

Synthesis of nanocrystalline and nanostructured oxide materials by controlled precipitation in a polyol medium

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A novel approach in utilizing the polyol method was used for the preparation of nanocrystalline and nanostructured undoped and Tb³⁺-doped Y₂O₃ materials. By this method, particles in colloidal solution and re-dispersible powders with spherical shape and luminescent properties were formed. The materials were characterised by High Resolution Transmission Electron Microscopy (HRTEM) and Luminescence Spectroscopy (LS). Oxide nanoparticles 5 to 6 nm in size, with homogeneous distribution, good morphology and high crystallinity were obtained, being colloiddally stable for weeks. In the case of the re-dispersible powders, nanostructured aggregates 300 to 400 nm in size were observed, containing ultra-small individual nano-oxide bcc crystallites. In addition, the nanocrystalline and nanostructured Tb³⁺-doped Y₂O₃ materials showed luminescent properties.

Keywords: Nanocrystal; Nanostructured materials; Luminescence; Y₂O₃; Green emitting material.

1. Introduction

In recent years, most studies have been focused to prepare nanometric and nanostructured ceramics for technological applications. Particularly, yttrium oxide has various applications such as high index oxide for optics, namely dielectric mirrors for high power UV lasers at 351 nm, as catalyst support or even catalysts, and as transparent matrices for phosphor materials when doping with rare earth metals such as Eu, Tb and Pr [1,2]. In addition, Tb-activated Y₂O₃ is one of the most efficient green-emitting phosphors. Under UV or cathode ray excitation, terbium activated yttrium oxide phosphor shows bright characteristic green luminescence and could be used in the manufacture of coloured fluorescent lamps, cathode ray tubes and plasma display panels [3,4]. Usually, Tb-doped Y₂O₃ phosphor synthesis is performed by ceramic techniques, i.e. the direct firing of oxide mixtures; the phosphor manufacture could proceed also by the firing of some precursors previously prepared by sol-gel or homogeneous precipitation [5-8].

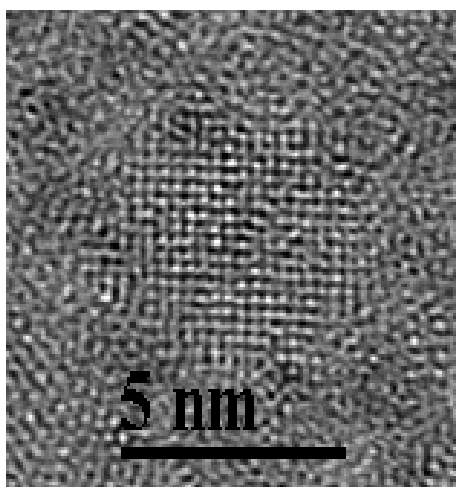
The preparation of colloids in a high boiling alcohol, diethylene glycol (DEG), generally called the *polyol* method, has been successfully used to obtain a large variety of materials, including oxides [9-11], sulfides [12], phosphates [13], and elemental metals [14,15]. Since the alcohol acts as a surface capping agent [16], the *polyol* method allows a close control of the particle size. Additionally, the size of the agglomerates can be adjusted by

varying some synthesis parameters such as temperature or the concentration of the cations introduced. In the case of rare earth based oxides, the nature of the precursor is crucial for determining the state of agglomeration of the particles formed. When starting from chlorides, some colloidal solutions stable for months were prepared [17], whilst suspensions of sub-micrometric agglomerates (0.1-0.5 µm), each of them composed by nanometric particles (3-5 nm), were obtained when nitrate precursors were used [18]. In the other hand, it was found that carbonates and acetates do not effectively lead to direct oxide precipitation [12,13].

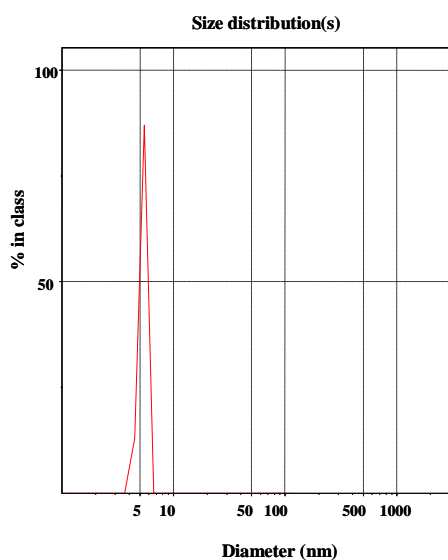
In this work, nanocrystalline and nanostructured undoped and Tb-doped Y₂O₃ materials are reported using a synthesis route based upon a direct colloidal precipitation route in diethylene glycol (DEG), generally called the polyol method.

2. Experimental

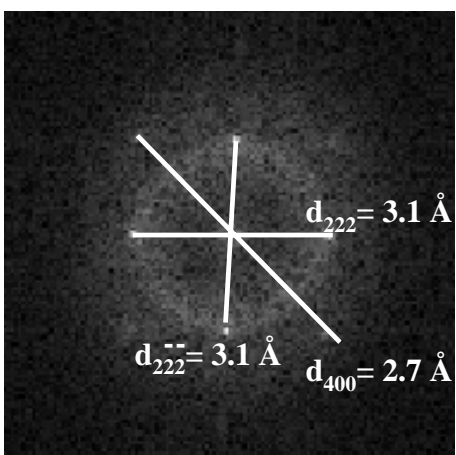
Undoped and Tb-doped Y₂O₃ ceramics were prepared as follows. The suitable precursors (YCl₃, TbCl₃, Y(NO₃)₃ and Tb(NO₃)₃ 99.99% Aldrich salts) were dispersed in 100 mL of diethylene glycol (99%, Aldrich) to obtain a 0.1-0.5 mol L⁻¹ global metal concentration. The whole mixture was heated at for 1 h and then the clear solution obtained was subjected to vigorous stirring at 180°C for 2h in refluxing diethylene glycol. The dehydrating properties of the alcohol, associated with the high temperature of the



a)



b)



c)

Figure 1. Characterization of undoped Y_2O_3 nanoparticles. a) HRTEM micrograph of a nanocrystallite; b) size distribution obtained from dynamic light-scattering experiments; c) Fourier transform of a selected area diffraction pattern.

solution during the synthesis, favored the formation of oxide, as opposed to hydroxide particles. Suspensions of nanometric and sub-micrometer particles dispersed in the organic solvent were obtained. In the case of the nanostructured phosphors, they could be easily separated from DEG by precipitation and filtration through a $0.2\ \mu\text{m}$ sieve and later washed with ethanol. The white precipitates were dried in a stove at 100°C for 1h and the resulting powder were subsequently characterized.

3. Characterization

Direct size distribution measurements of the nanoparticles and ultra fine powders suspended in diethylene glycol were performed by Photon Correlation Spectroscopy (Zetasizer 3000 HS PCS). High Resolution Transmission Electron Microscopy (HRTEM) was used to obtain detailed information about the shapes and size distribution of the colloidal dispersions. The HRTEM measurements were made with a TOPCON microscope operating at 200 kV. The samples for HRTEM were prepared by depositing a drop of a diluted colloidal solution on a carbon grid. Crystal structure was determined by analyzing the high resolution electron micrographs of selected area diffraction patterns. In the case of the ultra fine powders, the size distribution was evaluated by scanning electron microscopy, SEM (Zeiss DSM 940A Scanning Electron Microscope). Fluorescence spectra were obtained for all the samples, using excitation with a Xe lamp and a JYH10D monochromator set at $\lambda=280\text{nm}$ (hamamatsu R1477). Light was collected with an UV optical fiber coupled to a JYTRIAx 320 and a CCD camera (1200grooves/mm grating and 0.25-mm slits, giving 1-nm resolution). The spectra measurements were carried out at room temperature.

4. Results and discussion

The particle size was determined by a combination of HRTEM and dynamic light-scattering experiments. In the high-resolution micrograph shown in Fig. 1a, a particle around 5-6 nm size appears as a regular crystalline lattice, superimposed on an amorphous background due to the carbon support and to the DEG; a similar particle average size (5 nm) was obtained from the dynamic light-scattering experiments, as can be seen in Fig. 1b. The nature of the crystalline phase was inferred from the indexation of the inter-reticular planes visible in the particle; the precise inter-reticular distances between the planes were obtained from the Fourier transform of the image (Fig. 1c). The crystalline lattices are consistent with the usual bcc structure of yttrium oxide (space group $\text{Ia}\bar{3}$); the reticular distances observed ($3.1\ \text{\AA}$ and $2.7\ \text{\AA}$) and the angle of around 110° between the crossed fringes, correspond to the (222) and (400) planes of a Y_2O_3 cubic phase with a cell parameter close to $10.6015\ \text{\AA}$, in agreement with the JCPDS file (41-1105).

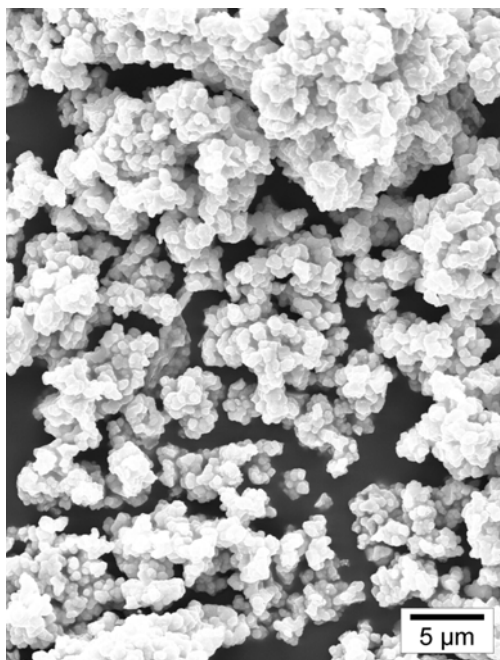


Figure 2. SEM image of an undoped Y_2O_3 powder just after precipitation.

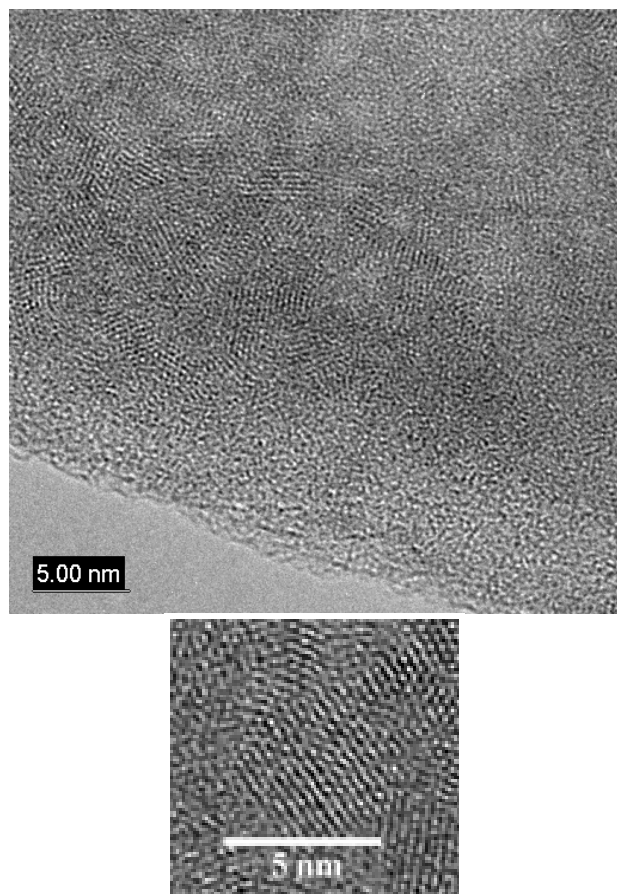


Figure 3. TEM image for a spherical aggregate; (inset) nanoparticle 5 nm.

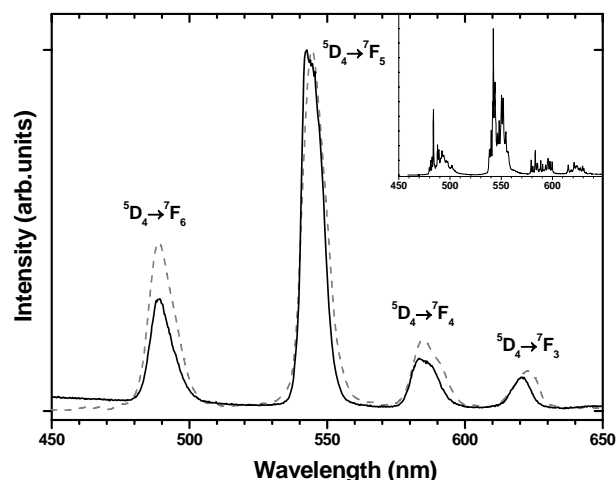


Figure 4. Emission spectra of Tb^{3+} -doped Y_2O_3 nanoparticles (dashed line), nanostructured and bulk materials (inset), excited at 280 nm.

The morphology and structure of the nanostructured powders obtained were determined by SEM, HRTEM and dynamic light-scattering experiments. SEM observations (Fig. 2) show that the precipitate consists of large agglomerates composed of spherical grains ranging from 300 to 400 nm in diameter. TEM observations of the starting material were performed to evaluate the structure of the powders; as can be appreciated in Fig. 3, they are formed by the aggregation of nanometer-sized spherical primary particles. The HRTEM micrograph presented as an insert in the same figure shows the high crystalline nature of these primary entities, where each agglomerate is composed of nanoparticles with a size lying between 5 and 6 nm.

Fig. 4 gives the emission spectra of Tb^{3+} -doped Y_2O_3 nanoparticles and nanostructured materials, measured at an excitation wavelength of 280 nm; the inserted spectrum in Fig. 4 corresponds to the bulk material. The emission transition of Tb^{3+} ions is clearly indicated by the large emission bands at 489, 542, 583 and 620 nm, due to the inner shell transition from the excited level to the lower levels: $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 6, 4, 3$ respectively). The broadening in the bands can be attributed to a disorder induced by the increase in the surface/volume ratio resulted from the decrease in the size of the particles, to confinement effects, or to the deteriorations of the electronic band in the host matrix [19].

5. Conclusions

In this study, a very simple and efficient chemical route to prepare nanocrystalline and nanostructured oxides is presented. Undoped and Tb^{3+} -doped sesquioxides have been synthesized and structurally characterized. According to the HRTEM observations, the nanocrystalline and nanostructured materials obtained possess the same average particle size (5-6 nm). From the analysis of the Tb^{3+} based oxides luminescence spectra, it was found that

the transitions within the cubic form of Y_2O_3 correspond to the known inner shell transition $^5\text{D}_4 \rightarrow ^7\text{F}_j$, which indicates that luminescent centers are formed efficiently by this direct precipitation in a high-boiling alcohol. Both nanocrystalline and nanostructured materials show identical luminescence spectra, confirming that they are constituted by particle of the same average size.

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References

- [1] M. D. Fokema and J. Y. Ying, J. Catal. **192**, 54 (2000)
- [2] O. M. Bordum, J. Appl. Spectr. **69**, 430 (2002)
- [3] E. T. Goldburn, B. Kulkarni, R. N. Bhargava, J. Taylor and M. Libera, J. Lumin. **190**, 72 (1997)
- [4] N.V. Gaponenko, O.V. Sergeev, V.E. Borisenko, J.C. Pivin, P. Skeldon, G.E. Thompson, B. Hamilton, J. Misiewicz, L. Bryja, R. Kudrawiec, A.P. Stupak and E.A. Stepanova, Mat. Sci. Eng., **B81**, 191 (2001)
- [5] Y. L. Soo, S. W; Huang, Z. H. Ming, H. Kao, G. C. Smith, E. Goldburt, R. Hodel, B. Kulkarni, J. V. D. Veliadis and R. N. Bhargava, J. Appl. Phys. **83**, 5404 (1998)
- [6] S. Erdei, R. Roy, G. Harshe, H. Juwhari, D. Agrawal, F. W. Ainger and D. Agrawal, Mater. Res. Bull. **30**, 745 (1995)
- [7] R. N. Bhargava, J. Lumin. **70**, 85 (1996)
- [8] Yu-Chun Wu, Maricela Villanueva-Ibañez, Cécile Le Luyer, Jun Shen, Jacques Mugnier, Opt. Mat. Appl., Proc. SPIE. **5946**, 396 (2005)
- [9] L. Poul, S. Ammar, N. Jouini, F. Fiévet and F. Villain, Solid State Sci. **3**, 31 (2001)
- [10] C. Feldmann, Scripta Materialia. **44**, 2193 (2001)
- [11] J. Merikhi, H. O. Jungk and C. Feldman, J. Mat. Chem. **10**, 1311 (2000)
- [12] C. Feldmann, C. Metzmacher, J. Mat. Chem. **11**, 2603 (2001)
- [13] C. Feldmann, Adv. Funct. Mat. **13**, 101 (2003)
- [14] F. Fievet, Surfactant Sci. Ser. **92**, 460 (2000)
- [15] G. Viau, P. Toneguzzo, A. Pierrard, O. Acher, F. Fievet-Vincent, F. Fievet, Scripta Materialia **44**, 2263 (2001)
- [16] Y. Tian, J.H. Fendler, Chem. Mater. **8**, 468 (1996)
- [17] R. Bazzi, M.A. Flores, C. Louis, K. Lebbou, W. Zhang, C. Dujardin, S ; Roux, B ; Mercier, G. Ledoux, E. Bernstein, P. Perriat, O. Tillement, J. Coll. Interf. Sci. **273**, 191 (2004)
- [18] M. A. Flores-González, G. Ledoux, S. Roux, K. Lebbou, P. Perriat, O. Tillement, J. of Sol. Stat Chem. **178**, 989 (2005)
- [19] R.S Meltzer, S.P. Feofilov, B. Tissue and H.B. Yuan, Phys. Rev. B **60/20**, 14012 (1999).