

FORMATION OF MnS CLUSTERS INTO LAUMONTITE ZEOLITE

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Aqueous ion-exchange and impregnation procedures were used to isolate MnS in laumontite zeolite. XRD and FTIR measurements suggest that the clusters are formed inside the zeolite channels. ED analysis and Kubelka-Munk spectra proved that the impregnation procedure favors the formation not only of MnS clusters but also the formation of metal nanoparticles. Dispersion in the dimension of MnS clusters and metal nanoparticles was evidenced.

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1. Introduction

The multiple valence and the paramagnetism of manganese compounds are related to the electrons in the unfilled 3d orbital of manganese [1]. Low-dimensional chalcogenides represent an active area of research owing to their interesting optical or magneto-optical properties. Manganese sulfide is a compound member of the family of magnetic semiconductors whose crystalline structure may be type rocksalt (α -MnS) or zinc blend (β -MnS) or wurtzite (γ -MnS) [2,3].

Semiconductor embedded in zeolites are attractive for many technological applications as photocatalysis, nonlinear optics, sensors, etc. Magnetic semiconductor clusters in zeolite host represent a novel composite material. The well-defined cavities and channels of zeolites provide a convenient environment for preparing clusters with narrow size distribution or cluster array [4,5].

In this work we explore the use of natural laumontite zeolite (collected from Stanija, Romania) as host matrix into which the MnS clusters are created in situ to impose crystalline order and physical constraint [5,6].

Laumontite is a monoclinic mineral characterized by single 4 - ring tetrahedral chains as secondary building units and large channels of ten - membered tetrahedral rings ($4.6 \times 6.4 \text{ \AA}$) which are parallel to *c*-axis. The channels are occupied by Ca and H₂O [7,8]. The (Si, Al) distribution in the tetrahedral framework is nearly perfectly ordered.

The well-defined, one-dimensional channels provide the chance of growing single-size clusters and cluster wires, while the windows provide access for transporting reagents to the channels.

2. Experimental

Natural laumontite crystals with the approximate unit cell formula of the framework $\text{Ca}_4(\text{H}_2\text{O})_{18}[\text{Si}_{16}\text{Al}_8\text{O}_{48}]$ have been used. The semiconductor clusters were prepared by using two procedures: aqueous ion exchange and impregnation [9-11]. The zeolite crystals were first crushed and then submitted to an ion-exchange process in order to obtain the sodium cation form, Na/LAU.

In the aqueous ion-exchange procedure the zeolite powder was treated with 0.1 N aqueous manganese nitrate solutions at 296K and pH 5.5-5.8, using a solid/liquid ratio of 1/50 (Mn/LAU1). The ion loaded zeolite powder, was washed and dried at 378K and then submitted to a sulfidation

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process with 1M Na₂S solution, at room temperature, during 12h (MnS/LAU1). In such a process MnS clusters precipitate in the zeolite framework and Na-form of zeolite was regenerated [11,12].

Stirring 0.5 g zeolite powder, Na/LAU, in a 0.5 molar solution of manganese acetate for 10 minutes carried out the impregnation procedure. The dispersion was separated by centrifugation and the residue was dried in vacuum at 350K for 2 h (Mn/LAU). Afterwards it was stored in a H₂S atmosphere at 350K for 12 h (MnS/LAU). In both procedures small exchanged rates were intended.

The sample chemical compositions were examined by electron microprobe analyses (JEOL JEM2010).

The crystallinity of samples and crystal morphologies were estimated by X-ray diffraction (DRON 3) and SEM. Structural information was also obtained by Electron Diffraction (ED) patterns analysis, using JEOL 120CX microscope operating at 100 kV and JEOL JEM2010 microscope operating at 200 kV. The samples suitable for the TEM studies were prepared by finely crushing the material and gluing on copper grid or by mechanical polishing followed by ion milling of crushed material sandwiched between two Si wafers.

For IR spectroscopic studies, in Mid IR region, were produced pellets at a concentration of about 1% zeolite powder in KBr. For measurements in far IR region was used polyethylene powder instead of KBr powder.

Diffuse reflectance measurements were made on pellets from the pure zeolite powder with a spectrophotometer Perkin-Elmer, Lambda 18. The data were converted using the Kubelka–Munk formula, the obtained spectra being a good representation of the absorption spectra.

3. Results and discussion

Electron microprobe analyses evidenced that the chemical composition varies from one micro-crystal to another. In table 1 are presented some of the results, which were often observed.

Table 1. Chemical characterization of the samples.

Sample	Si/Al	Na at %	Ca at %	S at %	Mn at %	S/Mn
Na/LAU	2.30	0.72	4.10	-	-	
Mn/LAU	2.30	0.40	3.75	-	1.49	
MnS/LAU	2.30	0.34	3.67	0.10	0.35	0.28
MnS/LAU1	2.30	0.22	3.85	0.11	0.12	0.92

All electron microprobe analyses proved that only a small quantity of calcium ions were exchanged by sodium ions, that manganese ions exchange predominantly sodium ions and that the sulfidation process removes a part of manganese ions from the zeolite channels. In the conditions of our experiments, it was observed that the impregnation procedure favored the entrance of manganese into the laumontite channels and that the sulfidation process was very low. In both procedures the S/Mn ratio had a reduced value.

SEM micrographs and XRD patterns (Fig. 1 and Fig. 2) show that the structure of the zeolite matrix was not damaged and there were no significant MnS or Mn outside the zeolite channels. There are visible long and short prismatic single crystal [13].

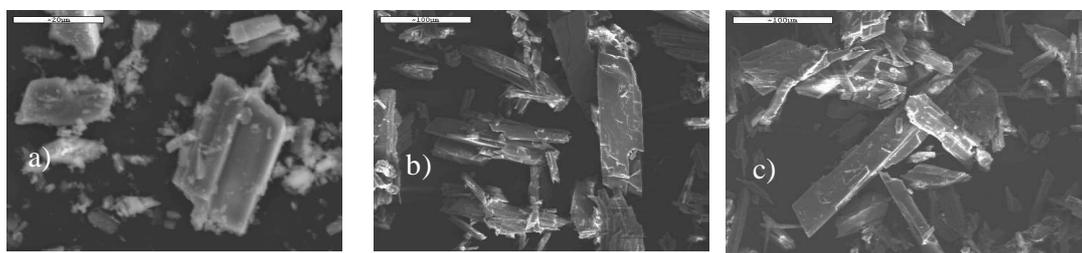


Fig. 1. SEM images: a) Na/LAU, b) MnS/LAU1, c) MnS/LAU.

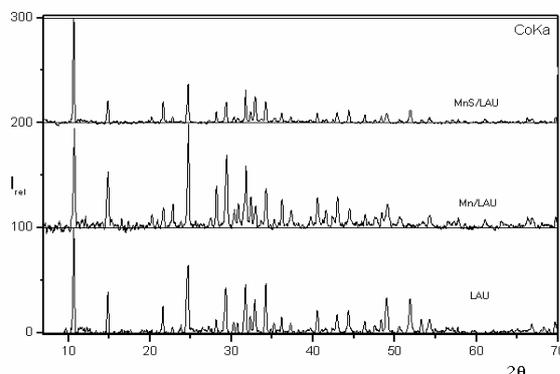


Fig. 2. XRD patterns of samples obtained using by the humid procedure.

The X-ray diffraction patterns of the samples show the diffraction peaks of laumontite. There is no evidence of MnS diffraction peaks, only small shifts of some peaks and changes in peak intensities. The calculated unit cell parameters evidenced a dependence on the unit cell content and a monoclinic symmetry, characterized by the spatial group C12/m1 (Table 2). The formation of MnS clusters along the zeolite channels causes a small increase in unit cell volume and a distortion of the unit cell.

Table 2. XRD structural characterization.

Sample	a(Å)	b(Å)	c(Å)	β	V(Å ³)
LAU	14.853	13.169	7.546	110.32	1384.0369
Mn/LAU1	14.822	13.212	7.529	110.11	1384.4531
MnS/LAU1	14.832	13.222	7.532	110.14	1386.6928

Typical electron diffraction patterns were obtained during a tilting experiment from the matrix material. The calculated interplanar distances and the angles between the reciprocal space planes confirm the monoclinic laumontite (PDF No. 47-1785) (Fig. 3). The angle between the two ED patterns measured during the tilting experiment is 48°, smaller than the theoretical value of 48.4°.

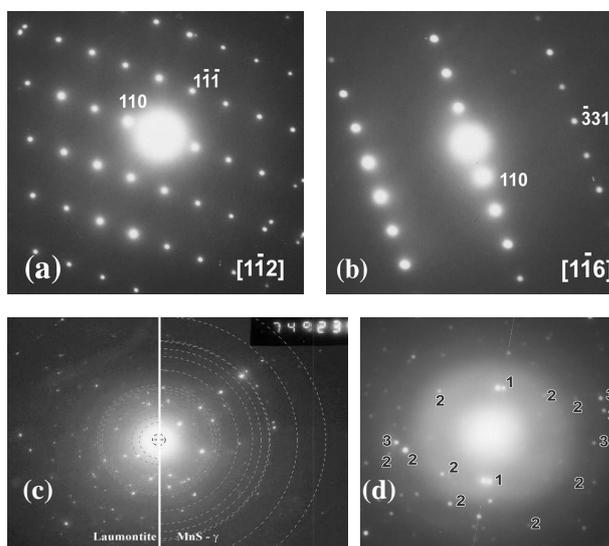


Fig. 3. Electron diffraction: - identifying the MnS/LAU matrix material: (a) $[1\bar{1}2]$ zone axis and (b) $[1\bar{1}6]$ zone axis – identifying the extra - framework phases: (c) MnS/LAU1, (d) MnS/LAU: 1-LAU, 2- γ -MnS, 3- α -Mn.

The ED patterns taken from a small area of the material, at an edge of a laumontite grain, using the smallest area aperture, or on a thick polycrystalline area, made possible the identification of clusters formed inside the zeolite channels. In this cases, due to the much higher scattering factor for electrons than X-rays, was possible to observe spots arising from small quantities of materials that are not detectable in XRD (Fig. 3 c) and d)).

For the sample resulted through the impregnation procedure three phases were identified from the calculated interplanar distances: (1) laumontite, (2) hexagonal phase γ -MnS (PDF No. 40-1289, $a=3.9792 \text{ \AA}$, $c=6.4469 \text{ \AA}$), (3) cubic phase α -Mn (PDF No. 32-0637, $a=8.912 \text{ \AA}$).

The ED patterns taken from the sample resulted through aqueous ion-exchange procedure enabled the identification of only two phases: laumontite and γ -MnS.

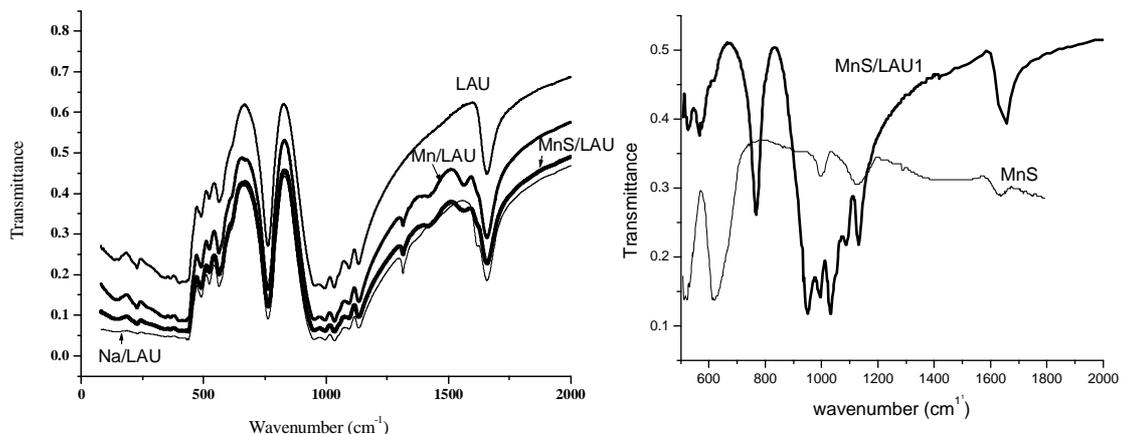


Fig. 4. FTIR spectra of studied samples and of a MnS powder synthesized in the conditions used for the aqueous ion-exchange procedure.

Vibrations of the framework of laumontite give rise to typical bands in the mid and infrared region. The vibration of bands due to vibrations of external linkages ($650\text{-}500 \text{ cm}^{-1}$) is often very sensitive to structure. In the far infrared region ($200\text{-}50 \text{ cm}^{-1}$) vibration of cations against the framework occur. Extra-framework species give rise to Lewis acid centers ($\approx 450 \text{ cm}^{-1}$) or Bronsted acid sites (1540 cm^{-1}) [14,15].

The formation of MnS clusters within the laumontite channels is evidenced by some small shifts in the framework tetrahedral atoms (Si, or Al) oxygen bonds (T-O bonds)(Fig. 4), which indicate a strong interaction between the MnS clusters and the zeolite framework

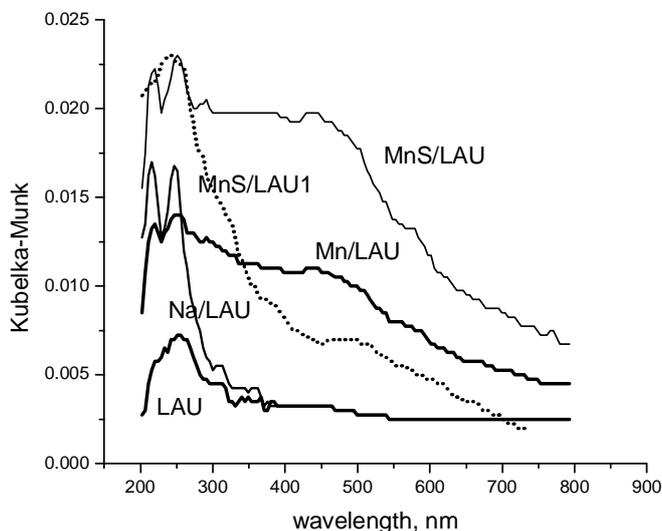


Fig. 5. UV-vis absorption spectra under ambient conditions.

The formation of Mn nanoparticles during the impregnation procedure is a process which must be avoided. The process of vacuum thermal dehydration involves autoreduction of manganese ions by intrazeolitic water and lattice oxygen and the formation of acidic centers (1569 nm and 1445 nm respectively)[16,17]

Fig. 5 shows the UV-vis absorption spectra of the samples exposed to ambient conditions. For Mn/LAU sample, obtained through the impregnation procedure, some reduced species of Mn and some dimeric and polymeric species of Mn are detected in line with familiar plasma resonance peak at 580-nm [18,19]. The sulfidation process implies only the not reduced species and increases the optical absorption. The optical spectrum of MnS/LAU, obtained through the aqueous ion-exchange procedure, shows quantum excitonic peaks at 387, 309 and 266 nm and a large band peaking at 495 nm[20]. We consider that the large band observed may be attributed to some MnS aggregates formed on the zeolite surface.

It is important to realize that if the size of MnS cluster is well defined, the size of the wire or supercluster is not. Ion-exchange method cannot fill up the zeolite channels. In addition defects and disorder exists with the current preparation procedures.

4. Conclusions

MnS clusters can be isolated in laumontite zeolite. The aqueous ion-exchange procedure is better than the impregnation one. The impregnation procedure favours the formation of Mn nanoparticles and MnS aggregates.

Both procedures cannot fill up the zeolite channels and disorder exists. The sulfidation process influences the repartition of manganese through the channels.

The different content in Mn and S of small single crystals also introduce inhomogeneities in the cluster size distribution, which is the reason for the broad excitonic absorption peak.

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