JOURNAL OF MATERIALS SCIENCE **36** (2001) 2253–2255

Use of preformed sols in the synthesis of luminescent lanthanide ion-doped yttria

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Luminescent erbium-doped yttria powders were directly synthesized from commercially available colloidal yttria preformed sols, after heating at temperatures up to 1200°C. The materials characterization and luminescence properties are described. Differences with analogous preparations employing preformed alumina sols are mentioned.
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1. Introduction

Lanthanide ion doped nanocrystalline Y_2O_3 is an efficient luminescent phosphor [1, 2]. Traditional sol-gel methods for the preparation of Y_2O_3 utilize high-purity metal alkoxide precursors [3], or the nitrate aqueous route [4]. We report herein the characterization and first luminescence study of this doped material prepared by a new technique from a commercially-available preformed sol. The use of preformed sols in synthesizing sol-gel materials has previously been considered for catalytic applications [5], since different preformed sols with defined particle sizes are commercially available. In addition, we show that the use of these colloidal-scale building blocks provides a rapid, easy and inexpensive method for synthesizing luminescent materials. Er^{3+} was chosen as dopant ion due to its well-characterized energy level scheme and efficient luminescence properties, which have previously been exploited in optical-fibre and waveguide applications [6].

2. Experimental

Y_2O_3 sol obtained from PQ Corporation, USA, as 14% colloidal Y_2O_3 dispersed in acetate solution at pH 7. The nominal particle size was listed as 10 nm so that this sol is further abbreviated as $10Y_2O_3$. Al_2O_3 sol was obtained from Vista Chemical Company, USA, as ca. 12% colloidal dispersions in nitric acid. The particle-size distributions of the sols were measured by a Coulter N4+ particle size analyzer. The preparation of the Er^{3+}-doped single oxide was performed via the mixing of the preformed $10Y_2O_3$ sol colloidal dispersion, the appropriate amount of $Er(NO_3)_3$ solution, together with about 1% by mass of the the gelation catalyst 1.0 M HNO_3. An opaque gel formed after about 1 hour. This was followed by a vacuum oven treatment (80 °C, 4 h) and a series of higher temperature heat treatments (at 110, 400, 1000 and 1200 °C, 8 h). The resulting products were white powders, which were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and diffuse reflectance infrared Fourier transform spectrometry (DRIFTS).

Powder X-ray diffraction patterns were recorded in the range $2\theta = 10–80°$, using a Philips X′pert X-ray diffraction system, with Cu-Kα radiation. The tube voltage and current were 40 kV and 55 mA respectively. The results were compared with library spectra from the JCPDS Database, and also with powders prepared from the preformed yttria and alumina sols. Fourier transform infrared (FTIR) spectra were recorded by a Perkin-Elmer Spectrum 1000 instrument, either in the absorbance mode, using samples dispersed in KBr discs; or in Kulbelka-Munk Units, from samples dispersed in KBr (3% by mass), using the PE DRIFTS Accessory. For the latter, 100 scans between 400–4000 cm^{-1} were averaged. The resolution was set at 4 cm^{-1}. Room-temperature luminescence and excitation spectra of powders were recorded by a SLM Aminco 4800C spectrofluorometer (SFM) at room temperature, with a resolution of 5 nm. Scanning electron micrographs were obtained from gold- or graphite coated samples using a Jeol 820 Instrument. Energy-dispersive X-ray analysis was used to identify the compositions of Y, Al and Er individual particles, or to map the concentrations over a selected area and compare with the direct SEM image.

CHN-analyses of powders were performed upon 1–10 mg mass of samples using a Vario EL CHN Analyzer equipped with an autosampler. EDTA was used as calibration standard.

3. Results and discussion

The manufacturer's specifications for the developmental $10Y_2O_3$ preformed sol listed a particle size of 10 nm. Our measurements by photon correlation spectroscopy (Fig. 1) showed that the mean particle size of the yttria sol was rather smaller: 2.54 nm (s.d. 0.52 nm). SEM

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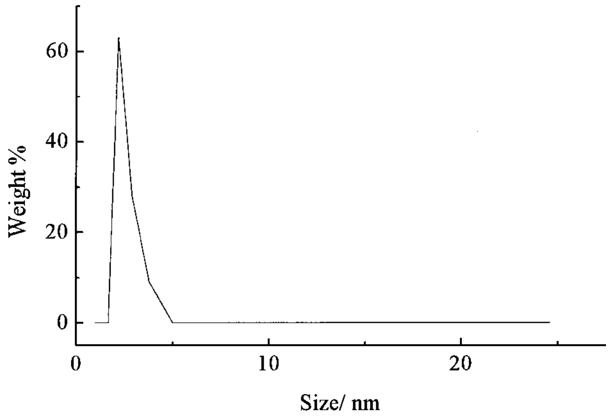

Figure 1 Particle size distribution of $10Y_2O_3$ preformed sol.

micrographs were taken of $Y_2O_3 : Er^{3+}$ samples with 1 to 2 mol % Er^{3+} dopant concentration, which had undergone heat treatment at 400 °C and at 1000 °C. The particle sizes of the irregular-shaped microcrystals ranged from 0.3 to 60 μm for the sample treated at 400 °C, and from 1 to 200 μm for that heated at the higher temperature. Fig. 2a shows a large particle for a sample heated to 1000 °C, and the yttrium and erbium density mappings are shown in Fig. 2b and c respectively. The Er^{3+} ions are observed to be randomly distributed in the material without clustering.

Y_2O_3 crystallizes in the cubic space group Ia3, with the Y^{3+} ions occupying two distinct sets of sites [7]. Recently, however, it has been shown that Y_2O_3 nanoparticles in the range 4 to 20 nm crystallize in the monoclinic phase [1]. The results of our powder diffraction patterns show an amorphous phase for the sample heated to 400 °C (Fig. 3a), but the $Y_2O_3 : Er^{3+}$ sample heated at 1000 °C gives a powder pattern matching the cubic Y_2O_3 reference (Fig. 3b and c).

Chemical (CHN) analysis of several Y_2O_3 gel products heated at 110 °C showed that they contained $13.6 \pm 0.3\%$ by mass C, and 3.2%H by mass. These analyses suggest that the composition of this material is similar to that of a nearly equal mixture of Y_2O_3 and $Y(CH_3COO)_3$, with $x H_2O$, (x between 2 to 3). The DRIFTS spectra of the sample heated at 110 °C (Fig. 4) show the presence of broad stretching and bending modes due to hydrogen-bonded water/hydroxide groups, together with ν(C=O) and ν(C-O) stretching modes of acetate groups. The compositional changes in the gel were conveniently followed by DRIFTS (Fig. 4), following the heating processes. Acetate bands are absent from the spectrum of the powder heated to 400 °C, but the broad water/hydroxide group bands persist even for samples heated at 1000 °C. These bands are absent from the spectrum of the sample heated at 1200 °C, which matches the infrared transmission spectrum of cubic Y_2O_3 [8], with the Y-O stretching mode at 561 cm^{-1}.

The luminescence of Er^{3+}-doped Y_2O_3 has previously been reported [9] and rationalized [10]. In our preliminary experiments we have investigated the relative emission intensity of our products under 385 nm excitation, as a function of Er^{3+} dopant ion concentration. The samples of Er^{3+}-doped yttria heated at 110 °C and 400 °C exhibited extremely weak luminescence, attributed to quenching via nonradiative energy transfer to water/hydroxide ion multiphonon modes. The intensity was much stronger for samples heated at 1000 °C. Fig. 5 shows the relative emission intensities of the (green) $^2H_{11/2},^4S_{3/2} \rightarrow {}^4I_{15/2}$ emission at this temperature, as a function of dopant ion concentration. The maximum intensity of emission was found for the 1 mol% Er^{3+} dopant ion concentration. The quenching effect at higher concentrations is attributed to the cross-relaxation process:

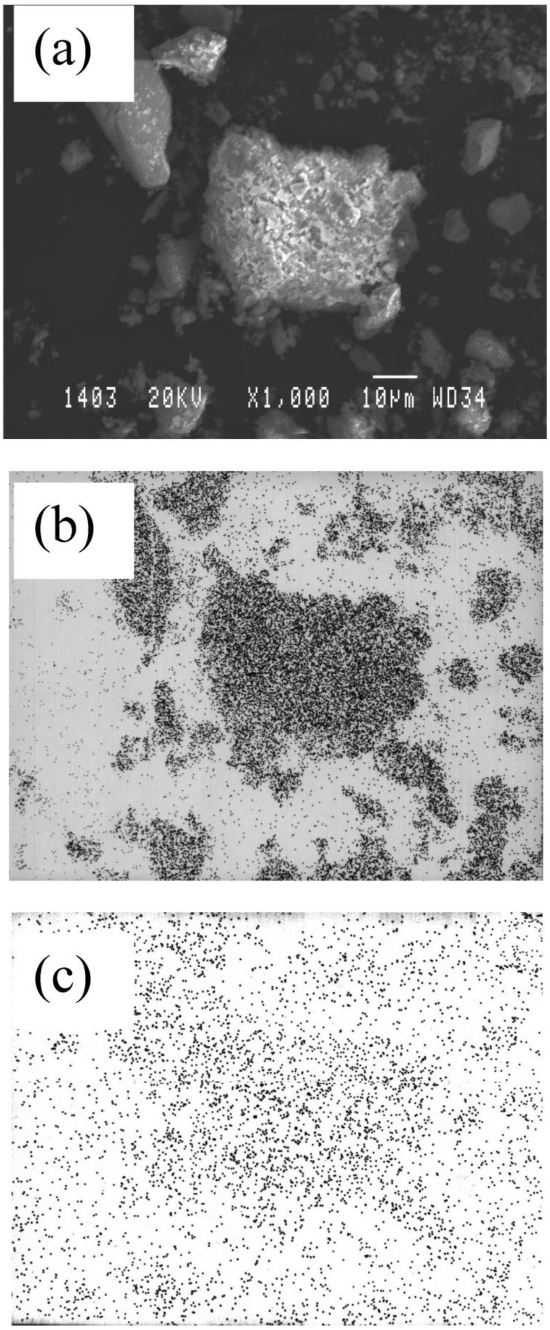

Figure 2 SEM micrographs of ca. 40 μm particle of $Y_2O_3 : Er^{3+}$ product (Er^{3+} concentration 1.0 mol%) after 1000 °C heat treatment: (a) digital image, (b) yttrium and (c) erbium density mapping.

$$^2H_{11/2},{}^4S_{3/2}\ \text{(ion 1)} + {}^4I_{15/2}\ \text{(ion 2)}$$
$$\rightarrow {}^4I_{13/2}\ \text{(ion 1)} + {}^4I_{9/2}\ \text{(ion 2)}$$

which has also been observed in $YAG : Er^{3+}$ [11].

We have conducted analogous preparations and characterization of properties for Er^{3+}-doped Al_2O_3

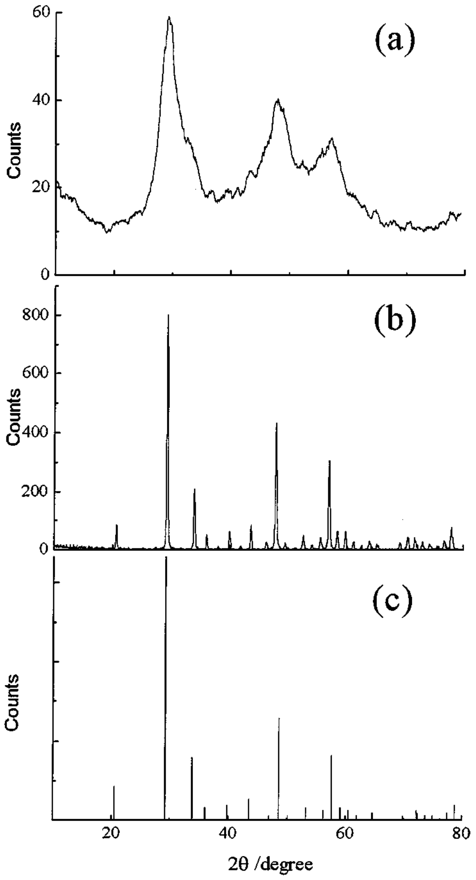

Figure 3 X-ray diffraction powder patterns for a sample of the $Y_2O_3 : Er^{3+}$ product heated at (a) 400°C and (b) 1000 °C. The library spectrum for cubic Y_2O_3 from the JCPDS Database is shown in (c).

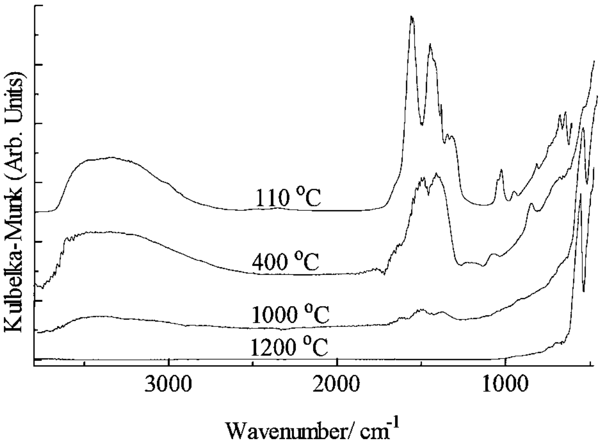

Figure 4 DRIFT spectra of Y_2O_3 samples after heating to various temperatures.

powders prepared from alumina preformed sols of nominal particle sizes between 50 to 415 nm. DRIFTS showed phase changes for samples heated from 110 °C to 1000 °C, from boehmite to γ-Al_2O_3. However, Er^{3+}-doped samples heated at 1000 °C were non-luminescent. Kurokawa *et al.* [12] have recently synthesized luminescent Er^{3+}-doped Al_2O_3 films by the sol-gel process for dopant ion concentrations as large as 15 mol% Er^{3+}. Since our DRIFTS spectra indicate the presence of hydroxide ion groups even for samples heated at 1000 °C, presumably nonradiative quenching at these defect sites occurs in our samples, and we will further investigate the dehydration processes.

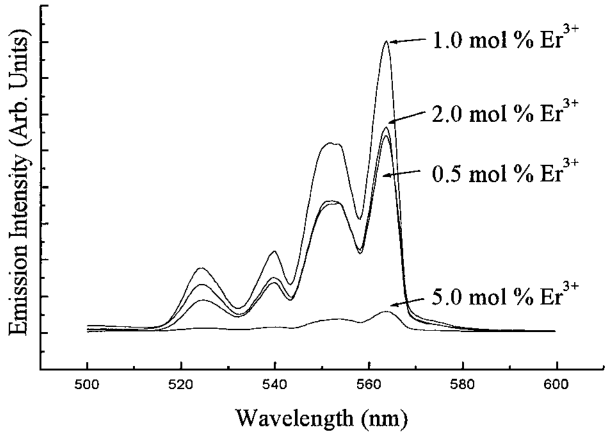

Figure 5 385-nm excited luminescence spectra between 500–600 nm of $Y_2O_3 : Er^{3+}$ products (1–5 mol% Er^{3+}) heated at 1000 °C.

Y_2O_3 is a suitable, high conductivity host for doping with rare-earth ions. However, conventional preparations from the melt are difficult since the melting point is above 2400 °C [13]. Bulk Y_2O_3 samples doped with Er^{3+} have alternatively been prepared by mixing Y_2O_3 with Er_2O_3, pressing the powders into pellets under 10 tons of pressure, and then firing in air for 24 hours [14]. The present method of preparation offers a lower-temperature route.

Acknowledgement

We thank the PQ Corporation and Vista Chemical Company for gifts of yttria and alumina preformed sols; and City University for financial support of this work under Strategic Research Grant 7000762.

References

1. K. S. HONG, R. S. MELTZER, B. BIHARI, D. K. WILLIAMS and B. M. TISSUE, *J. Lumin.* **76/77** (1998) 234.
2. E. T. GOLDBURT, B. KULKARNI, R. N. BHARGAVA, J. TAYLOR and M. LIBERA, *ibid.* **72–74** (1997) 190.
3. D. C. BRADLEY, *Chemical Reviews* **89** (1989) 1317.
4. P. K. SHARMA, M. H. JILAVI, R. NASS and H. SCHMIDT, *J. Lumin.* **82** (1999) 187.
5. S. J. MONACO and E. I. KO, *Chemtech* **28** (1998) 23.
6. G. N. VAN DEN HOVEN, A. POLMAN, C. VAN DAM, J. W. M. VAN UFFELEN and M. K. SMIT, *Optics Letters* **21** (1996) 576.
7. C. A. MORRISON and R. P. LEAVITT, in “Handbook of the Physics and Chemistry of Rare Earths,” edited by K. A. Gschneidner and L. Eyring (North-Holland, 1982) p. 564.
8. N. T. MCDEVITT and A. D. DAVIDSON, *Journal of the Optical Society of America* **56** (1966) 636.
9. W. F. KRUPKE, *Physical Review* **145** (1966) 325.
10. R. P. LEAVITT, J. B. GRUBER, N. C. CHANG and C. A. MORRISON, *Journal of Chemical Physics* **76** (1982) 4775.
11. A. LUPEI, V. LUPEI, S. GEORGESCU, I. URSU, V. I. ZHEKOV, T. M. MURINA and A. M. PROKHOROV, *Physical Review* **B41** (1990) 10923.
12. Y. KUROKAWA, T. ISHIZAKA, T. IKOMA and S. TERO-KUBOTA, *Chemical Physics Letters* **287** (1998) 737.
13. K. PETERMANN, G. HUBER, L. FORNASIERO, S. KUCH, E. MIX, V. PETERS and S. A. BASUN, *J. Lumin.* **87–89** (2000) 973.
14. J. A. CAPOBIANCO, F. VETRONE, T. D’ALESIO, G. TESSARI, A. SPEGHINI and M. BETTINELLI, *Phys. Chem. Chem. Phys.* **2** (2000) 3203.

Received 21 March
and accepted 4 October 2000