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Relationship between morphological and physical properties in nanostructured $CuMnO_2$

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ABSTRACT

In this study, crednerite CuMnO₂ nanostructures were prepared using a hydrothermal method at 100 °C with various amounts of NaOH mineralizator. Obtained nanostructured crednerite CuMnO₂ with monoclinic structure (space group *C2/m*) exhibits two morphologies: nanobelts with lengths of 1–1.5 nm and thickness of 15–25 nm, and nanoplates with diameters of 50–70 nm. Comparative analyses of the prepared samples reveal a close relationship between morphological and physical properties of nanostructured CuMnO₂. A low NaOH concentration promotes elongated crystal growth along the c-axis, resulting in nanobelt-shaped morphology. A strong base solution, on the other hand, promotes the formation of nanoplates. The different morphologies of nanostructured CuMnO₂ have different spectroscopic and magnetic properties. The Raman active A_{1g} mode at 637 cm⁻¹ and a modified Curie-Weiss behavior characterize the nanobelt-shaped sample. This phase has two magnetic phase transitions: ferromagnetic at 9.2 K and antiferromagnetic at 42 K. The nanoplate-shaped sample, on the other hand, exhibits typical behavior as reported in the literature, namely the Raman active A_{1g} mode at 688 cm⁻¹ and low-dimensional magnetism with antiferromagnetic ordering below 62 K. The variation in magnetic properties is presumably due to partial oxidation of Cu¹⁺/Cu²⁺ and Mn³⁺/Mn⁴⁺, as well as a change in Mn³⁺ spin states from low-spin in nanobelt-shaped samples to high-spin in nanoplate-shaped samples.

1. Introduction

Credner [1] discovered many year ago the mineral known as crednerite, which Rammensberg [2] described as having the chemical formula $3CuO \cdot 2Mn_2O_3$. However, the proper chemical stoichiometry was not determined until a century later by Kondrashev [3], who proposed to be of $CuMnO_2$ and crystal structure to belong to the space group C2/m. A detailed structural study of this compound was stated later, and a monoclinic structure was confirmed based on powder diffraction data [4]. The atomic positions of atoms were determined using single-crystal diffraction data, with the Cu atoms occupying the 2d position, the Mn atoms at the 2a position, and the O atoms at the 4i positions.

Because of its extremely broad range of potential applications, the CuMnO₂ material has sparked renewed interest in research over the last few decades. CuMnO₂ has been studied as a *p*-type semiconductor [5–7], electrode material [8] and in the context of photocatalytic activities for hydrogen production or storage [9–11], oxygen storage [12,13], energy storage [14,15], and multiferroic peculiarities [16]. Surprisingly, nanoparticles with diameters of 50–100 nm [6] or nanowires [15] can be obtained using a hydrothermal method. These findings pave the way for new avenues of investigation and application.

According to the available literature on the synthesis of CuMnO₂ one

https://doi.org/10.1016/j.physe.2022.115418 Received 15 January 2021; Accepted 30 June 2022 Available online 1 August 2022 1386-9477/© 2022 Elsevier B.V. All rights reserved. obtains this compound using a variety of methods, including hydrothermal methods [5,6], ion exchange reactions [10], and solid-state reactions [13,17,18], and sol-gel techniques [19,20]. The C2/m space group crystal structure and lattice parameters of samples from different preparations are essentially consistent with one another, but their physical properties differ dramatically. For example, the direct optical gap was discovered to have values ranging from 1.4 eV [5] to 4.6 eV [18]. Surprisingly, studies of magnetic properties reported for CuMnO₂ revealed a significant disparity as well. For the most part, an antiferromagnetic (AF) phase transition was established for bulk compounds below about 65 K [23,25-27]. However, complete incompatibilities were observed for nano-sized materials; AF order appears to occur below 42 K in nanoparticles with diameters of 50-100 nm [16] and is nonmagnetic for particles with diameters of 300 nm [28]. In our opinion, multiple mechanisms may be responsible for the diverse physical properties of CuMnO2. The various morphologies of nano-sized particles and bulk crystal structured CuMnO2 materials should be the first factor to consider. Aside from the exchange interactions between d-electron magnetic moments, dimensionality and dipole magnetic interactions are important components in the formation of a ground state at the nanoscale. The most natural method of preparing different morphologies of nanoparticles is one that can change the reaction

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conditions, such as the precursor solution and its concentration, the reaction temperature, the reaction time, and the pH value of the solvents. Changes in reaction conditions resulted in the successful synthesis of delafossite CuGaO₂ [29] or crednerite CuMnO₂ [15,30]. Fu et al. [15] demonstrated that the valence states of Cu^{1+} , Cu^{2+} , Mn^{2+} , and Mn^{3+} in samples can be adjusted by varying reaction temperatures. As a result, the morphologies of the CuMnO₂ nanoparticles change with increasing temperature, resulting in triangular sheets - nanowires - hexagonal prisms - octahedrons. In contrast, Zhang et al. [6] and Xiong et al. [30] used different amounts of NaOH and reaction components, as well as different temperatures. For a large amount of NaOH, the latter authors were able to obtain single-crystalline CuMnO2 nanoparticles with diameters of 50-100 nm at 80 K. Clearly, the morphology and size of nano-structured CuMnO₂ can be effectively controlled by reaction rates, which are governed by pH values and reaction temperatures, and this is a practical challenge in material research. However, the effect of nanostructured sample morphologies on optical and magnetic properties, in particular, remains an open question. In this paper, we describe the synthesis of nanostructured CuMnO₂ samples using a hydrothermal method that has been used in previous studies, such as that described by Krause and Gawryck many years ago [31] and reported in the literature for the synthesis of delafossites [15,30,32,33]. To change the reaction rates and degree of nucleation, we used different amounts of NaOH mineralizator, namely 1 g, 2 g, and 3 g per 35 ml of solution. The morphologies, chemical compositions, and crystallographic data of the obtained samples, as well as their spectroscopic (Raman and UV-VIS) and magnetic (dc-magnetization, ac-susceptibility) properties, are then determined.

2. Experimental details

All of the chemicals used in our experiments were of analytical grade and were used exactly as received, with no further purification. We used 35 ml of deionized water to dissolve 7.5 mmol of Cu(NO₃)₂·3H₂O and 7.5 mmol of MnCl₂·4H₂O, then a suitable amount of NaOH as a mineralizator was added to the above solution. To ensure the homogeneity of the blend, the reaction mixture was sonicated for 5 min and then stirred for 10 min. The growth solution was transferred into a 50 ml stainless steel Teflon-lined tube. For 24 h, the reaction was kept at 100 $^\circ\text{C}.$ The autoclave was naturally cooled to room temperature after the reaction. The precipitate was collected by centrifugation, washed several times with deionized water and absolute alcohol, and stored in an absolute alcohol solution. Before measuring physical properties, samples were air-dried. To investigate the influence of pH on the chemical process in CuMnO₂ synthesis, different amounts of NaOH, namely 1.0, 2.0, and 3.0 g, were added in successive synthesis. Following the procedures outlined above, we obtained three distinct nanostructured CuMnO₂ samples. The samples are denoted as No. 1, No. 2, and No. 3, respectively. Our synthesis procedure differs from that of Xiong et al. [30] only in terms of NaOH amounts and reaction temperature. The CuMnO₂ nanostructures obtained have been characterized in terms of morphologies, composition, and crystal structures, as well as lattice parameters and nanoparticle sizes. We used a Schottky eld-emission scanning electron microscopy (FESEM) system (JEOL JSM-7600F, 10.0 kV) equipped with energy-dispersive X-ray spectroscopy (EDX) and an XPert PRO diffractometer with monochromatic CuK_{α} radiation and an accelerating voltage of 40 keV and 30 mA for these purposes. The Rietveld refinement method was used to analyze measured X-ray powder diffraction spectra in the 10-80 deg. range using the FullProf program [34]. Additional experiments have been carried out in order to determine the vibrational modes of molecules and atoms, as well as optical absorption by nanostructured particles. The Raman spectra were collected in this case using a LabRAM HR800 (Horiba) with a 632.8 nm excitation laser and a resolution of 1.0 cm 1. In contrast, the UV-visible reflectance mode was measured with an Agilent 8453 UV-visible spectrophotometer. Finally, magnetic quantities such as ac-, dc-magnetic susceptibility, and

magnetization were measured using the Quantum Design MPMS-XL7 in temperatures ranging from 2 to 300 K and magnetic fields of up to 7 T.

3. Results and discussion

3.1. Morphological, chemical, and crystallographic analysis

The SEM and EDX spectra for nano-sized CuMnO₂ samples obtained by adding three different amounts of NaOH to the reaction solution are shown in Fig. 1. We can see from comparing the observed SEM images that pH of the used solvents has a significant effect on morphologies. The synthesis with 1 g of NaOH yields CuMnO2 nano-belts with lengths ranging from 1 to 1.5 mm, widths ranging from 50 to 80 nm, and thicknesses ranging from 15 to 25 nm. It should be noted that, to the best of our knowledge, crednerite CuMnO2 nanobelts were successfully synthesized by us for the first time. In contrast to the 1 g NaOH preparation, the nanoparticles obtained from the 2 or 3 g NaOH synthesizes have morphologies of nanoplate-like geometry and are of 50-70 nm in diameter. However, there is a difference in morphologies between these latter samples due to the presence of an agglomeration of nanoparticles in sample No 2 but well separately nanoparticles in sample No 3. Our findings can be compared to those of Fu et al. [15], who demonstrated that CuMnO₂ nanowires and nanoplates can be obtained at temperatures as low as 160 °C. The nanowires were found to grow along the (002) plane, which is similar to our sample's oriented growth along the (001) plane.

The elemental analyses of CuMnO₂ by EDX are shown in the right panels of Fig. 1. The current peaks confirm the presence of Cu, Mn, and O elements. However, the atom ratio of Cu:Mn:O does not match the ideal 1:1:2 ratio. Given that the at.% of O is less than 50 and there also is presence of a small amount of at.% of Cl, we anticipate that the Cl atoms will share some places with the O atoms in the 4*i* position. Furthermore, we see that the at.% of Cu is greater than that of Mn, implying that the Cu atoms may share with Mn at 2*a* position. Previous research on the crednerite CuMnO₂ revealed that it has the chemical formula Cu_{1+x}Mn_{1-x}O₂ with *x* up to 0.2 [22–24]. Based on this idea, we suggest that the chemical stoichiometry of our samples be Cu_{1+x}Mn_{1-x}O_{2-y}Cl_y with *x*~0.15 and *y*~0.05. However, we acknowledge that proper stoichiometry of prepared samples should be determined using more sophisticated methods than those used in this study.

Fig. 2 depicts the X-ray powder diffraction patterns of the investigated samples. We analyzed the experimental data with respect to these structure types because the compound CuMnO2 has previously been reported to crystallize in a monoclinic structure with space group C2/m[22] and possibly in a delafossite-type hexagonal (trigonal) with space group $P6_3/mmc$ (R-3m) [35]. In turn, our X-ray patterns do not support hexagonal or trigonal structures, but rather conform to the monoclinic structure. We must emphasize that no foreign impurity is detected within the instrument detection limit. The strong peak at $2\theta = 15.8$ deg. for hkl = 001 and $2\theta = 31.5$ deg. for hkl = 002 is clearly visible in the X-ray pattern for sample No 1, indicating that the grains preferentially align along the *c*-axis. The broadness of the peaks in all spectra is due to the product's weakly crystalline nature, as it is composed of nanoparticles.

To calculate average crystallite sizes of the samples we used the Si (111) single crystal standard and Scherrer's equation:

$$L = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where *L* is the mean size of the ordered grains, *K* is a shape factor constant assumed to be 0.9, λ is the X-ray wavelength and β is the peak width at FWHM of the Bragg angle θ . Our analysis yielded sizes of grains from 17 to 65 nm for sample No 1, from 16 to 30 nm for No 2, and from 15 to 24 nm for No 3, being consistent with the SEM data.

The refinements result in good agreement between the theoretical



Fig. 1. SEM image (Left side) and corresponding EDX spectrum (Right side) of the $CuMnO_2$ nanostructures grown using 1 g, 2 g, and 3 g NaOH per 35 ml of the reaction solution, shown in the top, middle and bottom panel, respectively.

(solid line) and measured (open symbols) profiles (see Fig. 2). The following are the refined convergence parameters: for No 1, $R_p = 2.7$, $R_{wp} = 4.2$ and $\chi^2 = 4.5.1$; for No 2, $R_p = 2.0$, $R_{wp} = 2.4$ and $\chi^2 = 2.0$; and for No 3, $R_p = 1.9$, $R_{wp} = 2.6$ and $\chi^2 = 2.0$. In Table 1 we give the obtained lattice parameters, which match well with previously published data [16,18,22,36]. We discovered that even the smallest amount of NaOH causes a decrease in the unit cell's parameters *a* and *c*. As a result, it is worth noting that the parameter *a* is associated with the geometry of the MnO₆ octahedron and the *c* parameter is associated with the O–Cu–O length. The results presented here show that different NaOH concentrations in the synthesis have an effect on the distinct stoichiometry, crystallographic parameters of the prepared product, and, of course, its morphology.

3.2. Spectroscopic properties

The frequency dependence of the Raman shift in the studied samples is shown in Fig. 3. According to the data reported in the literature, the delafossites CuMO₂ (M = Cr, Fe) have two Raman active modes: A_g and E_g . The active mode A_{1g} appears around 700 cm⁻¹ which corresponds to the vibration of the O–Cu–O linkage along the *c*-axis, whereas the two weak Raman active E_g modes appear between 350 cm⁻¹ and 420 cm⁻¹ corresponding to the vibration of MO₆ octahedra along the *a*-axis [21, 37]. Spectral data of nanostructured CuMnO₂ samples show a strong peak at 637 cm⁻¹ in a sample from 1 g NaOH synthesis and 688 cm⁻¹ from 2 to 3 g NaOH synthesis. Apparently, these Raman peaks are undoubtedly attributed to the A_{1g} wagging vibrational modes.

In the lower wave number range, there are very weak anomalies at 305 and 382 cm⁻¹, and they presumably represent the E_g stretching modes. In addition to these peaks, we find a prominent singularity near 570 cm⁻¹ in samples No 2 and No 3. This mode may be attributed to Mn–O bending because it resembles the vibration of the Co–O linkage in

LiCoO₂ [38]. It is worth noting that the position of the main Raman peak in sample No 1 has been moved down by 50 cm⁻¹ when compared to samples No 2 and 3. Furthermore, the linewidth of this peak is wider. The distinct behavior of sample No 1 may be related to the previously discussed lattice parameters and nanoparticle sizes.

Fig. 4 depicts the spectral characteristics of the absorption coefficient of nanostructured CuMnO₂ films prepared with three different amounts of NaOH. In our prepared samples, we see a pronounced absorption peak at 287 nm and a broadened knee in the range 480–580 nm. The presence of these peaks indicates the presence of d - d transitions in the electronic band structure. According to Hiraga et al. [39], the first absorption peak is excitonic absorption combined with a transition from the valence band of O-2*p* to the conduction band of Cu-3*d*4*s* states, and the extended knee in the absorption spectrum may be due to electron excitation from the valence band to Mn t_{2g} orbitals.

The Tauc relation [40] is used to determine the energy gaps in the absorption spectrum (Fig. 4):

$$h\nu^{1/n} = A \left(h\nu - \boldsymbol{E}_g \right) \tag{2}$$

where *A* is a constant, E_g is the optical bandgap of a given material, and exponent *n* is equal to 1/2, 2 or 3/2 for indirect, direct, or direct forbidden transitions, respectively [41]. In Fig. 5, we show the photon energy dependence of experimental ($hu^{1/n}$) data for n = 2 on the left and n = 1/2 on the right scale.

Fitting eq. (2) to the data results in direct gaps ranging from 3.17 to 3.74 eV and indirect gaps ranging from 0.98 to 2.29 eV. Experimental values from our measurements are significantly higher than those reported by several groups [5,6,42] of only 1.36–2.53 eV, but lower than those reported by Shukla et al. with E_g of 4.6 eV and 4.90 eV, respectively [18].

Keep in mind, however, that the Tauc method was designed to be used with amorphous materials possessing energy state localization.



Fig. 2. XRD patterns of the CuMnO₂ nanostructures synthesized by using different amounts of NaOH. The experimental data are denoted by open symbols, while the theoretical profiles by solid lines. The vertical scores spell the positions of Bragg reflections indexed in the *C*2/*m* space group. The line at the bottom is the difference between the experimental and theoretical data.

Because the measured absorption involves the convolution of the broadening of the generated electron-hole pair's initial (i) and final (f) states, the gaps calculated with the Tauc equation would be underestimated for polycrystalline samples [43].

Following a method developed by Delgonos et al. [44], we have fitted the equation:

$$\alpha^2 \propto \left[1 - \frac{2}{\pi} \arctan\left(\frac{E_g - h\nu}{\Gamma}\right)\right]^2 \tag{3}$$

to the experimental data. In Eq. (2), Γ is a parameter of energy broadening, that is accounted by broadening time constant \hbar/τ . The values of the direct gaps calculated via this method are given in the tab. I. Noticeably, the latter values are larger than those from the Tauc method. Since the energy broadening parameter has a value in the range of 0.15–1.2 eV, the difference in the direct gap values between the two calculation methods by the amount of $\sim \pi\Gamma/4$ is acceptable.

3.3. Magnetic properties

The study of magnetic behavior in Figs. 6–10 clearly establishes the influence of pH on the physical properties of nanostructured CuMnO₂ samples. An examination of the inverse magnetic susceptibility, $\chi^{-1}(T)$, of sample No 1 in a field of 0.15 T versus temperature (Fig. 6) reveals

Table 1

A comparison of the EDX, crystallographic, Raman, UV-VIS and magnetic data of three nanostructured CuMnO₂ samples obtained via adding 1 g, 2 g and 3 g NaOH to reaction solution. Direct gaps and Direct gaps are fitted values using the Tauc equation and the method developed by Dolgonos et al., respectively.

Quantities	1 g NaOH	2 g NaOH	3 g NaOH
O (at. %)	42.4	45.0	45.0
Cu (at. %)	31.0	29.8	31.2
Mn (at. %)	24.3	24.3	23.8
a (nm)	0.55034	0.55865	0.55737
b (nm)	0.28931	0.28855	0.28852
<i>c</i> (nm)	0.58793	0.58986	0.59058
Raman peak (cm ⁻¹)	637	688	688
Direct gaps (eV)	3.52, 3.74	3.41, 3.72	3.17,
			3.68
Direct gaps (eV)	4.38, 5.47	5.68, 8.10	5.37,
			5.97
Indirect gaps (eV)	1.54, 1.91	1.45, 2.29	0.98,
			1.17
Ordering temp.	$T_{\rm C} = 9.2$ K, $T_{\rm N} = 42$	$T_{\rm N}(2) = 40$ K, $T_{\rm N}(1) =$	$T^{*} = 42K$
	К	62 K	
Mag.	MCW, 3D	CW, LD	CW, LD
characteristics			
μ_{eff} ($\mu_{\rm B}/{ m mol}$)	2.22	4.23	4.08
θ_p (K)	-89	-775	-719
J/k_B (K)	-	-39	-41



Fig. 3. Raman scattering spectrum of the nanostructured CuMnO₂ synthesized by using different amounts of NaOH.

that magnetic susceptibility above 100 K exhibits a modified Curie-Weiss (MCW) dependence:

$$\chi(T) = \frac{C}{T - \theta_p} + \chi_0 \tag{4}$$

with Curie constant C = 0.616 emuK/mol of transition metal (TM). The latter value corresponds to an effective moment value of $\mu_{eff} = 2.22$ (0.03) $\mu_{\rm B}/f.u$. Because the precise concentration of the ions at atomic positions is unknown, determining the effective moment for a specific ion is difficult. As a first approximation, we assume a chemical stoichiometry of $[{\rm Cu}^+][{\rm Cu}^2_x+{\rm Mn}^{3+}_{1-2x}{\rm Mn}^{4+}_x]$ O_{2-y}Cl_y, and estimate the effective moment $\mu_{eff} = 2.5 \ \mu_{\rm B}/f.u$., taking into account the theoretical values for Cu²⁺ of 1.73 $\mu_{\rm B}$, low-spin Mn³⁺ of 2.83 $\mu_{\rm B}$, and low-spin Mn⁴⁺ of 1.73 $\mu_{\rm B}$. The obtained effective moment closely matches the experimental value. Apparently, our findings differ from those of Trari et al., who discovered a high-spin configuration for Mn³⁺ in CuMnO₂ samples obtained through a solid-state reaction [23]. Furthermore, our experiments yield



Fig. 4. Absorption spectrum of the nanostructured $CuMnO_2$ synthesized by using different amounts of NaOH.

different results than those reported in the literature in terms of magnetic phase transitions. On the one hand, we find up to two transitions in our sample at $T_{\rm C} = 9.2$ K and $T_{\rm N} = 42$ K (see inset). Previous researchers, on the other hand, only reported one antiferromagnetic phase transition at around 65 K [23,25–27] for bulk or one transition at 42 K for a nano-sized CuMnO₂ material [16].

We conducted additional magnetic quantity measurements at low temperatures, magnetic dc-fields, and ac-frequencies to shed more light on complex phase transitions. The magnetization at 2 and 25 K reveals magnetic hysteresis below $T_{\rm C}$ but no hysteresis below $T_{\rm N}$ (see Fig. 7 a). Further evidence for ferromagnetic properties is shown in Fig. 7 b), where increasing the applied dc-magnetic fields raises the $T_{\rm C}$ values.

The anomalies in the ac-susceptibility's real and imaginary components (Fig. 8) attach to a ferromagnetic support for this sample below $T_{\rm C}$. We should note that the ac-susceptibility measurements do not show a loss peak in the imaginary component at $T_{\rm N}$ (which is not shown here), implying that the transition at $T_{\rm N}$ is most likely antiferromagnetic.

Fig. 9 depicts the magnetic behavior of sample No 2. Magnetic measurements in fields up to 1 T appear to reveal two magnetic phase transitions at 62 K, denoted as $T_N(1)$, and 40 K, denoted as $T_N(2)$. The data collected in several low magnetic fields reveal a broad maximum that shifts slightly lower with increasing applied fields, confirming the antiferromagnetic nature of the transition at $T_N(2)$. It is also discovered that the temperature dependence of the inverse magnetic susceptibility in the paramagnetic regime has unambiguous properties that differ from the sample No 1. First, a Curie-Weiss (CW) law description of $\chi(T)$ in the temperature range 200–300 K yields an effective moment of 4.23 μ_B /mol and a Curie-Weiss temperature of $\theta_p = -775$ K. A high μ_{eff} value indicates the presence of high-spin Mn³⁺ and Mn⁴⁺ ions.

In this case, we can calculate a theoretical moment of $4.26 \mu_B$, which corresponds to the experimental value. Second, the broad maximum in the $\chi(T)$ curve around 150 K may reflect the low-dimensional nature of the Mn²⁺ ion antiferromagnetic interactions. Our findings support the findings of Jia et al. [45], who demonstrated that the magnetic coupling between Mn layers is weak, implying a 2D characteristic. Despite the fact that CuMnO₂ has been identified as a frustrated system due to the kagome lattice of moment arrangements, the exchange constant between nearest neighbours J_1 was found to be much larger than those between next-nearest neighbours J_2 and next-next-nearest neighbours J_3 [45]. In the first approximation, the Heisenberg model is applied to chain Mn-based systems in CsMnCl₃ [46], [(CH₃)₄N][MnCl₃] [47], and CsMnBr₃ [48]. For the sample under consideration, we used Fisher's



Fig. 5. UV-VIS data of nanostructured CuMnO₂ samples synthesized by using different amounts of NaOH. The dotted and dashed lines are respective fits of indirect and direct gaps to the Tauc equation, whereas the solid lines present fits of the direct gaps using a method proposed by Delgonos et al. [44].

[49] model:

$$\chi(T) = \frac{N_A g^2 S(S+1) \mu_B^2}{k_B T} \frac{1+u}{1-u}$$
(5)

where
$$u = coth \left\{ \frac{[2JS(S+1)]}{k_B T} - k_B / [2JS(S+1)] \right\}$$
, N_A is the Avogadro



Fig. 6. Temperature dependence of the inverse magnetic susceptibility of nanostructured CuMnO₂ obtained by using 1 g NaOH. The solid line is a modified Curie-Weiss fit. The inset presents the temperature derivative of the magnetization.



Fig. 7. a) The magnetization collected at 2 and 25 K as a function of applied magnetic strengths and b) Temperature dependence of selected magnetization curves of nanostructured CuMnO₂ obtained by using 1 g NaOH.

number, $k_{\rm B}$ is the Boltzmann constant, g is Lande factor and J is the antiferromagnetic exchange constant coupling between nearest neighbours. For the exchange of magnetic Cu²⁺, Mn³⁺, and Mn⁴⁺ moments, we assume an effective spin S = 3/2. Taking g = 2, the theoretical curve



Fig. 8. a) Temperature dependence of a) the real part and b) imaginary part of ac-magnetic susceptibility of nanostructured CuMnO₂ obtained by using 1 g NaOH, measured with amplitude of the excitation field $H_{ac} = 3$ Oe and frequency f = 1500 Hz.



Fig. 9. Temperature dependence of the inverse magnetic susceptibility of nanostructured CuMnO₂ obtained by using 2 g NaOH. The dashed line is a fit of modified Curie-Weiss law and the dotted is the S = 3/2 Heisenberg model fit to experimental data. The inset depicts the magnetization collected in several fields versus temperature.



Fig. 10. Temperature dependence of the inverse magnetic susceptibility of nanostructured CuMnO₂ obtained by using 3 g NaOH. The dashed line is a fit of modified Curie-Weiss law and the dotted is the S = 3/2 Heisenberg model fit to experimental data. The inset depicts magnetization collected at 2 as a function of applied magnetic field strengths.

shown as a dotted line in Fig. 9 was obtained for $J/k_B=$ - 39 K and $\chi_0=0.3~\times~10^{-4}\,$ emu/mol. The good agreement between the theoretical model and the experimental data suggests that the Heisenberg model is fully applicable to the magnetic susceptibility properties of CuMnO_2 No 2.

Fig. 10 depicts the magnetic properties of CuMnO₂ No 3. In general, the high-temperature susceptibility does not differ significantly from that of sample No 2. We obtain $\mu_{eff} = 4.08 \mu_B$ /transition metal ion and Curie-Weiss temperature $\theta_p = -719$ K from the Curie-Weiss fitting. A broad maximum in $\chi(T)$ around 150 K is observed once more, which is a feature of low-dimensional (LD) magnetism. The theoretical curve of eq. (5) is found to be in good agreement with the experimental data, and we calculate $J/k_B = -41$ K and $\chi_0 = 0.32 \times 10^{-4}$ emu/mol (see dotted line).

Around 42 K, an anomaly denoted as T^* appears, below which the susceptibility rapidly increases with decreasing temperature. Some ferromagnetic interactions between next-next-nearest neighbours, as determined by Jia et al. [45], may begin to play a role. However, in samples 2 and 3, large negative values of paramagnetic Curie temperature θ_p as well as Heisenberg exchange interaction coupling *J* indicate a net antiferromagnetic interaction between the Mn³⁺ magnetic moments. Magnetization at 2 K does not exhibit hysteresis, as expected (see inset of Fig. 10), and a ferromagnetic ground state in samples 2 and 3 can be ruled out.

4. Summary

The nanostructured CuMnO₂ samples were synthesized using a lowtemperature hydrothermal method. The obtained samples were characterized in terms of morphologies, chemical compositions, and crystallography, as well as spectroscopic (Raman and UV-VIS) and magnetic (dc-magnetization, ac-susceptibility) properties. Table 1 contains the physical parameters obtained from the measurements. Our results show that morphological and preferred crystal growth of nanostructured CuMnO₂, as well as their physical properties, can be tuned using appropriate amounts of NaOH mineralizator in the growth solution.

The SEM and Xray powder diffraction experiments reveal that a pure CuMnO₂ phase with a monoclinic structure can be prepared in the form of nano-belts with lengths of up to 1.5 m or nanoplates with diameters of 50–70 nm. The physical property measurements indicate that these samples behave differently. The Raman peak of the CuMnO₂ nano-belts is at a lower Raman number than that of the nanoplates. We used the

standard method based on the Tauc equation to calculate indirect and direct gaps. The direct gaps were also estimated using the method proposed by Dolgonos et al. Larger values of the direct gaps obtained by the latter method are due to broadening absorption spectra that were not taken into account in the standard method.

In terms of magnetic properties, the nanobelt sample shows two successive magnetic phase transitions at lower temperatures. The most important discovery in this study is that varying the amount of NaOH mineralizator used influences the morphologies and preferred crystal growth, which in turn affects the physical properties of the crednerite CuMnO₂. The magnetic behavior can be attributed to Cu¹⁺/Cu²⁺ and Mn³⁺/Mn⁴⁺ partial oxidations. Surprisingly, the change in the spin states of Mn ions from low-to high-one correlates with the change in sample topologies, i.e., from nanobelt-shaped to nanoplate-shaped. We believe that our findings broaden our fundamental understanding of the atomic processes that underpin the morphological modulations of the CuMnO₂ material, opening up a new avenue for obtaining selected nanoparticles with desirable properties.

Credit author statement

Thi Quynh Hoa Nguyen: Sample preparation, EDX spectrum, Raman spectroscopic and optical properties measurements. Vinh Hung Tran: Conceptualization, X-ray and Magnetic properties measurements, Formal analysis, Writing & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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