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In situ pulsed laser deposited thin films of ternary molybdenum cluster sulfides $Cu_xMo_6S_8$ $(2 \leq x \leq 4)$

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Abstract

Thin films of $Cu_xMo_6S_8$ have been deposited in situ by pulsed laser ablation on $(110)_R$ sapphire substrate. The high quality of films has enabled us to perform chemical treatments. Desintercalation reactions carried out in hydrochloric acid solution has led to metastable Mo_6S_8 as shown by X-ray diffraction (XRD) and Rutherford Backscattering Spectroscopy (RBS). In some cases an exchange reaction has been shown to take place between copper and silver, which comes from the silver paint used to stick the substrate and has allowed us to obtain ≈ 1 $AgMo_6S_8$ film. The copper reinsertion performed on a desintercalated film has succeeded, proving the reversibility of the desintercalation reaction. © 1997 Elsevier Science S.A.

Keywords: Chevrel phases; Thin film; Laser ablation; Desintercalation; Intercalation

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1. Introduction

Besides their superconducting properties, the Chevrel phase $M_xMo_6S_8$ compounds (where M is a cation) present a structure which is also very interesting for desintercalation–intercalation experiments. This structure is based on Mo_6S_8 building blocks. The arrangement of the latter creates channels which develop along the three rhombohedral axes [1]. When M is a small cation it displays a high mobility in these large cavities and can reversibly get in and out of the structure in mild conditions [2]. This behavior can be controlled by electrochemical experiments as many studies have been reported on rechargeable batteries [3–5]. In order to build solid state batteries, high quality thin films which have good mechanical properties are very important to obtain efficient electrodes. Many experiments have been devoted to $Cu_xMo_6S_8$ because besides this property, they exhibit superconducting transition properties at temperatures depending on their composition.

$Cu_xMo_6S_8$ presents a solid solution and the concentration of the cation can be varied continuously from $x = 4$ to $x = 1.8$ (and even to $x = 0$ in metastable conditions). Flükiger et al. [6] have established the low temperature phase diagram for this compound in the range 1.5–3.5 and have shown the dependence of the superconducting critical temperature (T_c) on the copper content. This characteristic is very useful in following the intercalation–desintercalation experiments.

In a previous work [7], we have described the first synthesis of $Cu_xMo_6S_8$ thin films in-situ deposited by laser ablation. In this article, we report on the chemical desintercalation carried out in hydrochloric acid

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solutions and subsequent chemical reintercalation of copper in these films. The characteristics of the films have been followed at different stages of the chemical treatment.

2. Experimental

2.1. Thin films growth

The films were grown in situ by pulsed laser deposition from a home-made target (26.3 mm in diameter and approx. 5 mm thick) of composition $Cu_3Mo_6S_8$. The target was sintered by hot pressing under vacuum (1000°C, 100 bars) from previously synthesized Chevrel phase powders. Thin films were deposited in a stainless steel vacuum chamber (MECA 2000) under vacuum (pressure approx. 10^{-6} mbar) using an XeCl ($\lambda = 308$ nm) excimer laser (SOPRA SEL 520), onto $(110)_R$ Al_2O_3 single crystal substrates (R-cut sapphire). Before deposition the substrates were ultrasonically cleaned in alcohol and fixed with silver paint on the stainless steel substrate holder the temperature of which ranged between 400 and 790°C.

2.2. Thin films characterizations

The thin films composition has been analyzed by Rutherford Backscattering Spectrometry (RBS) on the accelerator ARAMIS in Orsay [8]. The helium incident beam has an energy of 3 MeV and a typical diameter of 1.5 mm. The films discussed here have an excess of molybdenum but the transfer of composition between the target and the sample remains congruent for the copper–sulfur ratio.

The structural characteristics of the films have been studied by X-ray diffraction using an INEL CPS 120 diffractometer with a curved position-sensitive detector (CuKα1 radiation). In the case of epitaxially grown films, we have used a decoupled θ–2θ diffractometer (CuKα1 radiation). XRD patterns have shown that between 490 and 760°C the films present a powder like X-ray diffractogram whereas for a deposition temperature between 770 and 790°C the films grow with a $(100)_R$ preferential orientation. Moreover, the in-plane alignment determined by φ-scans using an X-ray texture diffractometer has shown that films are epitaxial.

Thin film morphology has been observed by scanning electron microscopy (SEM). The surface of the samples is smooth except for a low density of small droplets (approx. 3 for 10 μm^2) which is a typical characteristic of the laser ablation process. The films have a mirror like aspect and a good adherence to the substrate.

The superconducting transitions have been recorded from inductive measurements performed at 119 Hz.

2.3. Desintercalation–reintercalation experiments

Previous to desintercalation experiments, the silver paint which remains on the back of the substrate was removed as much as possible. A layer of protective resin was used to protect the film before etching silver with a ferric nitrate solution.

The films desintercalation has been carried out in hydrochloric acid solution (2.6 N or 1.0 N) [2]. The films were immersed for many hours in the solution, the desintercalation steps being followed by X-ray diffraction and superconducting characterization, the ultimate composition was determined by RBS measurements.

The intercalation has been carried out on previously desintercalated films. The sample was put in a quartz tube with a titanium–zirconium alloy foil and a small metallic piece of the element to insert. This ampoula was sealed under primary vacuum, the titanium–zirconium was then heated in order to act as an oxygen getter; afterwards the tube was sealed again to keep the film apart. Finally it was heated at 450°C for 5 h. The intercalated film was studied by X-ray diffraction, inductive measurements and RBS.

3. Results

Table 1 summarizes the characteristics of the three samples at each step of the chemical treatments.

Table 1
Characteristics of the three samples at different stages of the chemical treatment

Sample	Composition Cu–Mo–S	Desintercalation duration	Composition Cu–Mo–S	Insertion	Composition Cu–Mo–S
L31	3.6:7.6:8.0	20 h	0.05:7.6:8.0	—	—
L32	4.0:9.8:8.0	31 h	0.06:9.8:8.0	—	—
L42	3.5:6.6:8.0	3 h	0.2:6.6:8.0	450°C for 5 h	3.4:6.7:8.0

3.1. Desintercalation reaction

The desintercalation in the $M_xMo_6S_8$ compounds is an oxydo–reduction reaction.

The ternary compounds is oxidized and the proton is reduced:

$$M_x^{n+}Mo_6S_8 + nx(H^+,Cl^-) \rightarrow$$

$$Mo_6S_8 + x(M^{n+},nCl^-) + nx/2\,H_2\uparrow$$

The oxidation of the ternary compounds entails a loss of electrons for the molybdenum cluster.

3.1.1. Desintercalated films

The desintercalation process mentioned above successfully removes copper out of the initial phase, as evidenced by the RBS spectra displayed in Fig. 1. The initial composition of the L31 sample deduced from the area ratios of the RBS peaks was Cu–Mo–S = 3.6:7.6:8.0. The spectrum after desintercalation (overlaid on Fig. 1) exhibits a strongly reduced copper peak, whereas the Mo–S ratio remains unchanged, leading to a composition Cu–Mo–S = 0.05:7.6:8.0. XRD patterns taken at different steps of the desinsertion are represented in Fig. 2. Since they are very noisy, the unit-cell constants can not be accurately determined, but the most striking feature is the shift of the $(100)_R$ peak (in the rhombohedral settings) and the splitting of the $(221)_R$, $(310)_R$ and $(311)_R$ ones, corresponding to the expected evolution from the $Cu_3Mo_6S_8$ to Mo_6S_8 structure. Moreover the desintercalated film is not superconducting at 4.2 K, like Mo_6S_8 which is superconducting only under approximately 1.7 K.

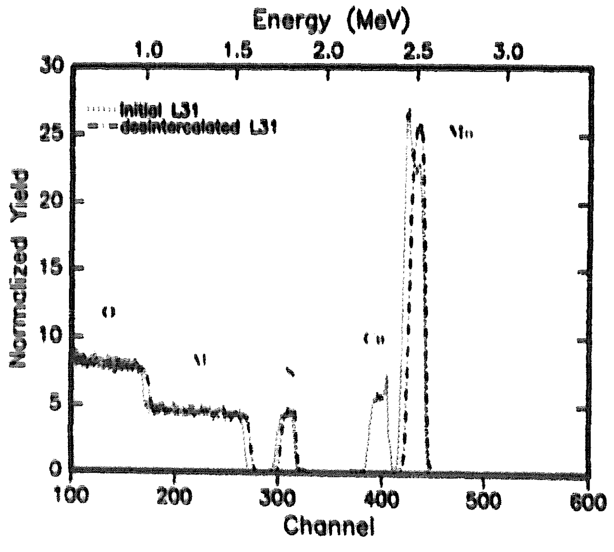

Fig. 1. Rutherford backscattering spectra (performed at 3 MeV) of the L31 sample: initially and after desintercalation.

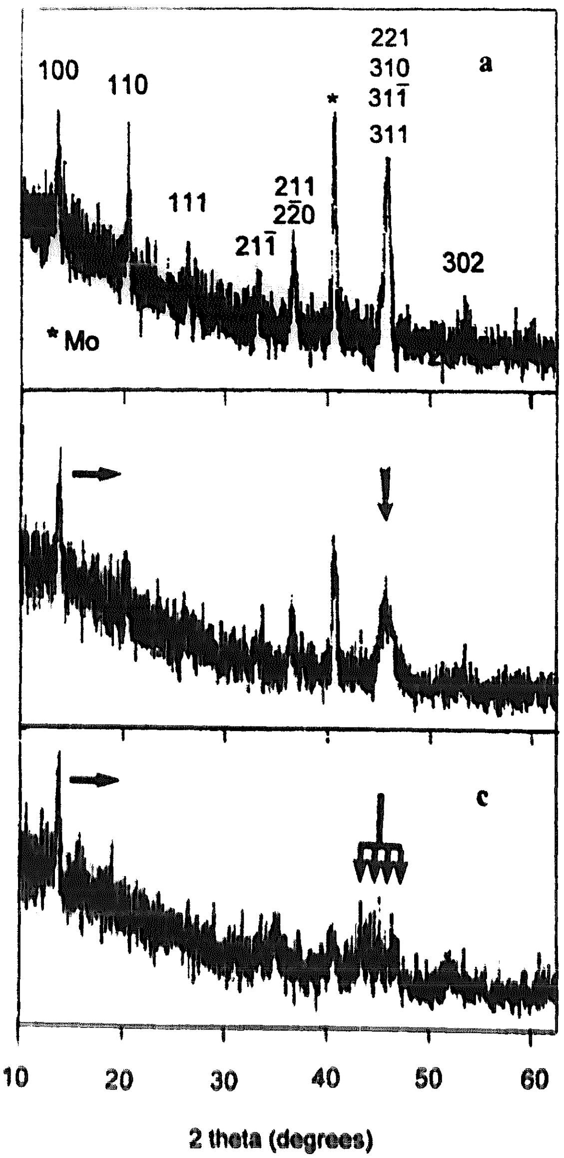

Fig. 2. XRD patterns of the L31 sample at different stages of the desintercalation (a: initially; b: after 2 h; c: after 20 h).

3.1.2. Exchange reaction

An alternative process has been evidenced, for instance in the case of the L32 sample, whose starting composition was close to the previous film, i.e. Cu–Mo–S = 4.0:9.8:8.0. The initial and after desinsertion RBS spectra are shown in Fig. 3. As previously, the copper peak is no more visible and at this stage there is no more than 1.5% of the initial copper content, as confirmed by an inductively coupled plasma analysis performed on the hydrochloric acid solution. However, the presence of a shoulder on the molybdenum peak suggests that some silver coming from the silver paste used to stick the substrate during deposition, which was not fully removed by the ferric nitrate etching, has diffused in the film via the solution. Fig. 4 represents the XRD patterns at dif-

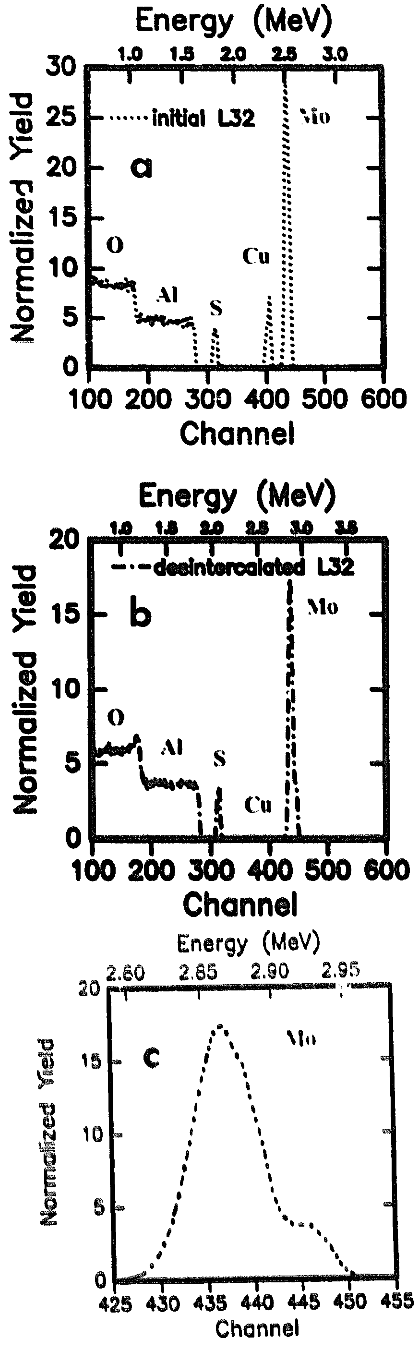

Fig. 3. (a) Initial RBS spectrum of the L32 sample performed at 3 MeV; (b) RBS spectrum of the desintercalated L32 sample carried out at 3.4 MeV; (c) enlargement of the molybdenum peak after desintercalation.

ferent desintercalation steps (initially and after 31 h in hydrochloric acid). They almost show the same evolution as the L31 samples (Fig. 2). Nevertheless, the final pattern has allowed us determine the unit-cell constants (a_R = 6.50 Å, α_R = 92.10°). These values correspond more closely to the unit-cell constants reported for $AgMo_6S_8$ than to those of Mo_6S_8 which was expected after desintercalation. Moreover, as shown in Fig. 5, the T_c of this thin film was reduced from 7.0 to 6.0 K, a value significantly above the T_c of Mo_6S_8 and electron microprobe analyses have clearly evidenced the presence of silver in the film. Despite a very low product of solubility for silver chloride in the acid solution, it remains a sufficient content of Ag^+ cations to react with the thin film. The silver acts as a reductive agent towards Mo_6S_8, in excellent agreement with the previously reported electrochemical potentials [9], so this system behaves like a battery and allows us to show the possibility of an exchange reaction in thin film.

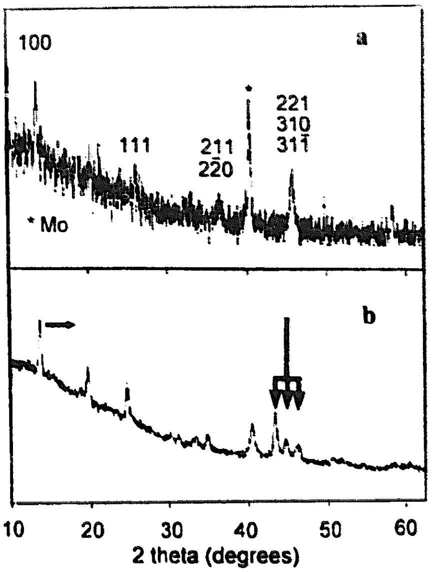

Fig. 4. XRD patterns of the L32 film at different steps of the desinsertion reaction (a: virgin; b: after 31 h).

3.2. *Reintercalated films*

The last set of experiments proves that the desintercalation process is reversible. The RBS spectra taken at three different stages for the L42 sample are shown in Fig. 6 (a: virgin, b: after 3 h of desinsertion, c: after copper reinsertion). During the different reactions the sulfur and molybdenum peaks do not change within experimental accuracy. As Fig. 6 (insert) shows, the copper comes in and out. Since the desinsertion time (3 h) is shorter than for the previous experiments (20 and 31 h), more copper is left during the desintercalation step, leading to a composition of Cu–Mo–S = 0.2:6.6:8.0, which has to be compared to the initial composition of Cu–Mo–S = 3.5:6.6:8.0. Interestingly, silver has been incorporated during the second step, but removed during the third one (it was probably expelled to give place to copper).

The XRD pattern (Fig. 7) on the reintercalated sample displays the usual diagram for $Cu_xMo_6S_8$, in full agreement with the composition obtained by RBS (i.e. Cu–Mo–S = 3.4:6.7:8.0).

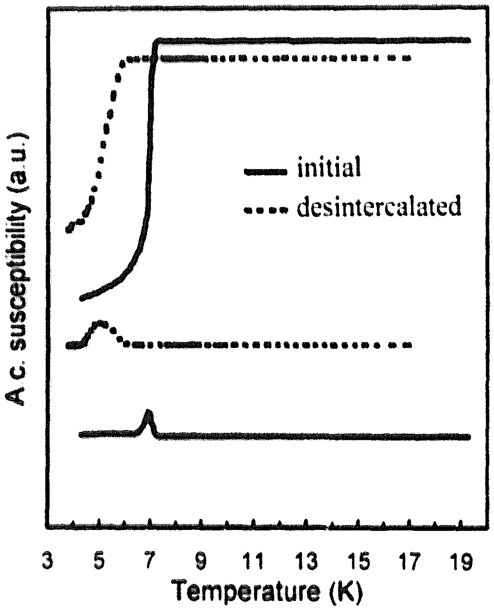

Fig. 5. The in-phase χ' and quadrature χ'' components of the a.c. susceptibility vs. temperature, showing the evolution of the superconducting transition for the L32 sample before and after desintercalation.

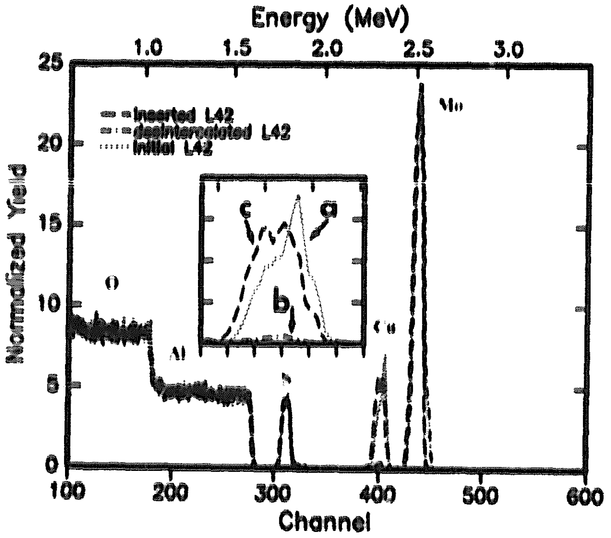

Fig. 6. RBS spectra for the L42 sample at different stages of the chemical reaction: a, virgin; b, after 3 h of desinsertion; c, after copper reinsertion. In insert: an enlargement of the copper peak.

4. Conclusion

In this article we have shown some preliminary results concerning chemical desintercalation–intercalation experiments performed on PLD grown $Cu_xMo_6S_8$ thin films. The success of such experiments is proof of the high quality of the samples. These results emphasize the strong reactivity of thin films and their ability to be used for further chemical and electrochemical studies.

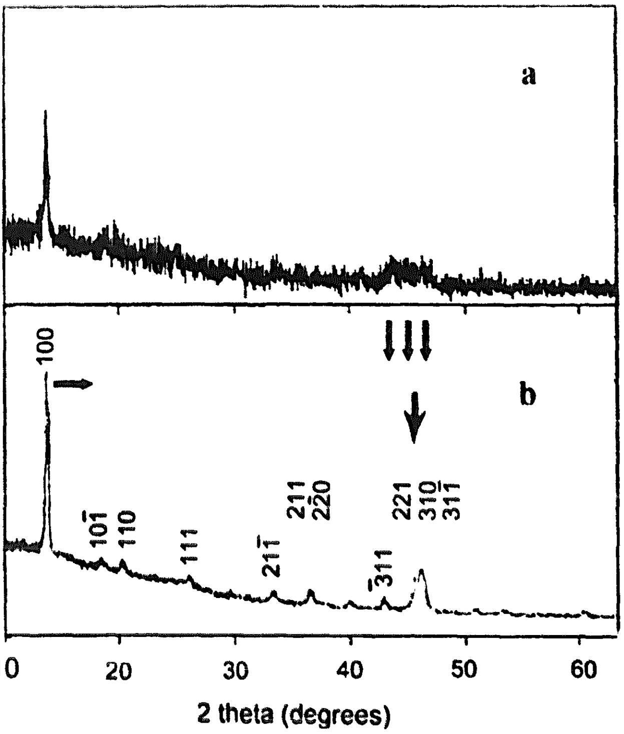

Fig. 7. XRD diffraction patterns of the L42 film: a, after desinsertion; b, after reinsertion.

The desinsertion–insertion reactions can lead to metastable compositions such as Mo_6S_8 and likely to new compounds with other cations even larger such as tin or lead, since the reintercalation of copper has succeeded. This possibility is very interesting since these Chevrel phases will be probably very difficult to synthesize in situ due to thermodynamical conditions during the growth.

Besides the intercalation by chemical vapor transport, the insertion using an exchange mechanism has been evidenced in the example of the copper–silver couple. This reaction could be very useful to insert a cation since it works even at room temperature and is very easy to apply.

On the other hand, the control of the obtention of actually desintercalated samples needs to fully remove silver, either by using another substrate sticking method or full silver removal using a lithography process.

In summary we have shown that the PLD method can be adapted to the Chevrel phase thin films syntheses and new studies about other cluster compounds should be expected.

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