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Preformed sol-gel synthesis and characterization of $YAlO_3$

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The synthesis of $YAlO_3$ is described from commercially-available yttria and alumina preformed sols which have nanometer particle-size ranges. The products have been characterized by X-ray diffraction (XRD), diffuse reflectance infrared Fourier transform (DRIFT) spectra, thermogravimetry—derivative thermogravimetry—differential thermal analysis (TG-DTG-DTA), scanning electron microscopy (SEM) as well as CHN-analysis, and are similar to those prepared by the alkoxide, nitrate and citrate routes. The proposed method is a simple, cheap and rapid synthetic route. *© 2003 Kluwer Academic Publishers*

1. Introduction

The conventional preparation of $YAlO_3$ (YAP) involves the high-temperature (ca. 2000°C) Czochralski growth in an inert atmosphere [1]. Other than the hydrothermal and glycothermal methods [2], sol-gel syntheses have employed the conventional alkoxide route [3, 4], as well as acetate [5], citrate [6], and some other methods [7–9]. Although high-purity alkoxides are available, the hydrolysis-condensation reactions:

$$Al(OR)_n + H_2O \rightarrow Al(OR)_{n-1}(OH) + ROH$$

$$Al(OR)_{n-1}(OH) + Y(OR)_n \rightarrow (OR)_{n-1}Al\text{-}O\text{-}Y(OR)_{n-1} + ROH$$

do not permit the step-by-step control of sol and gel formation.

The motivation of the present study was to explore the simple, low-temperature, rapid method of preparation of YAP. This is the first, crucial stage of a project to dope the resulting powders with lanthanide ions and to examine the luminescence of the phosphors under laser excitation. This method involved the use of commercial preformed sols in different size ranges on the nanometer scale. These materials are widely available, cheaper and more easily stored and used than alkoxides. Preformed sols are stable mixtures of dispersed particles which enable the sol and gel processes to be isolated and performed in two steps, offering potential control over the particle size, crystallinity and microstructure of the product. The preformed sol route has other advantages that *different-size* precursors are readily available in aqueous solutions, employed herein, or as dispersed powders.

2. Experimental

Preformed sols of 10 nm yttria and 90, 94, 180 and 415 nm alumina dispersed in aqueous solutions were donated by Nyacol Products Inc. USA, and by Condea Vista Company, USA. Some characteristics of these sols are listed in Table I. YAP powders were synthesized as follows:

2.1. Preformed sol method

In a typical preparation 5 cm^3 of 10 nm yttria was added, with vigorous stirring, to the determined volume of the alumina sol, (mol ratio Y:Al 1:1). The mixed sol was then stirred for 10 min to homogenize it. 0.5 cm^3 of 1 M HNO_3 was added over 1 min, and a vortex usually formed in the solution under rapid stirring within 1–5 min. The white wet gel mixture was stirred for a further 10 min, left at room temperature for up to 3–4 h, then dried for 10 h at ca. 110°C, prior to grinding into powder using a ceramic pestle and mortar. The white powder was subsequently heated for 2 h at higher temperatures between 400 to 1500°C, in ceramic or Pt crucibles.

2.2. Preformed yttria sol-aluminium nitrate method

A weighed amount of $Al(NO_3)_3{\cdot}9H_2O$ was dissolved in water and 5 cm^3 1 M HNO_3 was added. The clear mixture was stirred for 5 min. and then added dropwise to the preformed 10 nm Y_2O_3 sol that was rapidly stirred in a separate beaker. Subsequent procedures were as in method 1.

2.3. Nitrate-citric acid method

The appropriate amount of solid $Al(NO_3)_3{\cdot}9H_2O$ was added with stirring to $Y(NO_3)_3$ solution in a beaker. Solid citric acid was then mixed (mol ratio citric acid: metal ion 3:1). The mixture was evaporated at 85°C on a water bath until a pale yellow transparent, viscous gel

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TABLE I Properties of yttria and alumina preformed sols[a]

Property	Alumina sol					Yttria sol
Product name	Dispal 11N7-12	Dispal 14N4-25	Dispal 18N4-20	Dispal 23N4-20	Nyacol Al20DW	Nyacol Y_2O_3
Al_2O_3 or Y_2O_3 (wt%)	12	25	20	20	20	14
Air-dried solids content (wt%)	14	30	24	24	–	–
Surface area ($m^2\ g^{-1}$)	120	140	180	230	–	–
Average dispersed particle size (nm)	415	180	94	90	50	10
Viscosity (cP)	<50	<50	<50	<50	10	10
pH range of dispersion	6.5–7.2	3.8–4.0	3.7–3.9	4.3–4.7	4.0	7.0
NO_3^- (wt%)	0.02	0.22	0.29	0.38	–	[b]

[a] Technical data from Vista Chemical Company, PQ Corporation and Nyacol Products Inc.

[b] Counter ion is 2.5 wt% acetate.

was obtained (ca. 3–4 h). The gel was dried at 130°C for 24 h. Subsequent procedures were as in method 1.

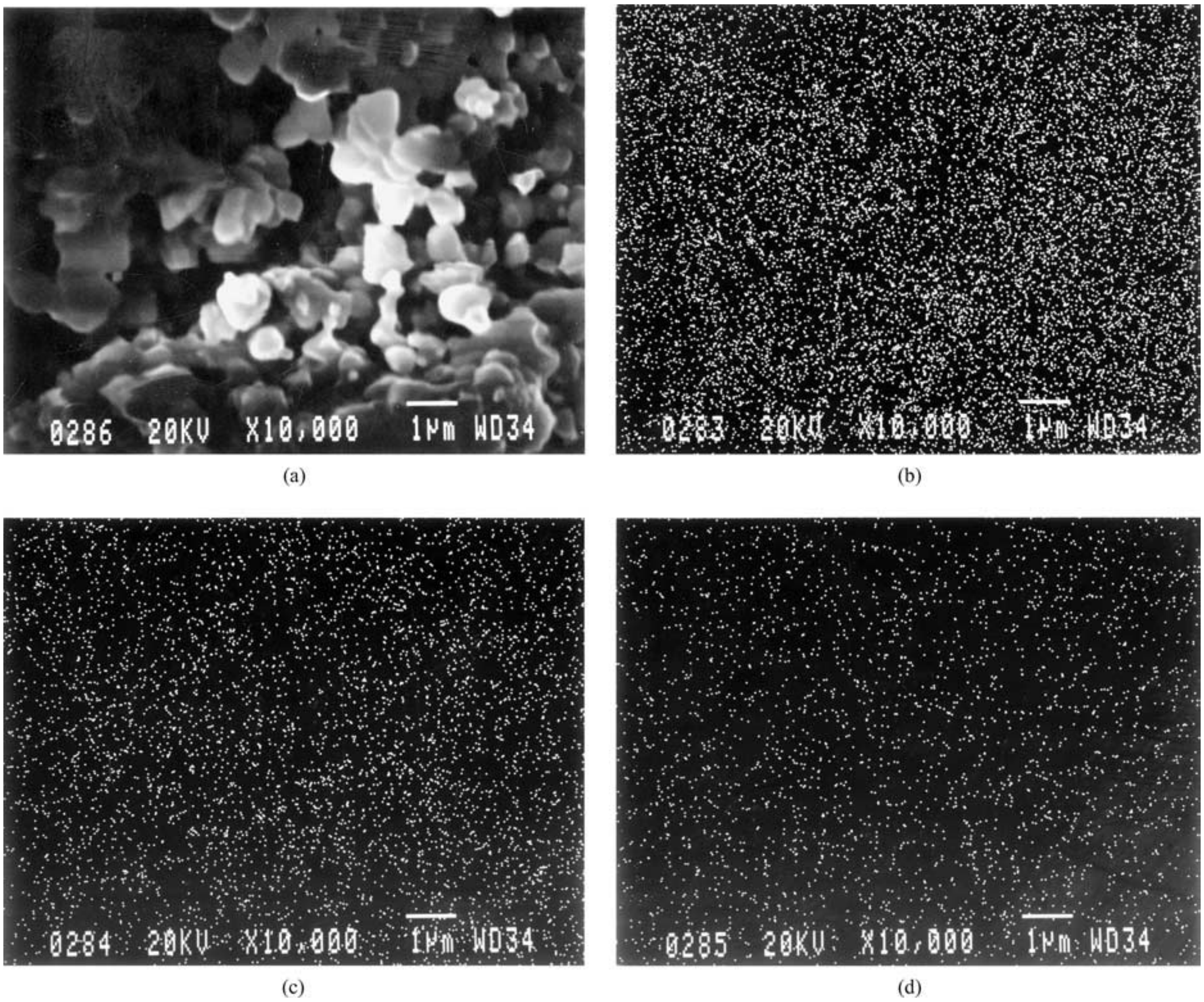
2.4. Alkoxide route

The preparation of YAP by the conventional alkoxide route used aluminium isopropoxide and yttrium isopropoxide (Gelest, Inc.). The preparations were conducted in a dry box and utilized dry ethanol or propan-2-ol as solvents, following the procedure of Jung *et al.* [4].

In all of the above preparations, the doping of YAP with lanthanide ions was achieved by adding the appropriate amounts of $Ln(NO_3)_3$ solutions at the first stage.

2.5. Measurements

Powder X-ray diffraction (XRD) patterns were recorded in the range $2\theta = 10$–$80°$, using a Philips X'pert X-ray diffraction system, with Cu K_α radiation. Thermogravimetry—derivative thermogravimetry—differential thermal analysis (TG-DTG-DTA) scans



(a) (b)

(c) (d)

Figure 1 (a) Scanning electron micrograph of $10Y_2O_3$-$50Al_2O_3$-$(Y_{0.95}Er_{0.05}Al)$-1.0A pre-heated at 1500°C showing the electron density mappings of (b) Y; (c) Al; and (d) Er.

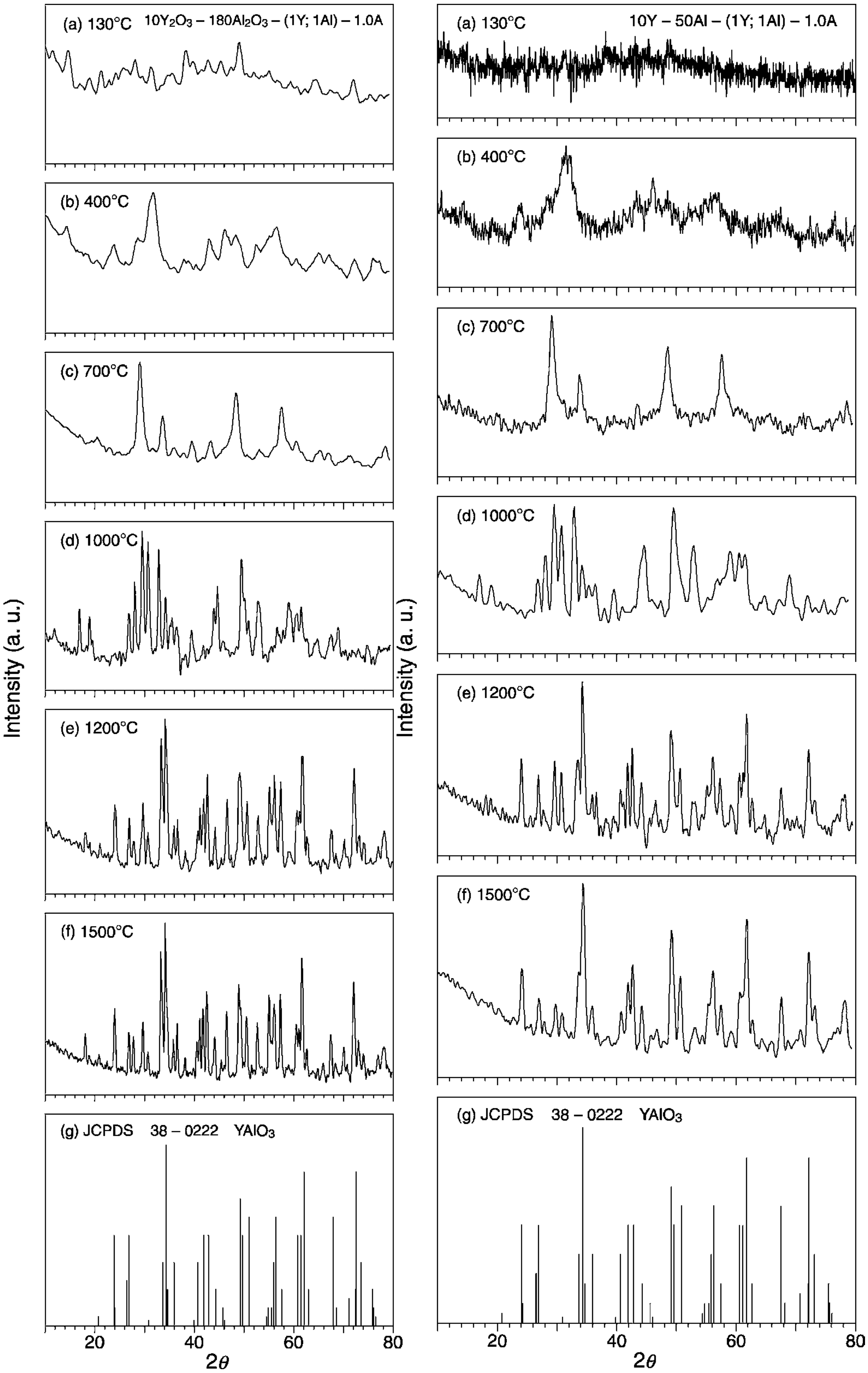


Figure 2 X-Ray diffractograms at stated temperatures of yttria-alumina products prepared from $10Y_2O_3$ and $50Al_2O_3$ or $180Al_2O_3$.

were performed between 40–1000°C under a He or O_2 atmosphere (300 cm^3 min^{-1}), with a heating rate 20°C min^{-1}, using a Seiko Instruments SSC5200H Thermal Analysis System. Fourier transform infrared (FTIR) spectra were recorded by a Perkin-Elmer (PE) Spectrum 1000 instrument, in Kulbelka-Munk (KM) Units, from samples dispersed in KBr (3% by mass), using the PE diffuse reflectance Fourier transform infrared spectra (DRIFTS) Accessory. CHN-analyses of powders were performed upon 1–10 mg mass of samples using a Vario EL CHN Analyzer equipped with an autosampler. Ethylenediaminetetraacetic acid was used as calibration standard. Scanning electron micrographs (SEM) were obtained from gold or graphite coated samples using a Jeol 820 Instrument. Energy dispersive X-ray (EDX) analysis was used to identify the compositions of Y, Al and Er in individual particles, or to map the concentrations over a selected area and compare with the direct SEM image.

3. Results and discussion

Fig. 1a shows a scanning electron micrograph of 5 mol% Er^{3+}-doped $YAlO_3$ prepared from $10Y_2O_3$ and $50Al_2O_3$, and heated to 1500°C. The particle sizes range from about 20 nm to 30 μm. No attempt was made to prepare nano-scale materials, which would involve an additional centrifugation step to separate large from small particles [10]. Fig. 1b–d show the homogeneity and different concentration regimes of Y, Al and Er from the electron density maps.

TG-DTG-DTA characterization under a He atmosphere of the sol-gel powders previously dried at room temperature showed that five distinct endothermic events take place between 77 to 486°C. Each one is associated with a mass loss, with the final mass being 56% of the initial mass. The major differences of the TG-DTG-DTA under an O_2 atmosphere from that under He, are the change from endothermic to exothermic nature for the mass loss near 400°C, and the greater overall loss in mass. The lower-temperature mass losses are associated with loss of water, whereas those near 400°C are assigned to the decomposition of organic matter giving CO in He or CO_2 in O_2 atmosphere. The nature of the organic matter became clear from the CHN analysis of material prepared either only from the Al_2O_3 sols, or from the Y_2O_3 sol, alone. In the first case, the carbon content was <0.6%, whereas it was 13.6 ± 0.3% for the Y_2O_3 powder which had been pre-heated to 110°C, so that the origin is attributed to the acetate present in the original Y_2O_3 preformed sol. Chemical analyses of samples of yttria-alumina powders prepared by method 1, and subsequently heated to 110°C, showed the presence of about 11% C, which dropped to <2% for the same samples after heating to 400°C, <0.5% for those after heating to 800°C, and <0.05% for those to 1200°C.

Yttria-alumina samples prepared from preformed sols were investigated by XRD, and Fig. 2 shows diffractograms for two preliminary samples prepared from $10Y_2O_3$ and $50Al_2O_3$ or $180Al_2O_3$. Broad features were observed for the powders heated at 130°C or 400°C, indicating amorphous phases. The three most prominent lines at 700°C, are at similar locations to the three lines in the Y_2O_3 sol heated at this temperature, showing that a mixture of yttria and alumina is still present. At 700°C, these lines are progressively sharper for increasing Al_2O_3 particle sizes, showing that there is evidently a memory effect at this temperature. Also, the patterns of samples heated at 700°C indicate more amorphous materials from methods 2 and 3, compared with method 1, presumably representing better mixing of the components. However, at and above 1000°C, new lines progressively sharpen up to 1500°C, and the powder diagrams are identified as $YAlO_3$. The X-ray patterns for powders heated at 1200°C or above, whether prepared by methods 1, 2 or 3, were similar to the JCPDS file for YAP. These samples were prepared on a small-scale with sols <0.5 cm^3 in volume, and the error in volume measurement is fairly critical and leads to the presence impurity phases, such as YAG. Larger-scale preparations (using 5 cm^3 $10Y_2O_3$ as in 2.1.) did not show other phases, as tested by the more sensitive technique of site-selective luminescence of lanthanide ion-doped samples.

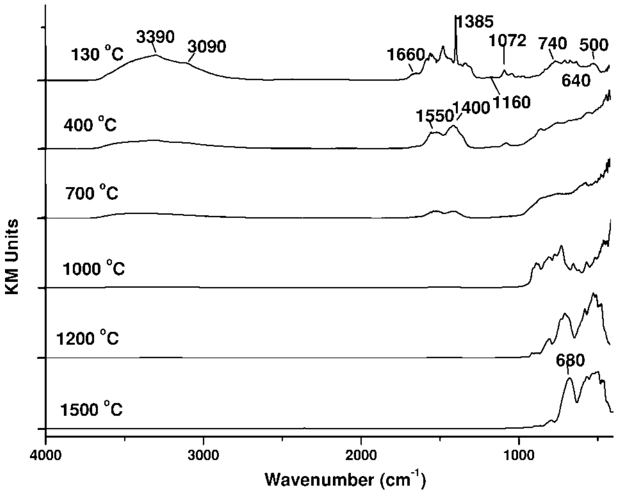


Figure 3 DRIFT spectra of gels prepared from 10 nm yttria and 50 nm alumina preformed sols (1Y:1Al) heated at various temperatures from 130 to 1500°C.

DRIFT spectra of the powders prepared by method 1 from 10 nm yttria and 50 nm alumina, which were then heated at 130°C (Fig. 3), show bands at ~3390, 3090 cm^{-1} (O—H stretching), 1660 (H—O—H bend), 1160, 1072 cm^{-1} (O—H bend), 740, 640, 500 (Al—O stretch and water librations) which are present in the spectrum of the alumina preformed sol treated alone in the same manner, to give boehmite, $AlO{\cdot}OH{\cdot}nH_2O$, at 130°C. The remaining bands are present in the spectra of the yttria sol, treated alone and heated to 130°C. In particular, the features at 1550 and 1400 cm^{-1} (COO^- antisymmetric and symmetric stretch, respectively) arise from acetate groups. The sharp peak at 1385 cm^{-1} is due to surface-adsorbed NO_3^-, and has previously been observed in samples of urban particulate matter and hydroxylated Al_2O_3 exposed to NO_2 [11]. The 130°C spectra of materials prepared using the different-size Al_2O_3 precursors are similar. On heating above 130°C, considerable changes occur in the spectra (Fig. 3), but these again represent a mixture of the spectra of the *individual* yttria and alumina materials. However, the spectrum of YAP is evident at 1000°C, albeit with some water/hydroxide remaining, but this is not present at 1200°C or 1500°C. As expected, the DRIFT spectra of samples prepared by methods 2 and 3, and subsequently heated to 130°C, are different from Fig. 3, but the final products at 1000–1200°C exhibit similar spectra. Although Raman data are available for $YAlO_3$ [12] and the calculation of the zone centre phonons has been performed, the only infrared data of $MAlO_3$ ($M = $ Y, Nd) are from reflection spectra [13, 14]. The highest energy transverse optic mode is at 676 cm^{-1} [13] or 681–684 cm^{-1} [12], in essential agreement with the lowest spectrum in Fig. 3.

The preparation of $YAlO_3$ is normally beset by the presence of different phases [15], particularly at high temperatures [16]. In summary, the preparation from preformed sols can give homogeneous products provided that accurate amounts of reactants are used; that these are thoroughly mixed and stirred in the gel forming process; and then subsequently ground, powdered and heated to 1200°C.

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