducting behavior of CuMnO<sub>2</sub> (Fig. 10); the thermal variation obeys to an exponential type law with  $\sigma_{300\text{K}}$  value of  $\sim 5 \times 10^4 \Omega^{-1} \text{cm}^{-1}$  [10,12]. The data are fitted by the least square method and the activation energy E<sub>a</sub> (=0.21 eV) is in conformity with a conduction mechanism by low polarons jump between mixed states Cu<sup>2+</sup>/Cu<sup>+</sup> in the (*a*, *b*) planes by phonon [2,12]. The electrons move by phonon assisted hopping between nearest sites owing to the electron phonon interaction. Indeed, the inter ionic Cu<sup>+</sup> Cu<sup>+</sup> distance, equal to the lattice constant *a*, is large enough to accommodate O<sup>2-</sup> ions (radius=0.140 nm) in the bi dimensional lattice of CuMnO<sub>2</sub>. An equivalent amount of Cu<sup>2+</sup> is formed (=2δ) to maintain the charge neutrality. The oxidation state of copper increases slightly and deviates from unity. Hence, CuMnO<sub>2</sub> exhibits *p* type behavior, thus allowing the oxide to be characterized electrochemically.

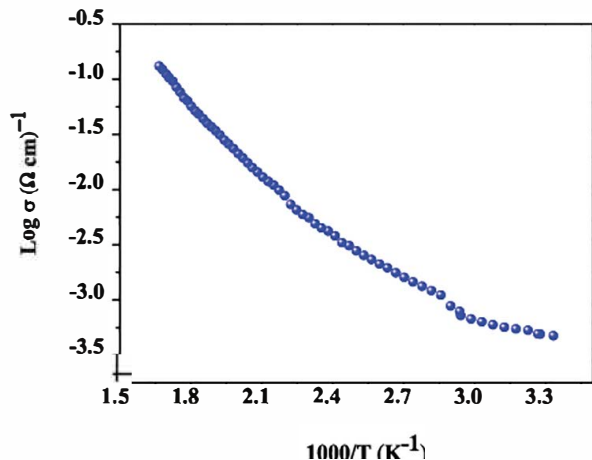
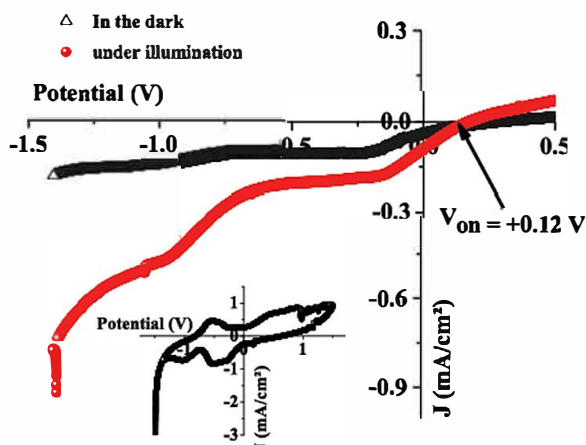


Fig. 10. Variation of log ( $\sigma$ ) versus temperature in the crednerite CuMnO<sub>2</sub> synthesized by sol-gel and annealed at 900 °C under N<sub>2</sub> flow.



**Fig. 11.** The variation of the current density ( $J$ ) versus the potential ( $V$ ) of  $\text{CuMnO}_2$  synthesized by sol-gel and annealed at  $900^\circ\text{C}$  under  $\text{N}_2$  flow, in the dark and under illumination in  $\text{KOH}$  solution ( $0.5\text{ M}$ ) at  $25^\circ\text{C}$ , scan rate  $10\text{ mV s}^{-1}$ . Inset: the  $J$  ( $V$ ) curve in the dark.

The photo electrochemical characterization of  $\text{CuMnO}_2$  is realized in  $\text{KOH}$  ( $0.5\text{ M}$ ) where the oxide exhibits an excellent chemical stability (Fig. 11). The intensity potential ( $J$   $V$ ) curve was scanned from  $-1.5\text{ V}$  toward positive potentials because of the  $p$  type conductivity. The dark current ( $J_d$ ) is smaller than  $1\text{ mA cm}^{-2}$ , indicating an electrochemical stability over a large potential range. While, the significant current above  $1\text{ V}$  is due to  $\text{H}_2\text{O}$  oxidation. The ( $J_d$   $V$ ) characteristic in the cathodic side intercepts the abscissa axis at a potential of the hydrogen evolution reaction (HER) and is function of the partial pressure of oxygen. In aerated solution, the potential of the couple  $\text{H}_2\text{O}/\text{H}_2$  ( $-0.75\text{ V}$ ) is obtained by prolonging the line to the potential axis. The peak at  $\sim 0.44\text{ V}$  (Fig. 11, inset) is due to the electrochemical couple  $\text{Cu}^{+2+}$  and is close to the standard redox potential [33], the electro neutrality condition implies oxidation of  $\text{CuMnO}_2$  according to the electrochemical process:



$\delta$  stands for the amount of inserted  $\text{O}^{2-}$  ions in the two dimensional lattice. The electrical charge under the anodic peak, determined by integration of the surface area, averages  $5\text{ mC cm}^{-2}$  and corresponds to the oxidation of  $\sim 3 \times 10^{16}$  at.  $\text{Cu}^+ \text{cm}^{-2}$ . The peak at  $\sim 0.33\text{ V}$ , is ascribed to the electrochemical couple  $\text{Cu}^{3+}/\text{Cu}^{2+}$ , and is close to that observed in  $\text{La}_2\text{CuO}_4$ , responsible of the superconductivity at  $\sim 40\text{ K}$  [34]. The peak at  $0.23\text{ V}$ , upon back scanning, corresponds to oxygen deintercalation but the difference exceeds the value  $0.06\text{ V/n}$  which indicates that the oxygen insertion is irreversible and the shape of the curve ( $J_{\text{ph}}$   $V$ ) and the increase of photocurrent  $J_{\text{ph}}$  along the negative polarization confirm  $p$  type behavior with holes as majority charge carriers.  $J_{\text{ph}}$  starts to appear at a potential of  $+0.12\text{ V}$ , thus corroborating the previous results [10] and increases gradually to attain a plateau region beyond  $0.15\text{ V}$ . Such saturation is mainly due to a neglected recombination process of ( $\text{e}^-/\text{h}^+$ ) pairs. Below  $0.3\text{ V}$ , the photocurrent  $J_{\text{ph}}$  reaches a maximal value which depends only on the light intensity and indicates that all generated ( $\text{e}^-/\text{h}^+$ ) pairs contribute to the photocurrent. The detailed electrochemical characterization is currently under progress and will be reported soon.

#### 4. Conclusion

Pure crednerite  $\text{CuMnO}_2$  was prepared by sol gel processing.

A monoclinic structure was obtained at  $900^\circ\text{C}$  under very pure nitrogen flow. The lattice constants were determined from the Rietveld refinement and the SEM images showed that the crednerite possesses a porous morphology having dense individual grains. The room temperature Raman spectrum showed a single peak assigned to  $A_{1g}$  mode in  $\text{MnO}_6$  octahedra. The direct optical transition in the visible region is attributed to  $\text{Cu}^+ d d$  transition. The thermal evolution of the electrical conductivity confirmed the semiconducting properties of the crednerite. The photoelectrochemical study showed  $p$  type behavior due to the oxygen intercalation in the layered crystal lattice.

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