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Stabilization of ScO(OH) dispersions in aqueous-alcoholic media by aminosilanes. Solution routes to scandia coatings

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Nanosized needles of ScO(OH) and lozenge shaped platelets of γ-ScO(OH) were prepared by hydrothermal syntheses (200 °C, 10 h) using $ScCl_3{\cdot}6H_2O$ as starting material. The influence of hydrothermal conditions on the nature of the phase, the morphology and the particle size was investigated. Characterization was achieved by XRD, TEM, FT-IR and TGA. Increasing the acidity of the reaction medium increased the particle size whereas increasing the concentration of the $ScCl_3$ solutions favored the formation of the platelet type ScO(OH). The NaCl and NH_4Cl mineralizers increased agglomeration between particles as well as the temperatures of transformation into oxides (480 to 530 °C). The point of zero charge was determined and found to be 6.7 for scandium oxide and 5.7 for the scandium oxohydroxide as prepared. Stabilization of the colloidal suspensions of ScO(OH) was achieved in aqueous-alcoholic media at $\mathrm{pH}=3$ by using [3-(2-aminoethyl)aminopropyl]-trimethoxysilane (DAMO). The stabilization is discussed in terms of surface coordination chemistry. These hybrid sols were used to obtain coatings of crystalline scandia on glass substrates by spin-coating. Thermal decomposition of scandium formate deposited by dip-coating *via* aqueous alcoholic media with PVP as an additive was an alternative for producing coatings of amorphous scandia with good optical properties.

Introduction

Solution chemical routes have largely been used as a way to decrease the crystallization temperature of metal oxides.[1] Classical sol–gel transformations, however, appear limited for scandium, yttrium and lanthanide oxides as a result of the stability of their hydroxides.[2] Indeed, the hydrated hydroxides decompose thermally *via* oxohydroxides MO(OH) and/or $M_2O(OH)_4$ giving the oxides, namely amorphous Sc_2O_3 at 450 °C and crystalline Y_2O_3 at 560 °C.[3,4] Cubic Sc_2O_3 is obtained between 400 and 500 °C by thermal decomposition of $Sc(OH)_3$. The stability of the carbonates (up to 900 °C) is another drawback for low temperature routes.

The interest in scandium materials for technological applications such as coatings for high power UV lasers at 351 nm[5] or solid state ionics such as $Sc_2(MO_4)_3$ ($M=Mo, W$)[6] and solid oxide fuel cells (SOFC)[7] has motivated the quest for other chemical routes. The recent papers of Sermon and Grosso[8] on obtaining ScO(OH) and scandia particles for optical applications starting from $Sc(acac)_3$ (acac = acetylacetonate) prompted us to report the results of our investigations.[9] The difficult access to large amounts of scandium alkoxides[10] led to the selection of other starting materials namely chloride or formate. These were treated by hydrothermal routes and thermal decomposition respectively. Hydrothermal treatment led to polymorphic particles of ScO(OH) which needed stabilization. Transparent coatings of crystalline and amorphous scandia were obtained by spin- and dip-coating methods.

Experimental

Scandium choride hexahydrate $ScCl_3{\cdot}6H_2O$ (Aldrich) was used as supplied. Ultra pure water ($R=18.2\ \mathrm{m\Omega\ cm^{-2}}$) was used for all experiments. Silanes (Hüls) and the various stabilizing reagents (Aldrich) were used as received. Scandium formate was prepared by heating scandium oxide and formic acid in water until dissolution. The $ScCl_3$ solutions were filtered, their concentrations (0.10, 0.20, 0.30 and 0.50 M respectively) were determined by gravimetric analysis. The pH of the medium was adjusted to 9, 7 and 4 using ammonia. The reactions were performed in a Parr autoclave in a 100 ml Pyrex feedstock. The temperature (200 °C over 10 h, pressure of 17 atm) was applied and controlled by a Binder oven. At the end of the experiment, the autoclave was cooled to room temperature and the powders were washed several times with distilled water after removing the surpernatant until the pH of the medium was neutral. After dialysis of the precipitates over 3 days, the powders were dried at 100 °C.

The as-prepared ScO(OH) powders were analyzed by FT-IR (Nicolet 550 serie II spectrometer) and by X-ray diffraction (XRD) at different temperatures using Cu-Kα radiation (Siemens D5000 diffractometer). The size and morphology were observed by transmission electron microscopy (TEM) with a Philips CM12 spectrometer at 100 kV. Drops of the suspension were deposited on a carbon film supported by a grid. Gravimetric and differential thermal analyses (TGA and DTA) were conducted under air using a Setaram system with a heating rate of 5 °C $\mathrm{min^{-1}}$. Particle sizes in solution and aging phenomena were determined by photon correlation spectroscopy with a Coulter NT 4 MD spectrometer. Determination of the pzc (point of zero charge) value was by acid–base titration.[11] The validity of the method was established with Y_2O_3 whose pzc value, 9, was available from the literature.[12]

The coatings were deposited at room temperature under stringently clean conditions by spin- or dip-coating either on soda lime glass plates or fused silica substrates. The coating suspensions were filtered through a 0.2 μm Teflon membrane before use. Transmission spectra were measured on a Unicam UV2 spectrometer (300–900 nm range), the background was

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measured with bare substrates, which gave access to the refractive index n and to the thickness e. The refractive indexes n were evaluated at a quarter wave optical thickness ($\lambda_0/4$) according to the expressions $n^2 = n_s(1+R^{1/2})/(1-R^{1/2})$ with $n_s = n$ of the substrate ($n = 1.48$ for glass, $n = 1.46$ for silica), R = maximum reflectivity = 1 minus the minimal transmission (absorption neglected) and $e = (L_1L_2)/2n(L_2-L_1)$ with L_2 and L_1 being twice the difference between two adjacent maxima and minima respectively.[13] The coatings were also analyzed by scanning electron microscopy using a JEOL JSM-T300 microscope after metallization of the substrate with a Au–Pd alloy.

Results and discussion

Hydrothermal transformations, identification of the phases

Hydrothermal transformations have been used in materials science for access to nanoparticles.[14] The transformation of $ScCl_3 \cdot 6H_2O$ under hydrothermal conditions (200 °C, 10 h) in the presence of ammonia afforded an oxohydroxide ScO(OH). Its identification was achieved by FT-IR as well as XRD. The FT-IR spectra of the powders showed absorption bands due to νOH vibrations at 3202 cm^{-1} indicating that condensation into the oxide had not been achieved. The absorption bands at 1079 and 935 cm^{-1} are actually diagnostic of γ-ScO(OH).[3] This assignment was confirmed by XRD (Fig. 1). Scandium oxohydroxide is actually polymorphous with various orthorhombic phases and a tetragonal phase, the latter being obtained at high pressure and high temperature.[15] The powders consist essentially of the orthorhombic γ-ScO(OH) phase[15a] ($a = 4.01$, $b = 13.01$, $c = 3.24$ Å) analogous to the lepidocrite γ-FeO(OH) and boehmite γ-AlO(OH) types.[16] Additional peaks were however observed in the XRD pattern. These were attributed to another orthorhombic phase with different lattice parameters namely $a = 5.150$, $b = 4.600$, $c = 3.197$ Å, which we named Γ-ScO(OH). Although this phase was reported previously,[15b] it was not reported by hydrothermal treatment of $ScCl_3 \cdot 6H_2O$ at higher temperature (350 °C, 160 atm, presence of ammonia),[15c] only γ-ScO(OH) was identified.[3] The same hydrothermal experiments applied to $YCl_3 \cdot 6H_2O$ showed that yttrium and scandium have quite different reactivity patterns.[9] The XRD patterns allowed the identification of a crystalline yttrium hydrated chlorohydroxide (JCPDS file 30-1445).

The ScO(OH) powders were also characterized by transmission electron microscopy which confirmed their polymorphic nature. Lozenge shaped platelets ($60 \pm 8 \times 30 \pm 5$nm), identified as γ-ScO(OH) and needles ($90 \pm 8 \times 18 \pm 5$ nm) corresponding to the Γ-ScO(OH) phase were observed as illustrated in Fig. 2. The lozenge shaped platelets are always the predominant species.

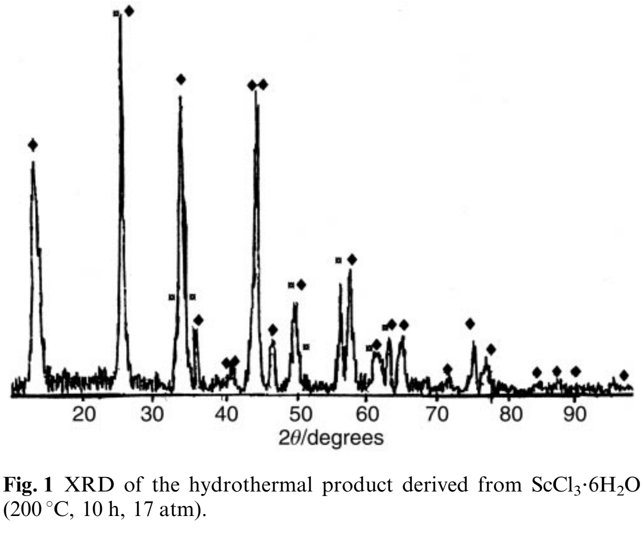

Fig. 1 XRD of the hydrothermal product derived from $ScCl_3 \cdot 6H_2O$ (200 °C, 10 h, 17 atm).

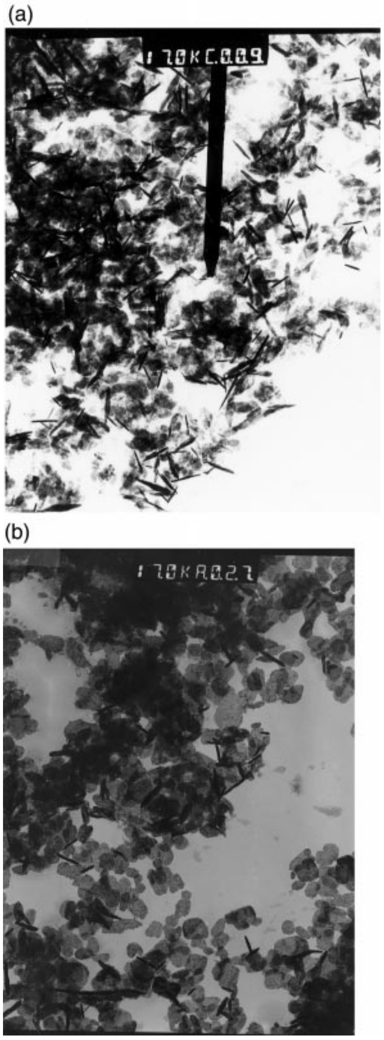

Fig. 2 TEM micrographs of powders resulting from hydrothermal treatment of $ScCl_3 \cdot 6H_2O$ at pH = 9 (a) and pH = 4 (b).

Influence of the hydrothermal conditions

The influence of the concentration of the $ScCl_3$ solutions, of the pH of the reaction medium and of mineralizers on the nature of the phase, the morphology, particle size and the temperature of transformation into oxide were investigated, all reactions being conducted at 200 °C for 10 hours.

The pH of a 0.1 M solution of $ScCl_3$ was adjusted to the desired value with concentrated ammonia solutions. Sodium hydroxide and urea, which are commonly used for preparing basic media, were avoided due to anticipated undesirable products and/or contamination. Indeed, basic lanthanide carbonates $Ln(OH)CO_3$ were obtained in such conditions. These decompose into oxide in two steps (610 °C for Y_2O_3).[17] The pH of the reaction medium had no significant effect on the distribution of the various ScO(OH) phases but tended to increase the particle size as shown by TEM micrographs. An EDX analysis showed that in acidic media, the powders remain contaminated by chloride residues despite dialysis. Increasing the concentration of scandium (0.1, 0.2, 0.3 and 0.5 M) in the reaction medium favors the formation of the Γ orthorhombic form although the γ form remains the major phase. At 0.5 M, the distribution was close to 1 : 1. The size of the crystallites also increases.

The effect of two mineralizers namely NH_4Cl and NaCl was evaluated. Mineralizer solutions (0.3 M, pH = 2) were added to

$ScCl_3$ solutions such that the final concentration of scandium was constant at 0.1 M. The mineralizers used did not affect the crystallinity of the powders only their temperature of decomposition into oxide. The temperatures of crystallization were evaluated by the presence of an exothermic peak in the thermogram. They increased from 460 to 530 °C. This might be attributed to a higher agglomeration of the particles. This hypothesis is also consistent with the fact that the temperature of crystallization increases with the concentration of the solution. Thus the lowest temperature of decomposition of ScO(OH) into crystalline oxide, 460 °C, was observed for the powders obtained with 0.1 M solutions of $ScCl_3{\cdot}6H_2O$ at $pH = 7$ in the absence of mineralizer.

Stabilization of colloidal suspensions

The ScO(OH) particules were obtained in the absence of any organic ligand [by contrast to those derived from $Sc(acac)_3$],[8] they were agglomerated and precipitated from the aqueous media without surface modification. Moreover, gelification was observed if the concentration was increased by $\cong 5\%$ and redispersion proved difficult. One can notice that a comparable behavior was observed for boehmite AlO(OH)[18] Many applications require strictly non-aggregated nanoparticles.[19] The best colloidal suspensions of ScO(OH) resulting from the hydrothermal syntheses were obtained in alkaline medium ($pH = 9.5$) without mineralizer. These suspensions were used as starting materials for stabilization studies either in aqueous or aqueous-alcoholic media. A large variety of stabilization reagents was used with the aim of obtaining blue sols stable for at least two weeks for optical applications.[13]

Surface modification involves weak adsorption of surfactants or polyelectrolytes or formation of a covalent coating.[20] A convenient measure of the propensity of a surface to become either positively or negatively charged as a function of pH is the value of pH required to give zero net charge surface. Acid–base titration has been widely used for the determination of the point of zero charge (pzc).[12] By contrast to yttrium, no values have been reported in the literature for scandium oxide and/or its hydroxide. The values obtained for the pzc were respectively 6.7 for scandium oxide (Rhone-Poulenc) and 5.7 for the oxohydroxide as prepared . Scandium oxide thus has a point of zero charge similar to the values observed for TiO_2, α-FeO(OH) or SnO_2.[21]

Blue sols stable for several weeks were obtained in aqueous media by adding sodium hydroxide up to $pH = 10$. However, TEM studies indicated that the platelets were dispersed whereas the needles remained agglomerated. This selective peptization confirms the presence of two different species having different surface properties in the system. Dendritic nanostructures were observed [Fig. 3(b)]. The possibility of steric stabilization was investigated with macromolecules such as poly(vinyl alcohol) $[CHOHCH_2CHOHCH_2]_n$ (PVA) or Pluronic $[(OCH_2CH_2)_n(OCH_2CHMe)_n(OCH_2CH_2)_p(OH)]$.[20] These polymers were successfully used for the stabilization of ZrO_2.[13a,22] However, in our case, they induced flocculation and swelling probably as a result of the flexibility of the organic chain as observed for boron derivatives.[20] Better results were obtained with propylene glycol aminoether $[MeCHNH_2\text{-}CH_2(OCH_2CHMe)_nNH_2]$ and stabilization up to a week could be achieved.

Simple or functional carboxylic acids were successfully used to obtain stable zirconia sols[22] whereas AlO(OH) could be redispersed with acetic or propionic acids.[22,23] A different behavior was observed for scandium oxohydroxide. Despite the fact that FT-IR showed some interaction between the particles and the acid functionality ($\Delta\nu_{CO_2} \approx 40\ cm^{-1}$ for instance for benzoic acid).[24] The results in terms of stabilization were rather disappointing independently of the pH of the medium. Amino acids such as glycine ($NH_2CH_2CO_2H$), *N*-dimethylglycine ($NMe_2CH_2CO_2H$), lysine $[NH_2(CH_2)_4\text{-}CHNH_2CO_2H]$, L-arginine $[NH_2C(=NH)NH(CH_2)_3CHNH_2\text{-}CO_2H]$ were able to disperse the particles but the stability of the sols was less than two days and thus insufficient for practical applications. Methacrylic and fumaric acids induced rapid flocculation. Formic acid and the polyfunctional 3,6,9-trioxaundecanoic acid $[O(CH_2)_2OCH_2CO_2H]_2$ which were used for the stabilization of ZrO_2 sols[22] led to the formation of soluble species.

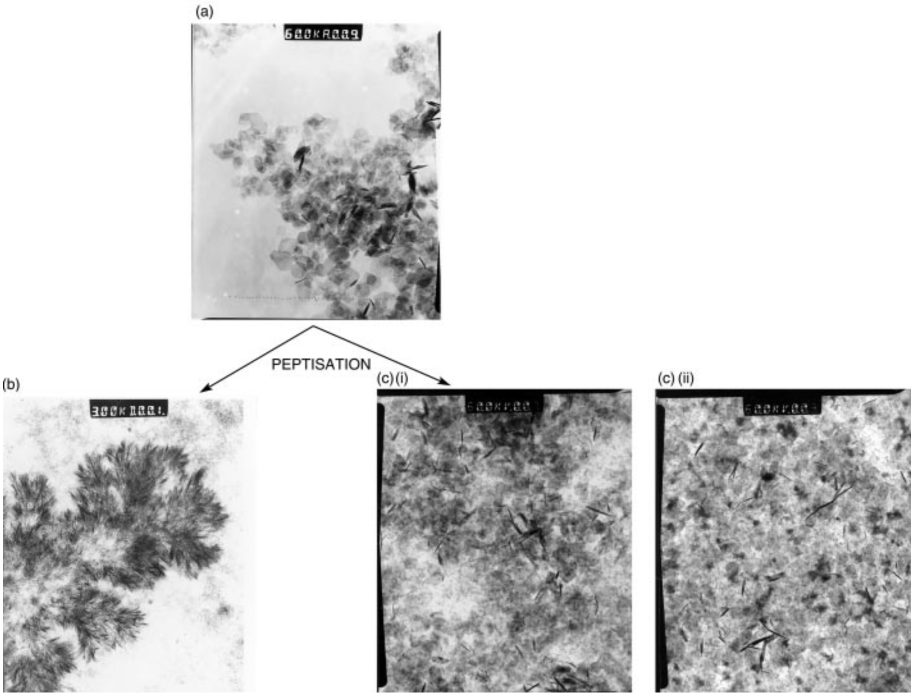

Fig. 3 TEM micrographs of ScO(OH) 0.1 M at $pH = 9.5$. (a) As-prepared (in aqueous solutions); (b) peptized with NaOH (up to $pH = 12$) in aqueous solution; (c) peptized with DAMO (0.2%) in aqueous-alcoholic media, (i) fresh; (ii) after 40 days.

Organically modified silanes (ORMOSILS) have been used recently for the dispersion of Fe_2O_3[23] or Au[25] particles. They offer acidic and basic sites whose properties might be tuned by the pH of the medium and an organic chain which might be grafted on the particle providing covalent surface functionalization. Such silanes allowed the concentration of the sols to be increased, up to 35% in the case of ZrO_2.[22] Aminosilanes such as 3-aminopropyltriethoxysilane $NH_2(CH_2)_3Si(OEt)_3$ (TRIA), 3-aminopropylmethyldiethoxysilane $NH_2(CH_2)_3Si(OEt)_2Me$ (DYNA) and [3-(2-aminoethyl)aminopropyl]trimethoxysilane $NH_2(CH_2)_2NH(CH_2)_2Si(OMe)_3$ (DAMO) were evaluated. Best results in terms of stability were obtained with DAMO in aqueous-alcoholic media (H_2O, EtOH 60 : 40% in volume). The amount of DAMO was varied from 0.001 to 1% for suspensions with 1% of ScOOH in weight. Fig. 4 represents the variation in stability which was observed for the sols. The optimal concentration of DAMO appears to be 0.2% on the basis of the stability experiments[26] and no precipitation was observed after 1.5 months. Good results were also obtained on varying the concentration of DAMO from 0.075 to 0.1%. DAMO can be grafted onto the particle without hydrolysis (in non-aqueous media), *via* the surface hydroxyl groups and elimination of alcohol. However, peptization of ScO(OH) is only effective in acidic media namely pH = 3 [Fig. 3(c)]. The $Si(OR)_3$ functionalities are hydrolyzed under such conditions as shown by solution ^1H NMR studies. Indeed, whereas no significant modification is observed for DAMO in D_2O at neutral pH, even after one month, modification is immediate at pH = 3. A third of the methoxy groups are hydrolyzed with elimination of methanol ($\delta = 3.35$ as compared to the chemical shifts of the Si–OMe groups at $\delta = 3.30$). Hydrolysis was also confirmed by ATR-IR as illustrated by the modification of the absorption bands of the νSi–O–C linkages between 1150 and 900 cm^{-1}. This hydrolysis is likely to form siloxanes and thus Si–O–Si chains by condensation. Several hypotheses such as hydrogen bonding between the surface hydroxyls and the Si–OH linkages or electrostatic interactions involving the amino functionalities which are protonated in the acidic conditions, can be considered for the fixation of DAMO on the particles.[20] An aminoalcohol having a formulation close to that of DAMO, $NH_2(CH_2)_2NH(CH_2)_2OH$ was used as peptization reagent. Decantation of the sols was observed in less than 15 h independently of the pH of the medium namely, 2, 3, 5, 7 or 12. The $Si(OR)_3$ groups and the formation of Si–O–Si linkages thus play a crucial role in the peptization by DAMO. The stabilization is thus an electrosteric one (Fig. 5). The high degree of polymerization of the aminosilane allowed concentration without precipitation or gelification up to 5% in weight.

By contrast to the oxohydroxide scandium particles, DAMO was a poor reagent for the stabilization of scandium oxide sols. Carboxylic acids such as benzoic or cinnamic acids appeared better especially for aqueous-alcoholic media but only some of the particles could be redispersed.

Coatings

Scandia coatings have been obtained by physical deposition methods[5] and very recently by dip-coating.[8b] Liquid deposition routes are low cost alternatives and have been used for high power lasers.[13] Aqueous-alcoholic sols (50/50%) concentrated to 2.5% of ScO(OH) and stabilized by DAMO (0.05 and 0.05%) at pH = 3 were used for elaboration of films on silica or glass substrates by spin-coating (900 rpm). Stackings can be obtained. The initial poor mechanical properties of the coatings can be improved by thermal treatment (15 min at 100 °C) without formation of cracks. Strengthening can also be achieved under gaseous ammonia at room temperature.[27] The siloxane character of the hydrolyzed DAMO can act as wetting reagent like PVA [poly(vinyl alcohol)] or PVP [poly(vinyl pyrrolidone)].[13] However, this also gives a polymeric character to the medium and increases the particle size, which might be close to $\lambda/10$, resulting in a scattering effect that precludes the measurement of the refractive index by UV-Vis spectroscopy. Conversion into crystalline scandium oxide was achieved after each deposition by thermal treatment at $\approx$500 °C for 30 min. Unfortunately, the coatings remained scattered and SEM micrographs showed the disordered growth of grains of cubic scandium oxide (Fig. 6).

In view of the interest of optical coatings of Sc_2O_3, alternate methods were envisioned. Scandium formate $Sc(O_2CH)_3$ appeared as an attractive precursor on the basis of its clean, sharp, one step decomposition into oxide which occurred at temperatures as low as 405 °C, as shown by TGA. Scandium formate was thus dissolved in a water–ethanol (0.15 M, 1 : 1 in volume) solution containing 0.06% of a water soluble polymer, PVA (molecular weight 15 000, $n = 1.51$). Deposition was achieved by dip-coating. Thermal annealing at 500 °C for 30 min gave an amorphous oxide. Several layers were required for a thickness higher than 100 nm. UV spectra (Fig. 7) indicated good transparency properties in the range

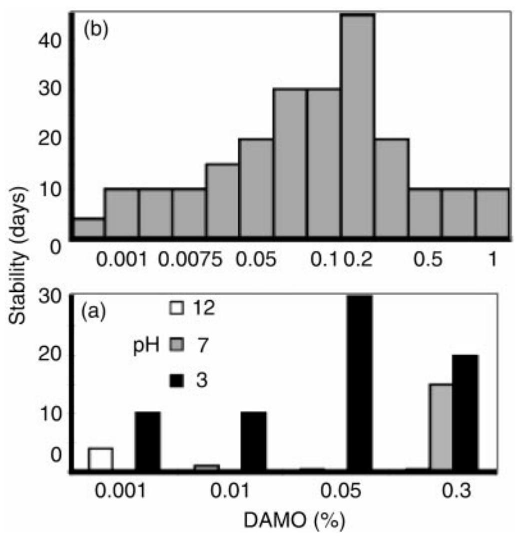

Fig. 4 Histograms showing the relative stability of the sols of ScO(OH) in H_2O–MeOH media (60 : 40%). (a) At various pH as a function of the amount of DAMO; (b) at pH 3 as a function of the amount of DAMO.

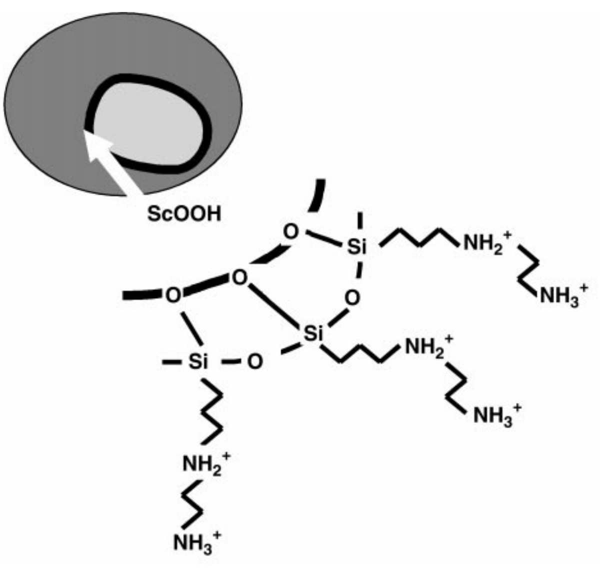

Fig. 5 Scheme showing the interaction between the particles of ScO(OH) and DAMO in aqueous-alcoholic media at pH = 3.

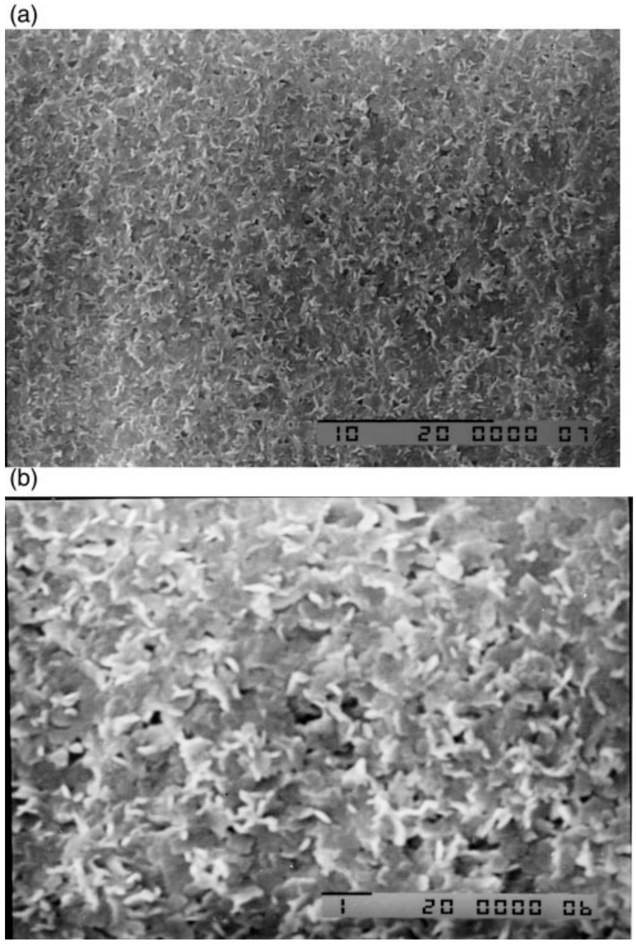

Fig. 6 SEM micrographs of a film of crystalline scandia obtained by spin-coating of a sol of ScO(OH) (3% stabilized with 0.2% of DAMO) and thermal annealing at 500 °C after each deposition (5 layers).

300–1000 nm, the transmittance decreasing with the number of layers. Deposition of 16 layers gave a thickness of 360 nm and a refractive index of 2.03 at 386 nm with a transmittance of 90%. Better wetting properties (necessary for homogeneity on circular wafers) were achieved by replacing PVA by 1% PVP (molecular weight 40 000, $n = 1.53$).[28] The larger amount of PVP, as compared to PVA, led to a decrease in the refractive index. (Table 1).

To evaluate high refractive index coating laser damage resistance, threshold measurements were carried out on amorphous scandium oxide (the sample with 12 layers) at 351 nm with a 3.3 ns pulse duration. A result of 5 ± 1 J cm^{-2} was obtained using a one-on-one irradiation mode. Such a value is encouraging for the use of scandia as a high index material in high power laser UV mirrors.

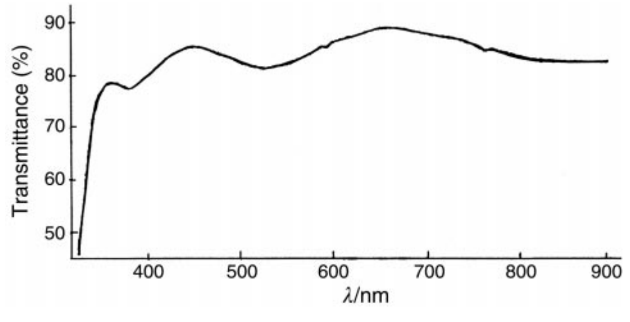

Fig. 7 Transmission UV-Vis spectrum of a film of 16 layers of amorphous scandia on a glass substrate.

Table 1 Properties of coatings of amorphous scandia on glass substrates

	With PVA (0.06%)		With PVP (1%)	
Number of layers	Thickness/nm	Refractive index *n*	Thickness/nm	Refractive index *n*
4	—	—	—	—
8	240	1.83	192	1.89
10			280	1.72
12	295	1.79	356	1.73
16	360	2.03		

Acknowledgements

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