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ORIGINAL CONTRIBUTION

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Synthesis of colloids and films of Pr, Er and Yb with nonaqueous solvents

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Abstract Colloidal dispersions of Yb, Er and Pr have been prepared by chemical liquid deposition. The metals were cocondensed at 77 K with 2-methoxyethanol and ethanol to produce solvated metal atoms. The particle size of the dispersions was determined by transmission electron microscopy to range from 52 to 1080 Å; the particles had spherical shapes. After solvent evaporation under vacuum, active solids and amorphous powder were deposited over Cu and Al metal. Dispersion stability, particle size, UV/Vis absorption and zeta potential were studied. The solids prepared by solvent evaporation were characterized by Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The films prepared on Al were studied by scanning electron microscopy. The most stable colloid was obtained using 2-methoxyethanol: several concentrations were stable for several months and the zeta potential indicated that this colloid stability is mainly due to solvation effects. FTIR spectroscopy of the solids indicated solvent incorporation in the film. This observation was corroborated by thermal analysis. Information on the thermal stability of the films was obtained by TGA. The UV/Vis absorption spectrum was measured at several concentrations under different conditions.

Key words Nanostructures – Thin films – Vapor deposition – Electron microscopy – Optical properties

Introduction

The stability of lanthanide colloids is quite similar to colloids of the block *d* elements [1–3]. Solvent evaporation produces metal films showing irregular surfaces different from the films of other metals of the *f* block [4]. In general, the atomic properties of rare-earth metal ions, are retained after formation of complexes with different ligands. Most metal ion complexes absorb visible and/or UV radiation but a few re-emit the absorbed energy as visible or UV radiation. In fact, the trivalent lanthanide ions and their complexes are known to luminescence, giving sharp bands corresponding to *f-f* transitions in the metal atom.

Crosby [5] reviewed the luminescence of organic complexes of lanthanides. Later on, Sinha [6] published studies on europium luminescence. The absorption and luminescence properties of rare-earth ions in solution were summarized by Cornall [7]. The great interest in studies on the luminescence properties of lanthanide ions and chelates is due to their potential applications. We observed some interesting behavior in the UV/Vis range of Yb-2-methoxyethanol colloids.

Experimental

Transmission electron microscopy

Electron micrographs were obtained on a JEOL JEM 1200 EXII with 4 Å resolution. A drop of the sample was placed on a carbon-coated copper grid of 100 mesh.

Statistical treatment and zeta potential

Each micrograph was divided into 81 squares; those without relevant information (too many clusters or undefined borders) were discarded. The remaining squares were analyzed with a RAN program and only 20% of the sources were considered. In these squares the particles were counted and their sizes were measured accurately. Then, the mean and standard deviation of the particle sizes were evaluated using the Statgraphics software package. The zeta potential was obtained directly using a Laser Meter 501.

UV-Vis

The absorption spectra between 200 and 800 nm were obtained by means of a Perkin Elmer UV/Vis Lambda 12 spectrometer. The solution concentration was 1×10^{-4} M, and the spectra were run under vacuum. The cells were pumped out up to 0.01 mbar, then the colloids were added under a nitrogen atmosphere.

Scanning electron microscopy

The films were prepared on metallic Cu and Al holders by evaporation of the colloid solution of Er, Pr and Yb in 2-methoxyethanol. After solvent evaporation, the films were heated from 25°C to 350°C under vacuum. SEM micrographs were obtained using a ETEC Model U-1 microscope.

Thermogravimetric analysis

A Perkin-Elmer model TGA7 instrument with a microprocessor-driven temperature control unit and a TA data station was used. The weights of the samples were recorded accurately and were generally of the order of 5 mg. The sample was placed in the balance system of the equipment and the temperature was raised from 25°C to 550°C at a heating rate of $10°\mathrm{C\ min}^{-1}$.

Fourier transform infrared (FTIR) spectroscopy

Infrared spectra were obtained using a Nicolet Magna 5PC FTIR. KBr pellets were prepared for all the films. Spectra were recorded at a resolution of $2\ \mathrm{cm}^{-1}$. One hundred and twenty-eight scans were accumulated for each spectrum.

Results and discussion

Due to the interest in the applications of luminescence properties of rare-earth elements, we were motivated to study the possibility of obtaining metal colloids using nonaqueous solvents. The following scheme shows the synthesis:

Colloid synthesis

$$\begin{tikzcd} X\mathrm{M}_{(v)} + Y\mathrm{SOLV}_{(v)} \arrow[r] & (\mathrm{M}_n)_x(\mathrm{Solvent})_y \arrow[d, "\begin{array}{r}\text{77 K,}\\ \text{vacuum}\\ 5\ \mu\text{Hg}\end{array}"', "\begin{array}{l}\text{1) Melt for1 h}\\ \text{2) 30 min : with flow}\\ \text{of } \mathrm{N}_{2(g)}\end{array}"] \\ & \begin{array}{l}(\mathrm{M}n)_x \text{ solvent } y\\ +(y-x)\text{solvent}\\ \text{Metal dispersions}\end{array} \end{tikzcd}$$

M : Pr, Er and Yb
SOLV. : $CH_3OCH_2CH_2OH$
CH_3CH_2OH

Colloid stability

The relative stabilities of Yb, Er and Pr in ethanol and 2-methoxyethanol are summarized in Table 1. It is necessary to point out that these metals behave chemically in a similar way due to their similar

Table 1 Stability of Yb, Er and Pr colloids

Metal-solvent[a]	Concentration[b] (mol/l)	Stability	E°(Vol) Ln + 3e = Ln	Atomic radius (Å)
Yb-2-metho	0.019			
	0.0035	Months	2.267	1.940
	0.0065			
Yb-ethanol	0.010	Flocculates		
	0.015	~24 h in $N_{2(g)}$		
Pr-2-metho	0.031			
	0.003	Months	2.462	1.828
	0.004			
Pr-ethanol	0.021	Flocculates		
	0.015			
Er-2-metho	0.015			
	0.005	Weeks	2.296	1.757
Er-ethanol	0.023			
	0.026	Flocculates		
	0.012			

[a] 2-metho=2-methoxyethanol
[b] Concentration based on metal evaporation

oxidation potential. Pr and Yb dispersions exhibit similar stabilities, and this is mainly due to the higher oxidation potential of Pr and to the larger size of Yb.

The 2-methoxyethanol colloids are the most stable. During the first 30–60 min partial flocculation occurs but then the remaining particles are stable in solution. It is quite interesting that Pr and Yb colloids remain stable at room temperature for several months, while Er colloids are stable only for a couple of weeks. Under a nitrogen atmosphere the stability does not change dramatically, but the Yb colloid changes from a light to a dark brown color.

The ethanol dispersions under normal conditions are not very stable and they oxidize easily with simultaneous flocculation. The light brown colloids change to colorless due to oxidation. Pr and Er flocculate faster than Yb, but under a nitrogen atmosphere the stability of Yb improves by about 2 days. Sometimes, depending on the colloid concentration, the colloid solution produces a gel after 24 h most probably Yb-ethoxide.

Transmission electron microscopy

The colloid sizes of Er-ethanol, Yb-2-methoxyethanol, Er-2-methoxyethanol, Yb-ethanol and Pr(surfactant + 2-methoxyethanol) are summarized in Table 2. The sizes of these colloids are around 100 Å and they are very similar to Au, Ag and Cu colloids with some polyethers [1], the main difference being the number of isolated particles in the last case. This is probably due to the easier oxidation and clustering of lanthanide metals [8]. For this reason it has been quite difficult to obtain the true value of their particle size. Especially in the case of Pr in 2-methoxyethanol, it was necessary to use a stabilizer in order to get the particle size; with ethanol it was not possible.

Schmid [9] observed gold colloids stabilized by ligands in which some growing features could be seen. These colloids are growing to the peripheries generating some irregular spacing. This kind of behavior is similar to our Er-ethanol colloids (Fig. 1a). The particles are growing in such a way that intertwined chains form leaving some spaces between the particles. This growing behavior for the Yb-ethanol colloid can be easily observed in Fig. 1b, where it is difficult to find isolated particles.

Table 2 Particle sizes of metal colloids

Metal-solvent	Concentration[a] (mol/l)	Sizes (Å)	SD (σ)
Er-ethanol	0.020	1080	342
Yb-ethanol	0.016	200	34
Yb-2-methoxyethanol	0.035	133	23
Er-2-methoxyethanol	0.025	42.7	6.2
Pr-2-methoxy ethanol[b] + surfactant	0.018	52	9

[a] Concentration based on metal evaporation
[b] [0.05 ml/50 ml]

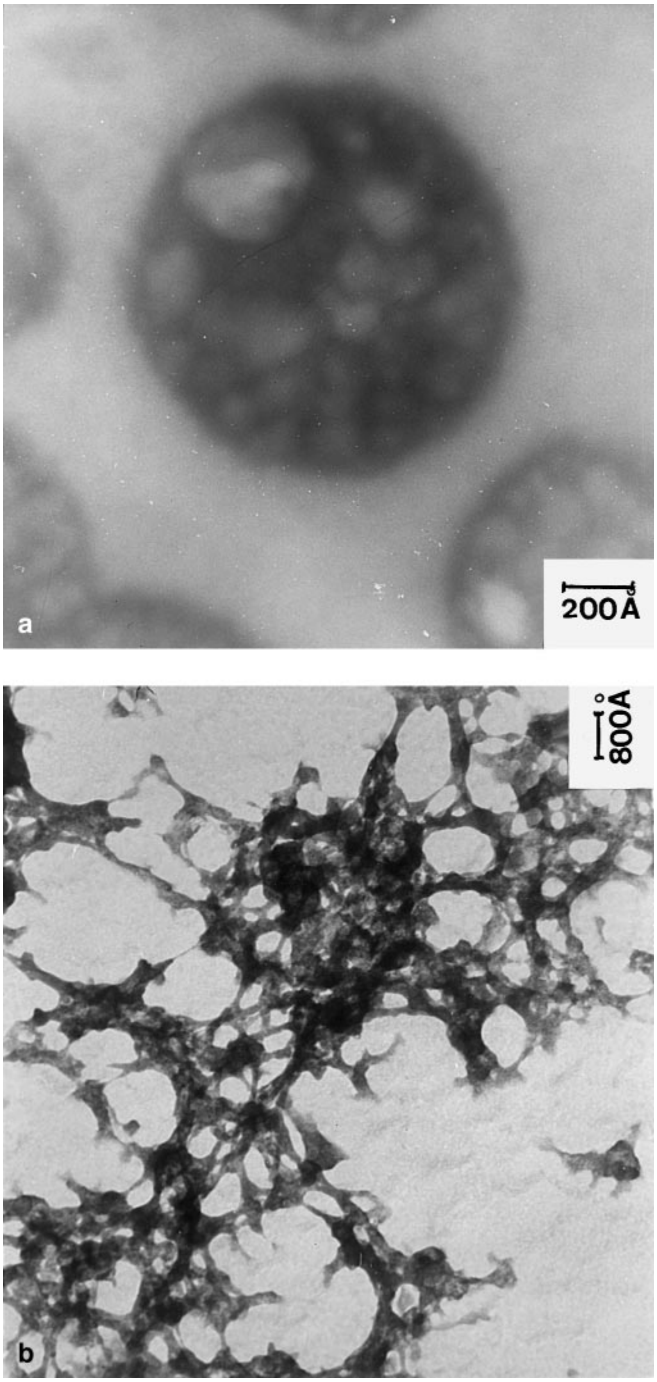


Fig. 1a, b Particle size of metal colloids. **a** Er-ethanol, size = 1080 Å, magnification 500 K; **b** Yb-ethanol, size = 200 Å, magnification 75 K

Yb-2-methoxyethanol colloids show agglomeration tendencies yielding three-dimensional branches of hundreds of particles (Fig. 2a). On the other hand, Pr-2-methoxyethanol in the presence of a surfactant exhibits well-dispersed particles of smaller size. Unfortunately, we were not able to get micrographs of the colloid without additives.

UV/Vis spectra

The absorption spectrum for Yb-2-methoxyethanol was studied between 200 and 600 nm. The UV spectra of several lanthanides have been calculated by Creighton

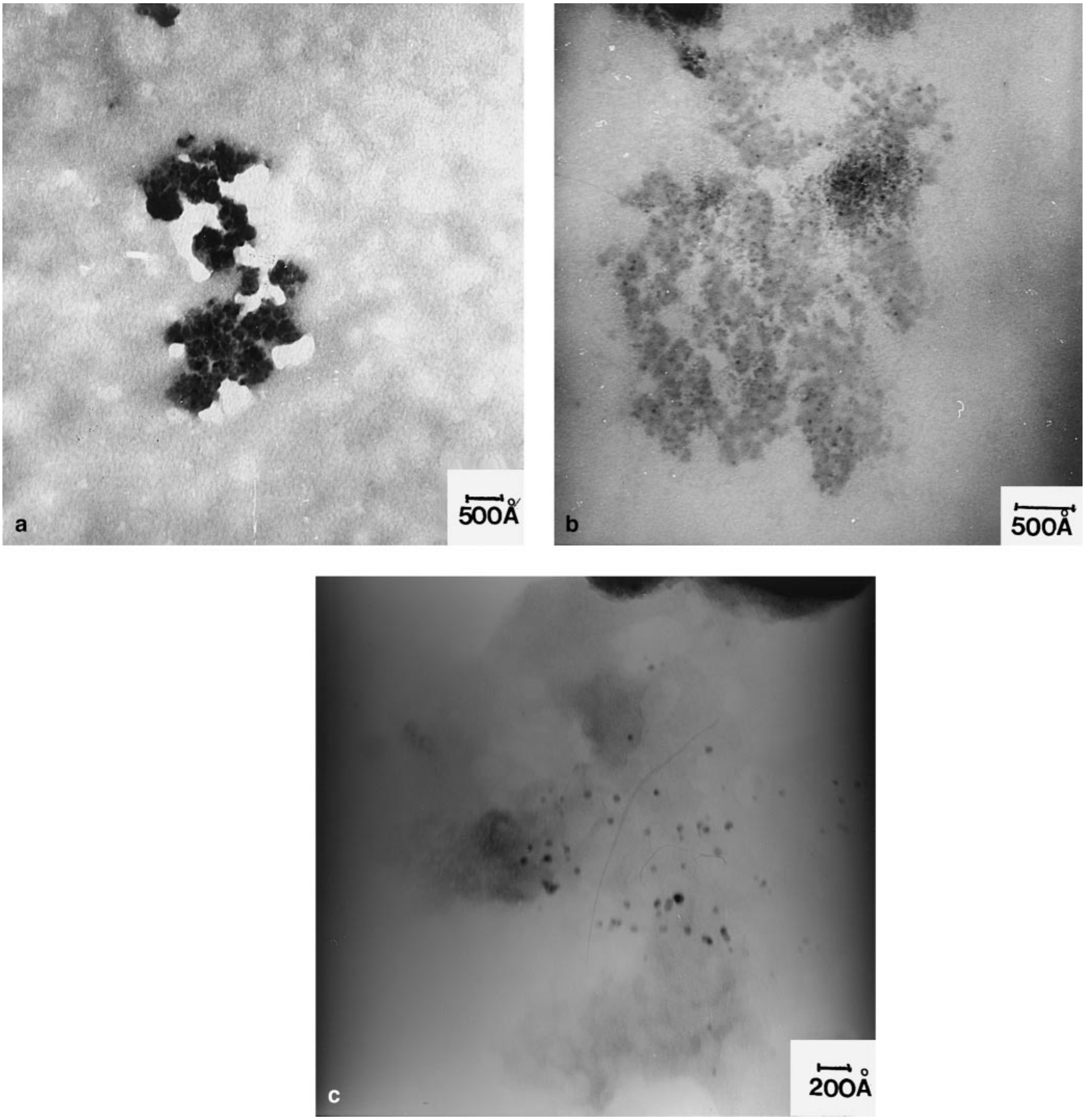


Fig. 2a–c Particle size of metal colloids. **a** Yb-2-methoxyethanol, size = 133 Å magnification 120 K; **b** Er-2-methoxyethanol, size = 42.6 Å, magnification 200 K; **c** Pr-2-methoxyethanol with surfactant, size = 52 Å, magnification 250 K

and Eadon [10] using the Mie approximation. According to Creighton and Eadon Yb shows electron-free metal behavior, and as a consequence the colloidal particles show an absorption plasmon band.

The spectrum of freshly-prepared Yb-2-methoxyethanol under vacuum is shown in Fig. 3. The spectrum of Yb1 corresponds to the absorption of a dilute colloidal sol (~1×10^{-4} M). Two bands appear: the first one at 235 nm is due to an interband transition ($4f^{14} \rightarrow 5d^{1}$), while the theoretical spectrum shows a band near 300 nm; the second band of lower intensity is at 302 nm and is most probably due to plasmon resonance.

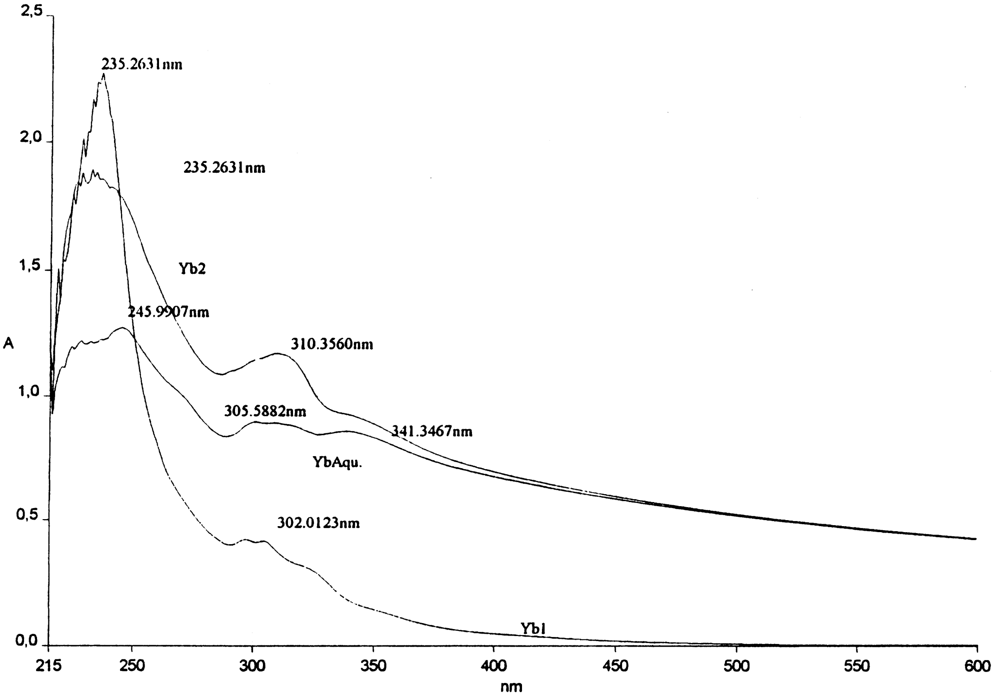


Fig. 3 UV/Vis absorption spectrum of Yb-2-methoxyethanol. *Yb1*: diluted solution; *Yb2*: initial concentration higher than Yb1; *YbAqu*: Yb2-2-methoxyethanol + H_2O

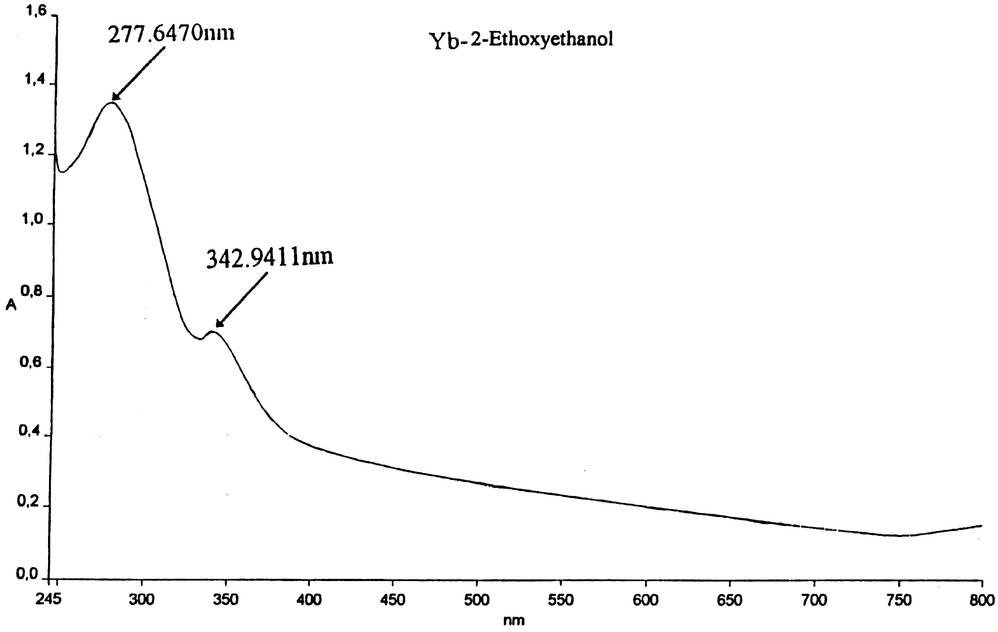


Fig. 4 UV/Vis absorption spectrum of Yb-2-ethoxymethanol

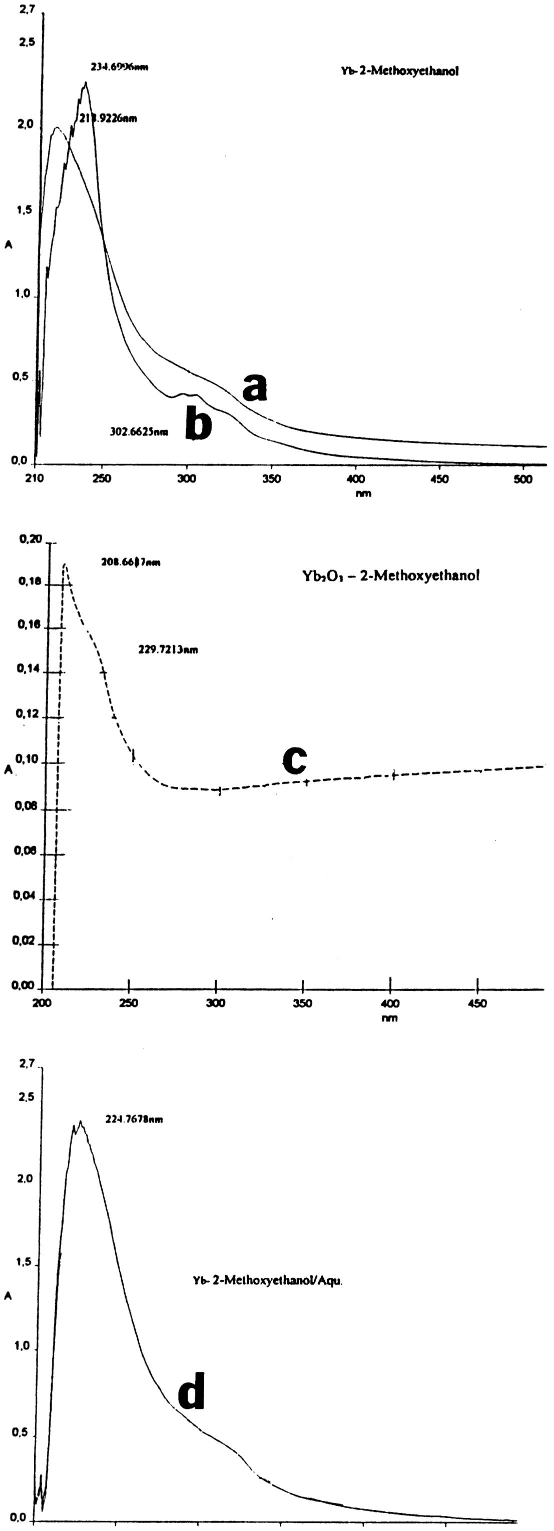


Fig. 5 UV/Vis spectrum of Yb-2-methoxyethanol: **a** after a week; **b** just prepared; **c** Yb_2O_3 in 2-methoxyethanol; **d** Yb-2-methoxyethanol plus water

Yb2 corresponds to a dispersion prepared with a higher initial metal concentration. The spectrum was recorded after dilution. The spectrum shows two bands: the first one at 235 nm is wider than was recorded for Ybl; the second one at 310 nm is well-defined and is more intense than in the Ybl case. This is probably due to a higher free metal concentration in the dispersion. In fact, the higher metal atom concentration increases the cluster sizes and the reaction speed decreases with the addition of solvent and as a consequence a lower alcoxide adsorption is produced (Yb^{3+} does not absorb in this region [11]).

Figure 3 shows the spectrum of the water-solvated Yb colloid (Yb Aqu) i.e. Yb2 after addition of water (0.05 ml H_2O/5 ml colloid). The band at 310 nm slowly disappears and another grows around 341 nm: this behavior can be attributed to a plasma absorption band shift. This shift is analogous to some extent to silver colloids where Ag_2O present interacts with metal clusters producing a band shift from 390 to 410 nm [8, 12]. In a more reductive medium there is a smaller solvent interaction with the free electrons of the solvent and the plasma absorption band should shift to a higher wavelengths.

Figure 4 shows the absorption spectrum Yb-2-ethoxyethanol. This solvent has been used to form Pd and Cu colloids from palladium acetate solutions [13, 14]. The band at 310 is shifted to 343 nm.

The Yb-2-methoxyethanol spectrum is shown in Fig. 5. After 1 week the band at 310 nm has disappeared and the band at 235 nm has shifted to 210 nm: the spectrum is very similar to the Yb_2O_3 dispersion in 2-methoxyethanol (Fig. 5b). This fact is evidence for metal oxidation. Even after adding water to the colloid, the spectrum does not change (Fig. 5c).

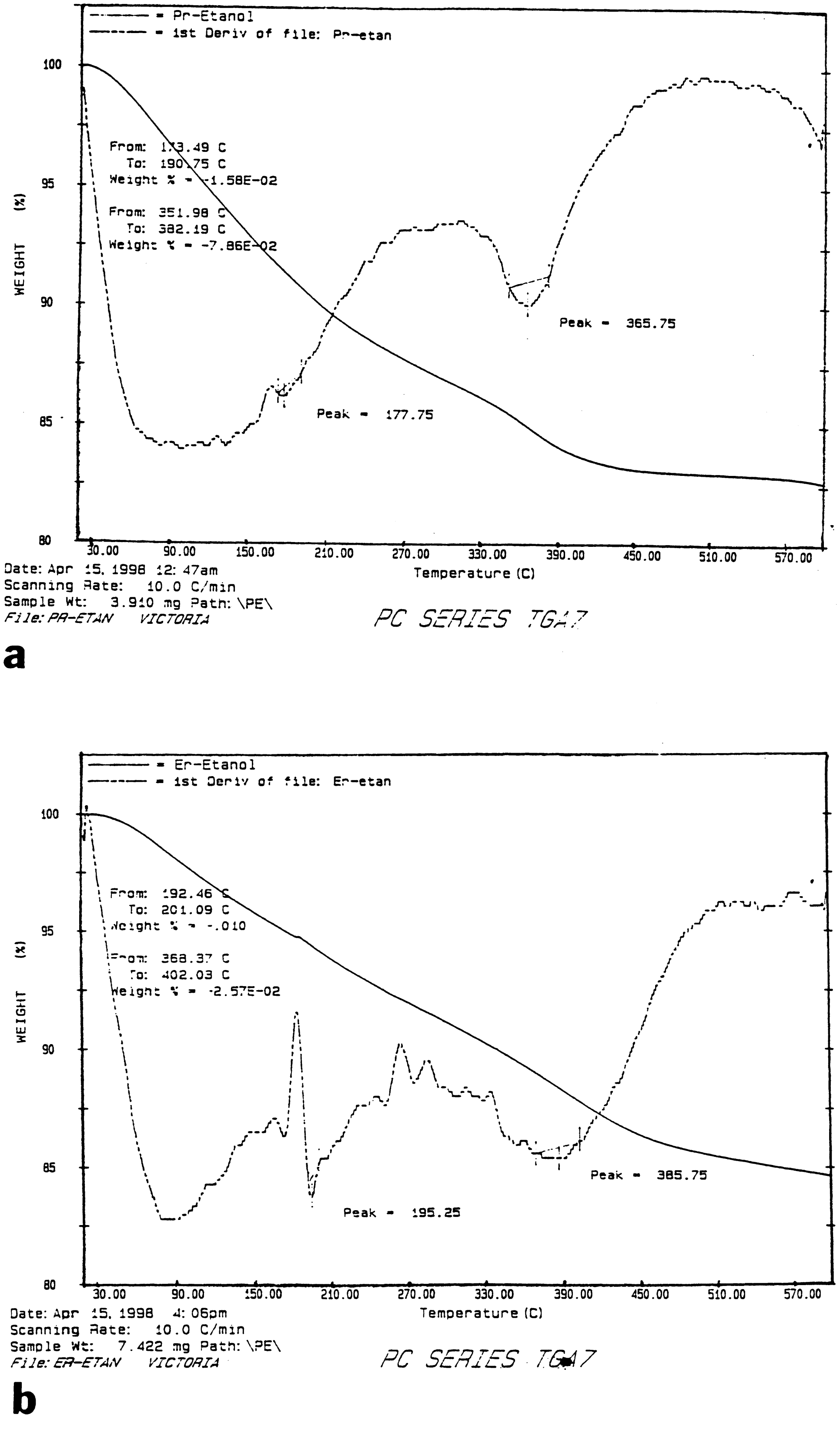
Thermogravimetric analysis

The thermograms of the Er, Yb and Pr-2-methoxyethanol films prepared by solvent evaporation showed one decomposition curve between 25°C and 500°C.

The results are summarized in Table 3. Figure 6 shows the thermograms of Pr-ethanol and Er-ethanol. The weight loss is very high: the values are analogous to the ketone metal films of the *d* block [15, 16].

The one-stage weight loss reveals the presence of the solvent (Table 3). For the ethanol series, the thermograms reveal two steps during the decomposition which is indicative of the presence of a mixture of ethanol and ethoxide trapped in the films (see Table 4). Due to the more electropositive character of Pr the two decomposition steps are clearly found. The weight loss in these films is lower than for, other films but higher than for active powders of ethanol prepared with transition metals [15, 17, 18].

Fig. 6 Thermograms of **a** Pr-ethanol and **b** Er-ethanol



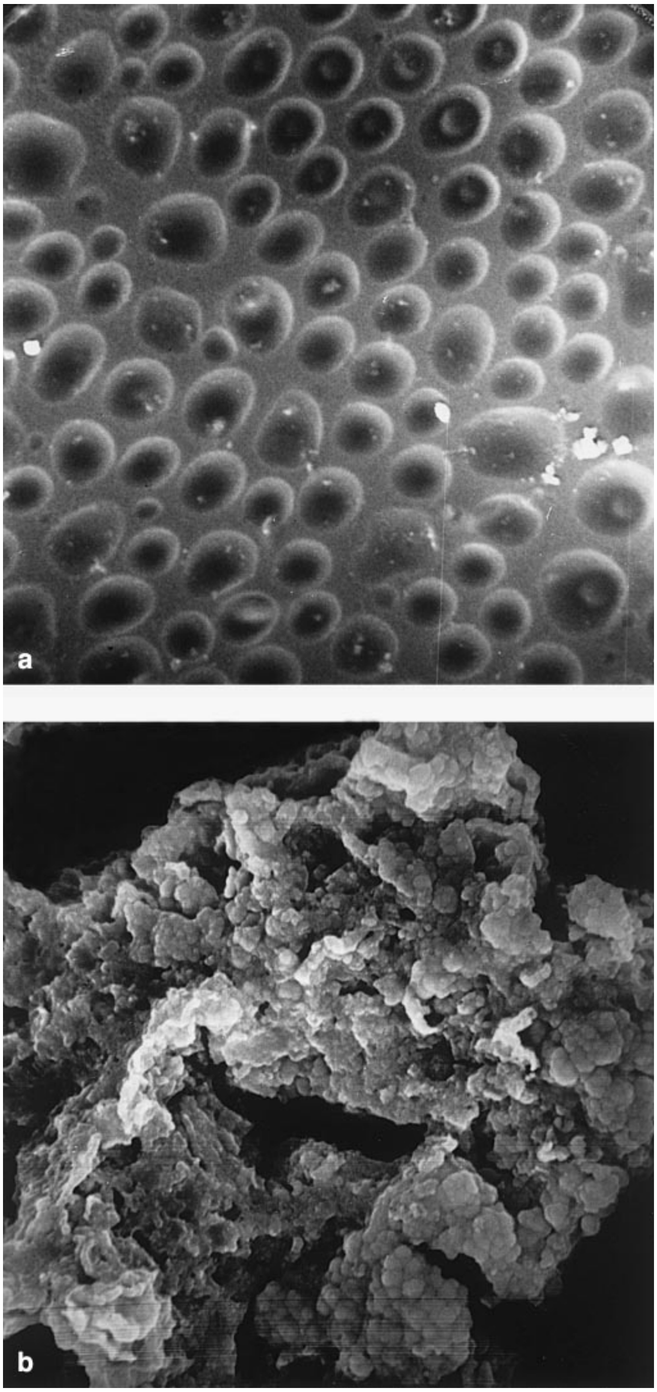


Fig. 7a, b Scanning electron micrographs of **a** Yb$_m$-(2-metho)$_z$/Al at 10 K magnification and **b** Er$_m$-(2-metho)$_n$/Al at 5 K

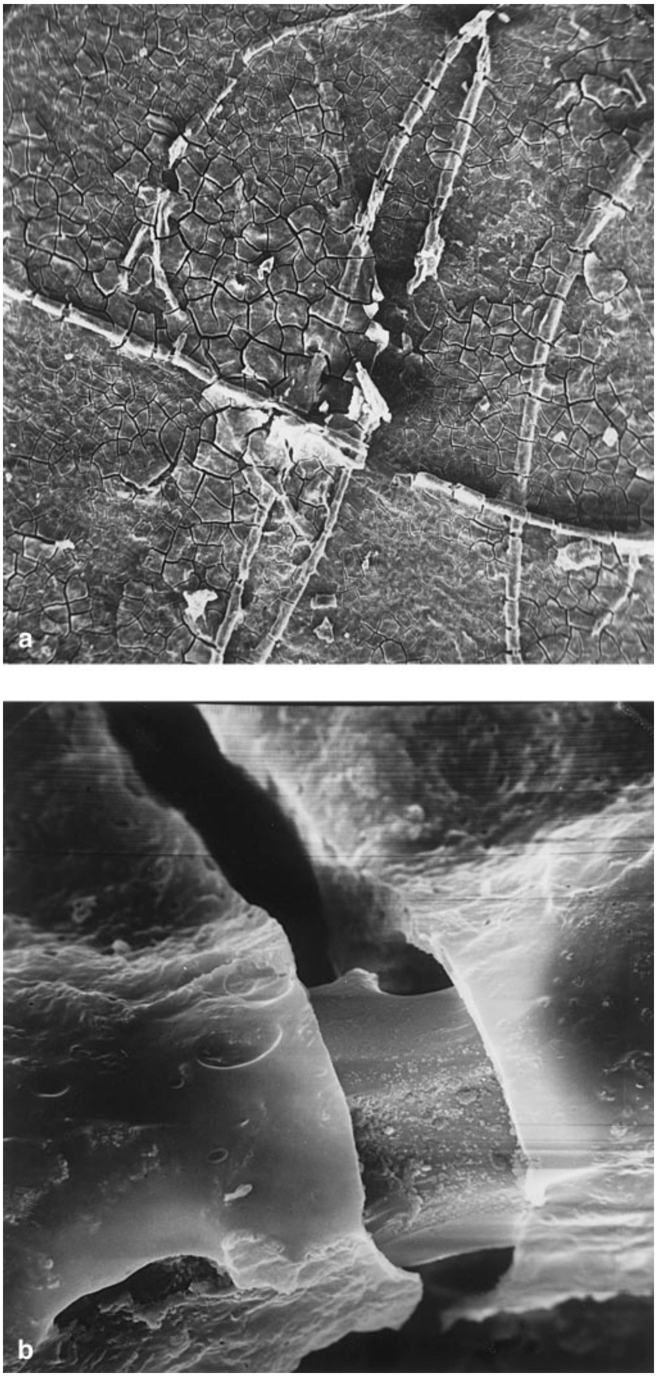


Fig. 8a, b Scanning electron micrographs of **a** Pr$_m$-(2-metho)$_n$/Al at 50 K magnification and **b** Pr$_m$-(2-metho)$_n$/Al at 2.5 K

Scanning electron microscopy

The films of Yb, Er and Pr deposited on aluminum were studied by SEM. Films of Yb$_m$(2-metho)$_n$/Al, Er$_m$(2-metho)$_n$/Al and Pr$_m$(2-metho)$_n$ were obtained by heating the films from 25 to 350°C. The electronmicrograph of the Yb$_m$(2-metho)$_n$/Al film is shown in Fig. 7a. It can be observed that films with several sheets are formed. On the sheets several spheres of similar size can be observed: these are most probably metal oxides.

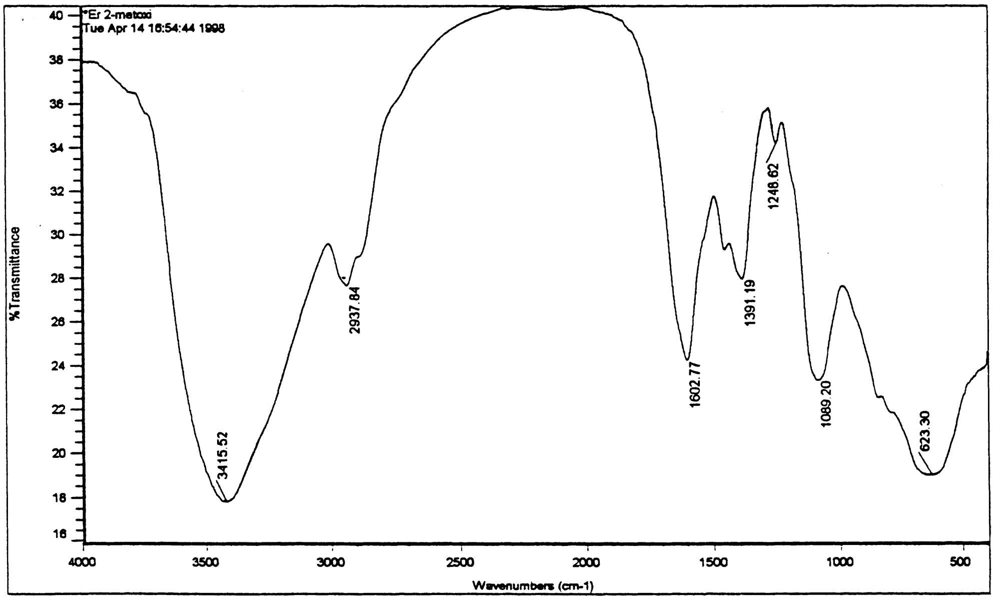


Fig. 9 FTIR of Er-2-methoxyethanol

Table 3 Percentage weight loss of Pr, Yb and Er films

Metal films/powder	Total % weight loss	Decomposition temp. T_o (°C)
Er-2-methoxyethanol	42.3	
Pr-2-methoxyethanol	42.8	177.75; 365.75
Yb-2-methoxyethanol	21.1	
Er-ethanol	15.0	195.25; 385.75
Pr-ethanol	17.4	177.75; 365.75
Yb-ethanol	10.8	217.75; 352.75

Table 4 FTIR of active solids[a]

Solid	O—H_s (cm^{-1}) stretching	C—O (cm^{-1}) stretching
2-methoxyethanol	3429.35	1125.64, 1069.28
Er-2-methoxyethanol	3415.52	1089.20
Pr-2-methoxyethanol	3450.49	1076.32
Yb-2-methoxyethanol	3436.40	1125.64, 1062.23
Ethanol	3406.19	1054.43
Er-ethanol	3422.82	1055.64 (weak)
Pr-ethanol	3433.05	–
Yb-ethanol	3420.81	1054.36 (v. weak)

[a] Films prepared in KBr

The films are similar to the surface of Sm/THF [4] but smoother, the difference in preparation being the heating of the Yb film. In fact, the morphology of the films depends on several conditions, such as preparation methods, temperature, solvents, metals and the supported surface [4] of $Er_m(2\text{-metho})_n/Al$. The electromicrograph of Er_m $(2\text{-metho})_n/Al$ is shown in Fig. 7b. This film exhibits clustering of several spheres with irregular shapes and forms sheets very similar to that reported for Sm/THF [4]. On the other hand, the Er films are very different to those of $Pr_m(2\text{-metho})_n$ shown in Fig. 8. The films are formed with long sticks which are shown as a sort of encapsulated material very similar to electrical wires.

Fourier transform infrared spectroscopy

The most relevant bands obtained from FTIR spectroscopy of the solids are summarized in Table 4. The Er, Pr and Yb-2-methoxyethanol films showed characteristic bands, ν_{OH} around 3450 cm^{-1} and ν_{C-O} near 1060 cm^{-1}. The bigger influence on the ν_{OH} band is mainly due to metal-solvent interaction. The ν_{C-O} band does not change with metal cluster presence due to the low amount of solvent (Fig. 9). On the other hand, the C—O and O—H bands of ethanol show some influence from the metal clusters. Most probably, there is a mixture of Metal-ethoxy and Metal-ethanol in the films.

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