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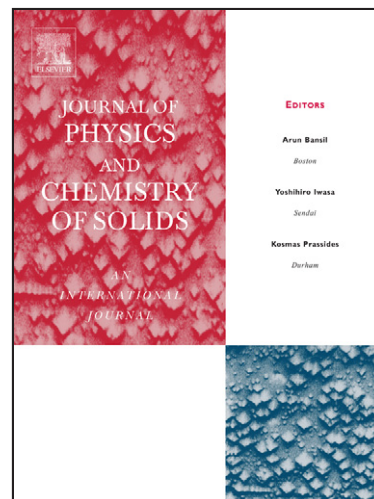
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**Powder and film of Nickel and Iron Layered Double Hydroxide:
Elaboration in polyol medium and characterization.**

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Abstract

Two main reactions occur in polyol media: reduction and hydrolysis. In the case of systems with two easily reducible elements Ni and Fe for instance, previous works have shown that bimetallic particles or the oxide spinel particles can be obtained. This paper shows that polyols can also be used to elaborate Layered Double Hydroxides LDH-Ni-Fe. In this case, the hydrolysis ratio must be adjusted to avoid both reduction and oxidation reactions in favor of hydroxylation. The compound can be obtained either in powder or gel forms. The gel enables elaboration of film by spin-coating process. The compound is poor-crystallised and exhibits a turbostratic character. Its interlamellar distance (12.89Å) is slightly higher than that of similar compound elaborated in aqueous solution via titration method (12.02Å). ^{57}Fe Mössbauer spectrometry allows to conclude to the presence of HS Fe^{3+} cations which occupy two different octahedral sites. XRD and Mössbauer studies reveal interesting preferential orientation features of the film with an anisotropy of the crystalline grains having their c axis perpendicular to the film.

Keywords: A. Inorganic compound, B. Sol-gel growth, C. X-ray diffraction, C. Mössbauer spectrometry, D. Microstructure.

Introduction

Since the pioneer work of Figlarz et al. an intense activity has been devoted to the synthesis of inorganic materials in polyol media [1]. For systems containing one easily reducible metal (cobalt for instance), competition occurs between hydrolysis and reduction [2]. This competition can be easily controlled by the hydrolysis ratio h defined as $n(\text{H}_2\text{O})/n(\text{M})$, allowing thus the synthesis of three inorganic material types: metal, oxide or layered hydroxysalt.

The aim of this work is to show that these rules can be extended to systems with two easily reducible metal elements. The nickel – iron system is chosen for this purpose. Since the synthesis of submicronic bimetallic particles NiFe [3] and spinel oxide NiFe₂O₄ nanoparticles has yet been reported [4], we focus here on the synthesis and characterization of the third term of the series namely the LDH-Ni-Fe. This will enable to discuss for the first time, the main parameters governing the elaboration in polyol medium of metal, oxide and hydroxide for bimetallic systems.

2- Experimental:

A pure LHD-Ni-Fe-Ac has been recovered for the following experimental conditions: a high hydrolysis ratio $h = 40$, (addition of 50 ml of water), Ni/Fe = 3 (Ni(CH₃COO)₂.4H₂O and Fe(CH₃COO)₂ used as precursors) and a working temperature of 120°C. The choice of these conditions of hydrolysis ratio and temperature will be discussed hereafter. The compound can be obtained in either ethyleneglycol, diethyleneglycol (DEG) and propane 1,2-diol or ethanol (60°C). However, the highest rate was observed for DEG which thus has been retained to elaborate the studied compound.

After cooling, the mixture is centrifuged, washed with ethanol and finally dried in vacuum at 60°C. A yellow-green gel (**Fig.1**) is recovered when the mixture is left settle for several days at 300K and the supernatant liquid regularly removed. A transparent yellow-green multi-layers film (Thickness = 30 μm) (**Fig.2**) is obtained from gel by spin-coating method and heating at 100°C. Before coating, the gel viscosity is adjusted by addition of small amount of ethanol before coating.

Chemical analyses and characterization were conducted using several techniques described in a previous work [5]. The ⁵⁷Fe Mössbauer spectra were recorded at 300 and 77 K in a transmission geometry using a ⁵⁷Co/ Rh γ-ray source, in zero magnetic field. The isomer shift

values (δ) were referred to that of α -Fe at 300 K. The sample consists of either 5 mg of Fe/cm² powder or a spin-coated film on a kapton foil.

Results and discussion:

- Synthesis of hydroxide in polyol for bimetallic systems: the case of LDH-Ni-Fe

Polyol medium present numerous advantages to elaborate inorganic compounds [11]: good homogeneity at the molecular level (formation of mixed diolates), no direct control of the pH, absence of carbonate due to the acidic character of polyol[12] and an easy control of hydrolysis, polymerization reactions. Furthermore, hydrolysis competes with reduction reaction due to the reducing power of polyol. As previously reported [2], this competition can be easily controlled thanks to the hydrolysis ratio. For bimetallic system Ni-Fe, when water is distilled off (hydrolysis ratio $h = 0$), the temperature can reach the boiling point of polyol (245°C). This favors the reduction and bimetallic NiFe submicrometer particles are obtained [3]. A low hydrolysis ratio (in the range of 1–6) (the temperature is slightly decreased: $T = 205$ °C) favors the oxolation reaction which leads to the formation of NiFe₂O₄ nanoparticles [4].

In the present work, we show that when the hydrolysis ratio is significantly increased ($h = 40$) and the medium temperature lowered ($T = 120$ °C), the oxolation reaction is inhibited and only hydroxylation is favored leading to the hydroxide compound LDH-Ni-Fe

- Chemical and physical characteristics of LDH-Ni-Fe powder and film:

Chemical analysis and ionic chromatography show that both acetate anion and polyol species are present in the final product. This has also recently been observed for Ni-Al-Ac LDH prepared in polyol medium [6]. Iron (II) is oxidized into iron (III) under these conditions as clearly established by potentiometric titration and Mössbauer analysis. Altogether these results led to the chemical formula Ni^{II}₃Fe^{III}(OH)₈ (CH₃COO)_{0.80}(DEG)₃H₂O. Elemental and TG-TD analyses confirm this composition: obs (calc) Ni: 31.39 (31.12); Fe: 9.32(9.87); C: 10.55 (10.83); H: 3.97 (4.39), (theo. loss: 46.2%, exp. loss: 45.1%). Regardless of the

amount of DEG, the same chemical formula was obtained when the material is prepared in aqueous medium by exchange reaction starting from the LDH-Ni-Fe-CO₃ compound [7].

The presence of both acetate anion and DEG species is confirmed by IR spectroscopy: indeed, bands at 1564 and 1408 cm⁻¹ are assigned to acetate anion, bands at 1124 and 1054 cm⁻¹ to DEG. The broad peak at 3580-3400 cm⁻¹ corresponds to hydroxyl groups and water molecules and band around 1570-1640 cm⁻¹ to $\delta(\text{H}_2\text{O})$.

At both 300 and 77K, the ⁵⁷Fe Mössbauer spectra of the powder (**Fig. 3**) present broadened line quadrupolar doublets which have to be fit with at least two distinct resolved quadrupolar components. The corresponding isomer shifts (0.46 and 0.47mm/s at 77K) are characteristic of HS Fe³⁺ located in different octahedral sites while the absence of Fe²⁺ is confirmed. The values of the quadrupolar splitting (0.43 and 0.69 mm/s) suggest non symmetrical environment around the Fe³⁺. The spectrum of the film oriented perpendicularly to γ -ray and recorded at 77 K shows dissymmetrical doublet (**Fig. 4a**). By rotating the film (45°) respect to the γ -radiation, one observes a significant change in the relative intensities of the two peaks, as shown in **Fig. 4b**: this allows to conclude to a preferential orientation of the crystalline grains according to previous works [8, 9].

The XRD patterns (**Fig. 5a**), are typical of layered material with a turbostratic disorder of the layers stacking: indeed, one observes sharp and symmetric reflections for the basal (00*l*) planes and broad and asymmetric reflections for the non-basal planes [10]. The interlamellar distance (12.86 Å) is slightly higher than that previously observed by Mendiboure et al.(12.03Å) [7]. The turbostratic feature is confirmed by TEM: LDH-Ni-Fe-Ac powder appears as aggregates of thin crumpled sheets with any definite shape (**Fig. 6**). Electron diffraction patterns are characteristic of hexagonal plate-like particles lying in the (00*l*) plane. The X-ray diffraction pattern of the film (**Fig. 5b**) reveals the disappearance of the (hk0) reflections. This highlights the presence of a preferential orientation {00.1}(c axis of the

hexagonal cell) of the grains parallel to the normal to film and an isotropy of their orientations in the plane of film, that is consistent with above Mössbauer results.

Conclusion:

We have shown in this work, that metal, oxide and hydroxide can be elaborated in polyol medium for bimetallic system thank to hydrolysis and reduction reactions which occur in this medium. The absence of water, inhibit hydrolysis and thus metal particles are obtained. A low amount of water favours the formation of oxide while a high amount leads to the formation of hydroxide (LDH-Ni-Fe). It is interesting to note that this method allows to obtain the LDH compound either in powder or gel forms. The later is likely suitable to obtain thin films with a preferential orientation of crystalline grains, making these materials good candidates for several applications. It is also important to emphasize that other bimetallic hydroxide compounds can be synthesized according to similar route.

References

1. Figlarz, M., F. Fiévet, and J.-P. Lagier, *patents*, 1982: Europe n°0113281; U.S.A n°4539041; Finlande n°74416; Japon n°04024402.
2. L. Poul, S. Ammar, N. Jouini, and F. Fiévet, F. Villain, *J. Sol-gel Sci. Tech.*, 26 (2003) 261.
3. Viau, G., F. Fiévet-Vincent, and F. Fiévet, *Solid State Ionics*, 84 (1996) 259.
4. S. Chkoundali, S. Ammar, N. Jouini, F. Fiévet, P. Molinié, M. Danot, F. Villain, and J. M. Greneche, *J. Phys. : Condens. Matter.*, 16 (2004) 4357.
5. M. Taibi, S. Ammar, N. Jouini, F. Fiévet, P. Molinié, and M. Drillon, *J. Mater. Chem.*, 12 (2002) 3238.
6. Prevot, V., C. Forano, and J.-P. Besse, *Chem. Mater.*, 17 (2005) 6695.
7. Mendiboure, A. and R. Schollhorn, *Rev. Chim. Min.*, 23 (1986) 819.
8. Greneche J.M. and F. Varret, *J. Physics C: Solid State Physics*, 15 (1982) 5333.
9. Greneche J.M. and F. Varret *J. Physique Lettres* 43 (1982) L233.
10. Yang, D. and R.F. Frindt, *J. Mater. Res.*, 11 (1996) 1733.
11. M. Taibi, S. Ammar, N. Jouini, and F. Fiévet, *J. Phys. Chem. Solids*, 67(2006) 932.
12. Hansen, H.-C.-B. and R.-M. Taylor, *Clay Minerals*, 26 (1991) 311.

Figure captions

Figure 1. Yello-green gel

Figure 2. SEM Edge-view of the transparent film (inset is the SEM view of the layers forming the film; thickness about 2 μ m)

Figure 3. 77 K ^{57}Fe Mössbauer spectrum of the powder

Figure 4. ^{57}Fe Mössbauer spectra of the film (a: perpendicular to γ -ray, b: with an angle of 45° with γ -ray)

Figure 5. XRD patterns (a: powder, b: film)

Figure 6. TEM image of LDH-Ni-Fe-OAc

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Figure 1

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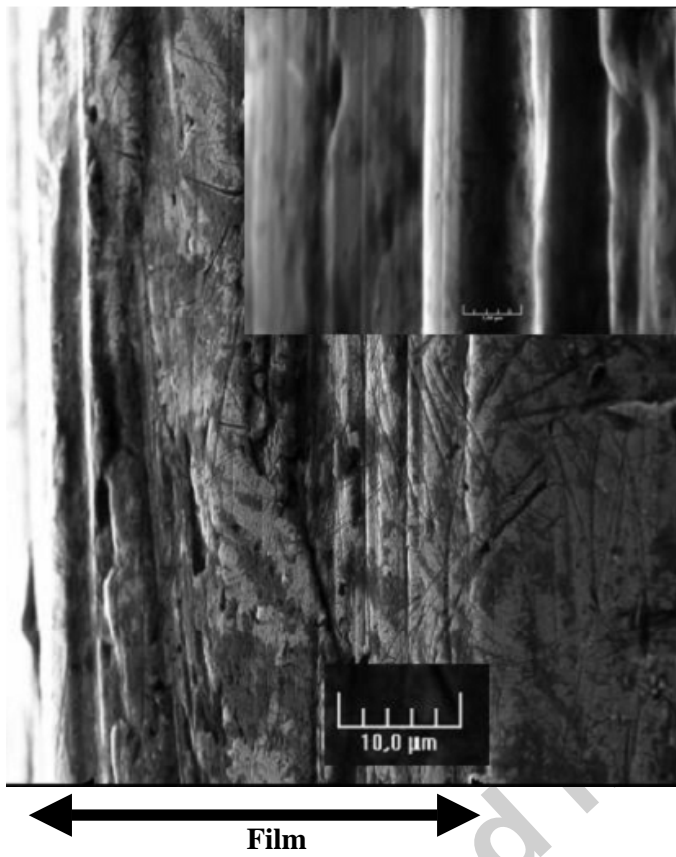


Figure 2

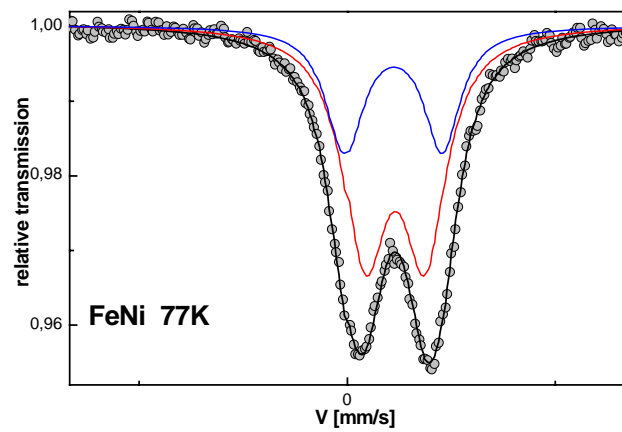


Figure 3

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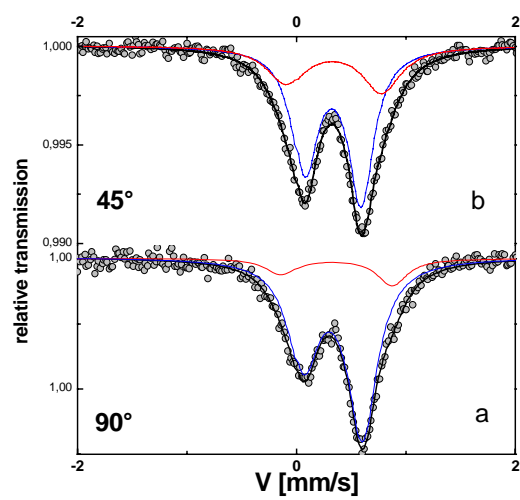


Figure 4

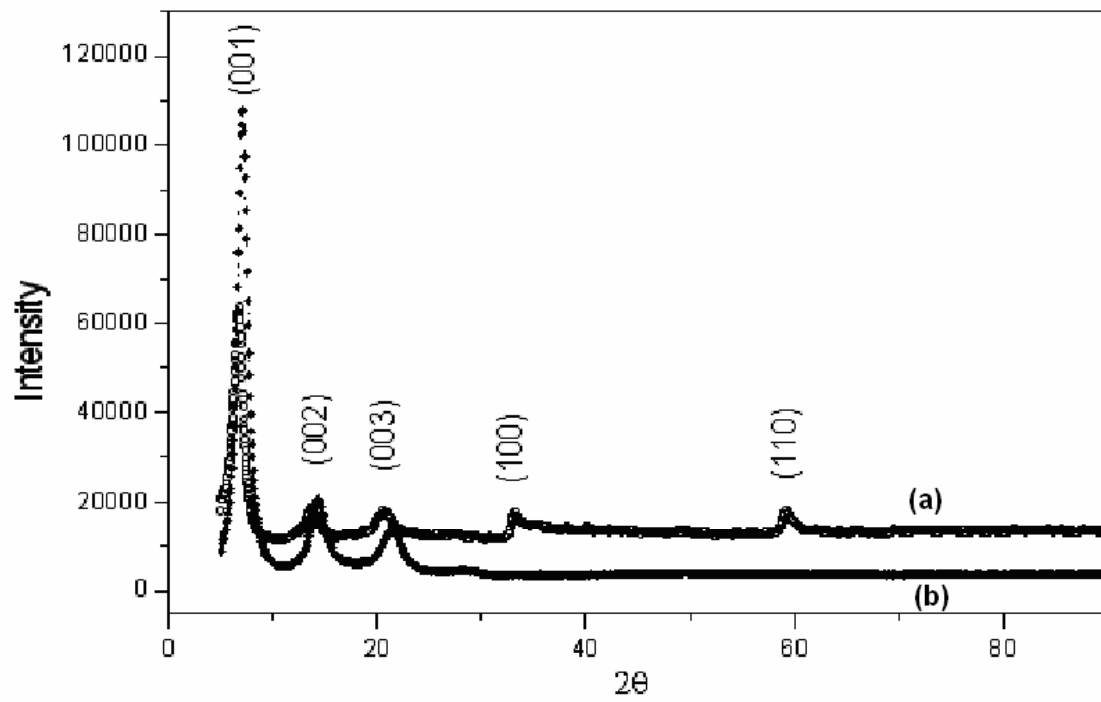


Figure 5 :

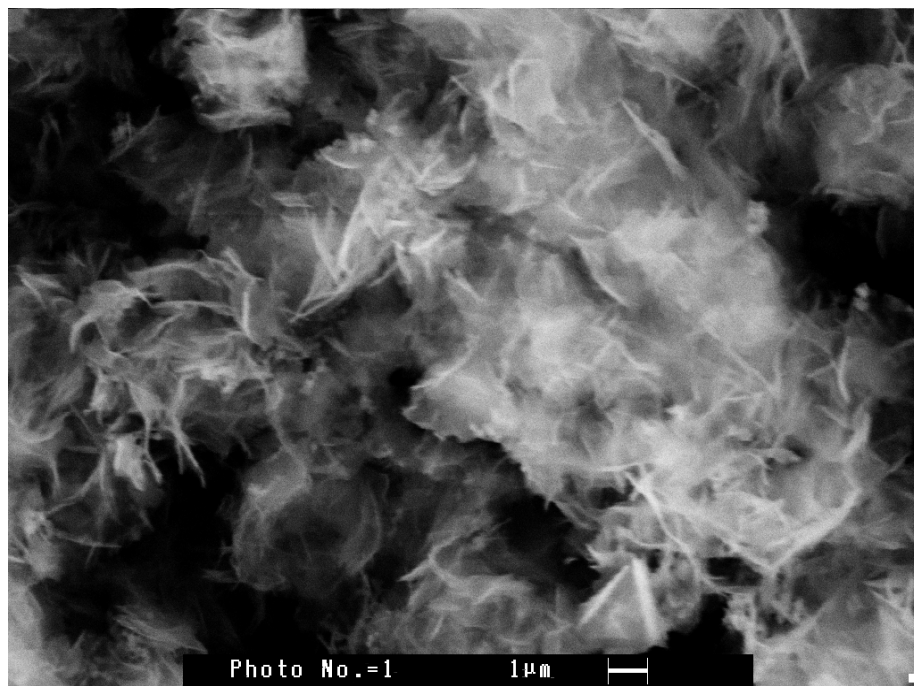


Figure 6