

A new thermoluminescence phosphor of Gd₂O₃ was synthesised by an aerosol technique which allows heavy doping with Eu. Annealing at 1,200°C increases the luminescence efficiency by ~1,000 times relative to the as prepared material. Data are presented both from morphological studies and the emission spectra. Emission is primarily from the red transitions of the Eu, but some short wavelength signal was detected at low temperature. There is evidence for a range of defect and luminescence sites in these Gd₂O₃:Eu phosphors related to the methods of sample preparation and annealing. Stability of some sites is enhanced by the presence of Eu so that the TL peaks appear at higher temperatures than the intrinsic defect TL of the host material. The synthesis of uniform and submicron sized spherical particles with nano-clustered inner structure was demonstrated with various analysis techniques (XRPD, FE-SEM and HR-TEM).

INTRODUCTION

High grade phosphors in the form of particles with a narrow size distribution, a spherical morphology and absence of agglomerates have been made using an aerosol approach with europium doped gadolinium oxide. High levels of Eu produce intense red emission. As initially fabricated the material lacks intensity and requires thermal treatments above 800°C, and then Eu improves further with 12 hours above 1,200°C. Reasons include removal of unwanted trace materials, improvements in the crystallinity of the mixture, alterations in surface sites, and dispersion and homogenisation of the Eu dopant. Further, the phase of Gd₂O₃:Eu changes with annealing temperature. Dopant levels with a Gd to Eu ratio of 9:1 were first used. High dopant values can generate clustering of the Eu ions into non-radiative sites, lattice strains intrinsic defects or induce phase separation and/or precipitation of the dopant ions into interacting clusters. All such scenarios can result in greatly reduced luminescence efficiency. Current results, with a higher dopant concentration of Gd:Eu of 8:2, are feasible because of the improvements from annealing. A monoclinic phase was observed after the sample powder was annealed above 1,100°C.

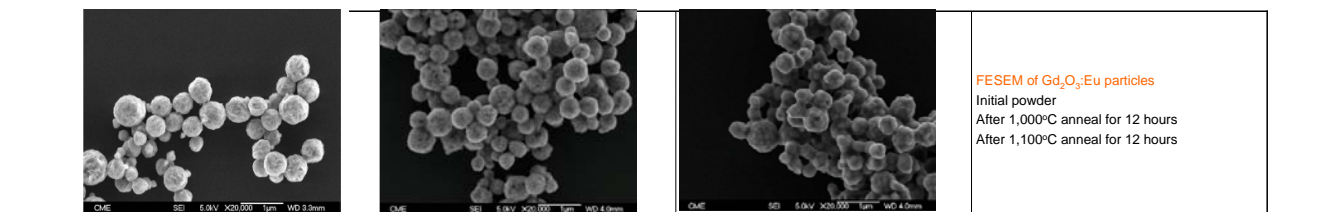
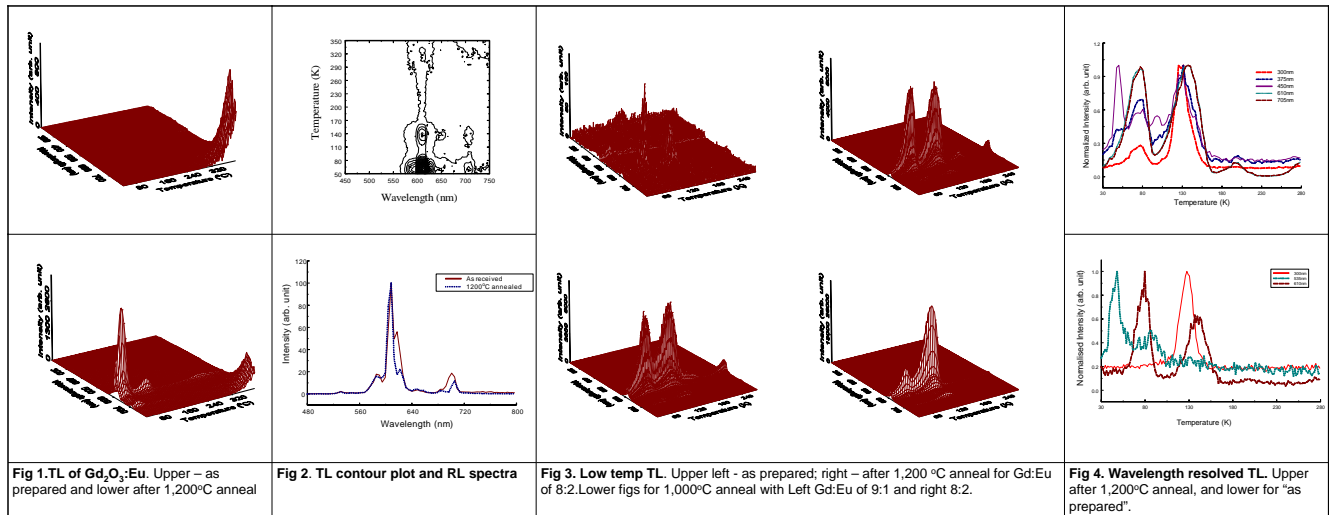
EXPERIMENTAL

Samples were prepared from solutions of Gd(NO₃)₃.xH₂O and Eu(NO₃)₃.xH₂O to obtain 0.080:0.020 Gd/Eu molar ratio. The solutions were atomized ultrasonically (piezo-transducer resonant frequency of 2.1 MHz), introduced into a high temperature tubular flow reactor with air as a carrier gas, and decomposed at 700°C. The gas flow rate was 1.5 l/min, and the corresponding droplet/particle residence time was 75 s. This resulted in a fine powder called "as prepared" which was subsequently thermally annealed. Annealing was made in air at temperatures of 800 to 1,200°C for periods of 12 hours. The TL emission spectra with a wavelength multiplexed spectrometer. Above room temperature the heating rate was 0.5 degrees per second, but 0.1 K/s for low temperature data. TL was excited by X-ray irradiation with 40 kV X-rays using 200Gy.

The crystal phases and particle morphology were determined by X-ray powder diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM). All peak positions were used for the determination of microstructural parameters. Structural refinements were carried out using the Rietveld based programs Fullprof. A FESEM was used in order to identify particle morphology.

THERMOLUMINESCENCE

The TL spectra reveal trap depths and presence of different sites (particularly at low temperature). There are major differences in intensity between the intrinsic short wavelength signals and those from the europium sites. Figure 1 contrasts the TL for original material and after annealing for 12 hours at 1,200°C. Eu emission intensity increases by ~1,000 times. Figure 2 shows contour and spectra plots. Figure 3 includes low temperature TL spectra from 25K and two Eu concentrations and Figure 4 separates the TL plots in terms of wavelength. The intrinsic signals are at the shorter wavelengths. The effects of annealing are apparent in terms of changes in lattice sites on the TL.



Rietveld based Fullprof refinement parameters

Temperature °C	Time (h)	Phase	Lattice parameter (Å)	Rp (%)	Rwp (%)	Rt (%)	Rb	χ ²
As prepared	700	Ia3	10.835(1)	11.1	14.2	8.93	9.88	2.82
As prepared	700	Fm3m	5.620(1)	11.1	14.2	10.1	13.9	2.82
800/12		Ia3	10.822(1)	11.60	15.6	25.4	14.4	1.5
900/12		Ia3	10.821(1)	11.60	15.6	25.4	13.9	1.5
1000/12		Ia3	10.818(1)	12.9	16.9	26.7	20.4	1.58
1100/12		Ia3	10.821(2)	13.6	17.6	34.8	22.0	1.71
1200/12		Ia3	10.8360(4)	10.3	14.0	14.7	6.78	1.70

Theoretical and empirical parameters of the monoclinic phase after annealing at 1,100°C

	JCPDS 43-1015	Experimental	R ₂ Miller indices
Space group	12 C ₂ /m	12 C ₂ /m	
Lattice parameters	a = 14.06, b = 3.55, c = 8.56	a = 13.6, b = 3.56, c = 8.6	
Angles	α = γ = 90° β = 100.1°	α = γ = 90° β = 100.6°	
Interplanar distances	h k l	h k l	
	8,6,2	8,6	0 0 1
	4,3,2	4,3	0 0 2
	3,1,58	3,15	1 1 1
	2,875	2,86	0 0 3
	2,755	2,759	-1 1 2
	2,431	2,43	4 0 3
	2,134	2.1	-2 1 3
	1,913	1.91	3 1 3

PARTICLE STRUCTURE AND MORPHOLOGY

XRD patterns implied the presence of two cubic phases in as-prepared powder sample; a main Ia3 phase and a secondary Fm-3m phase with the concentration of 12% wt. The latter phase is similar to Gd₂Te₂O₇. The table above summarizes the parameters. Only the Ia3 phase was found after annealing. It is evident the higher value of the cell parameter compared with c-Gd₂O₃ (a=10.81 Å), indicates the incorporation of Eu³⁺ into the matrix, since (Eu³⁺ - 0.095nm; Gd³⁺ - 0.094nm). Luminescence changes for as-prepared and thermally treated samples thus could relate to changes in the gadolinia crystal structure.

High resolution FE-SEM images show spheroidal geometry in the submicrometre range. Agglomeration occurs either as chains or clusters of particles of primary nano-particles. FE-SEM images clearly show differences with preparation history. On increasing the annealing temperature, the particle surfaces become smoother. Loosely sintered primary particles are evident inside agglomerates at 1,000 °C and at higher temperature interparticle collision and sintering are evident among the secondary particles, and decreases of the primary particle size dispersion, to smaller particles.

SAED patterns confirmed two polycrystalline cubic phases in "as prepared" samples: the main phase is bcc with Ia3 space group, and the unit cell parameter a ≈ 10.8Å; the secondary phase is a with Fm-3m symmetry and with the cell parameter of 5.6 Å. In samples treated at temperatures of 800-1000 °C for 12h, only the cubic Ia3 phase has been observed. TEM observations reveal existence of a well ordered phase for the samples treated at 1100 °C for 12 hours (which was not observed in the XRD patterns). The new phase is different from the cubic one, and the interplanar spacings indicate a similarity with a monoclinic phase. The details of this minority phase can be appreciated in an HR-TEM image in bright field of the sample treated at 1100 °C for 12 hours. Fast Fourier Transform revealed C2/m symmetry, confirmed with SAED patterns, indicating a monoclinic phase with the approximate unit cell parameters: a=13.6, b=3.56, c=8.6 (a:b:c = 3.82:1:2.41), β = 100.6° as summarized in the Table above. Defects formed along grain boundaries could be responsible for extra spots that are present in FFT of some areas of the image. For the case of the rare earth sesquioxides, a monoclinic phase is metastable at ambient conditions and could be obtained by quenching from high temperatures and under high pressure, however, the high heating rates associated with the aerosol route may favoured to the formation of the metastable monoclinic structure at temperatures ≥ 1,100 °C.

The Eu³⁺ occupies the three non-equivalent crystallographic sites in the monoclinic structure. For the case of the Gd₂O₃:Eu³⁺ cubic crystalline system, with space group Ia3, the Eu³⁺ ion can occupy two Gd³⁺ sites with a coordination number of 6 with C2 and S6 symmetries.

SUMMARY

An aerosol route was applied for the synthesis of nanostructure submicron sized spherical Gd₂O₃:Eu³⁺ particles. The particle morphology and phase content were evaluated by different analysis techniques (XRPD, FE-SEM and HR-TEM) and discussed in terms of the processing parameters and post-annealing temperature. XRD patterns implied the presence of two cubic phases in as-prepared powder: a main Ia3 phase and a secondary Fm-3m phase with the concentration of 12% wt. Only the Ia3 phase after the annealing was found. HR-TEM investigations proved the locally appearance of the metastable monoclinic C2/m structure at temperatures around 1,100 °C, whose formation is probably associated with the high heating and cooling rates during synthesis. In conclusion the TL signals demonstrate that there are numerous defect and luminescence sites in the Gd₂O₃:Eu phosphors which are a function of sample preparation, dopant concentration and annealing. The sites are somewhat independent in terms of their emission spectra and the stability of some sites is enhanced by the presence of Eu so that the TL peaks appear at higher temperatures than those of the host material.

Recent publications

- Mileosevic, O., Mantic, L., Rabanal, M. E., Yang, B. and Townsend, P.D., Structural and Luminescence Properties of Gd₂O₃:Eu³⁺ and Y₃Al₅O₁₂:Ce³⁺ Phosphor Particles Synthesized via Aerosol, Journal of the Electrochemical Society, 152, 707-713, 2005.
- Wang, Y., Mileosevic, O., Gomez, L., Rabanal, M.E., Torralba, J.M., Yang, B., Townsend, P.D., Thermoluminescence responses from europium doped gadolinium oxide, J Phys Condensed Matter 18 9257-9272, 2006.