Synthesis and Characterisation of Nanoparticle \(Y_2O_3:Eu\) and \(YAG:Ce\) Phosphors

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Abstract

Samples of nanoparticle \(Y_2O_3:Eu\) and \(YAG:Ce\) phosphors have been prepared using a micellar synthetic method for the control of particle size and morphology. The structural, morphological and luminescent properties of the nanoparticle phosphors have been characterized using X-ray powder diffraction, TEM, SEM, CL and PL spectroscopies.

Keyword: Nanoparticle, nanophosphor, crystallite, particle size, combustion synthesis

1. INTRODUCTION

The aim of this work was to prepare nanoparticle phosphors under conditions that enable their particle sizes and morphologies to be controlled. Furthermore, the synthesis of the phosphor nanoparticles needed to be as simple and cost effective as possible. With regards to these constraints, a straightforward method for the production of such phosphor nanoparticles has previously been developed using \(n\)-alkylammonium chloride chains with the general formula \(C_nH_{2n+1}NH_3Cl\) \((n = 10\) to \(16\)) as a particle size and morphology regulator \([1]\). It is confirmed herein that the method may be applied to the synthesis of \(Y_2O_3:Eu\), and it is shown that the method may also be applied to the synthesis of \(YAG:Ce\) nanophosphors for a number of possible lighting and display applications.

2. EXPERIMENTAL

The basic synthetic method for the preparation of sub-micrometre \(Y_2O_3:Eu\) phosphor particles has been previously described \([1]\), and the same method can be applied to the synthesis of nanocrystalline \(YAG:Ce\) sheets. It utilized a facile micelle self-assembly of \([Y(NO_3)_3\) and \(AlCl_3]\) and \(CeCl_3\) stock solutions mixed with dodecylamine hydrochloride in ethanol. The solutions formed micelles containing the \(YAG:Ce\) precursor composites, and they were reduced in volume by boiling until they became viscous. The viscous precursor materials were fired in alumina crucibles at a minimum temperature of \(1200\)\(^o\)C over a range of annealing times. The micelles were eliminated during the initial combustion of the precursor solution, this occurs after ca. 15 seconds of introducing the crucible into the furnace at the minimum temperature of \(1200\)\(^o\)C or above. The combustion process is completed after ca. 1 minute when the micelles and ethanol that constitutes the fuel driving the process have been consumed. During the combustion process, the precursor phosphor materials are converted to \(YAG:Ce\); further annealing then increases the emission intensities of the materials. Longer annealing times and higher annealing temperatures can lead to improved luminescence, but may cause sintering of the networked particles forming the sheets.

This preparative method can be described as a combustion synthesis and the foam-like white powder crust, which is obtained, is typical of materials formed using this technique.

A typical synthesis is described here, as follows. Dodecylamine hydrochloride was prepared from dodecylamine that was quaternised using excess dilute HCl in a warm solution of ethanol. The resulting yellow soapy mass was filtered at the pump, washed with acetone and recrystallised in warm ethanol; this was done twice. The resulting dodecylamine hydrochloride crystallised into thin soft white laths. A warm ethanolic (10 ml) solution of dodecylamine hydrochloride (0.7g) was added to the two stock solutions (12.5 ml) of \([Y(NO_3)_3\) and \(AlCl_3]\) and \(CeCl_3\) stock solutions mixed with dodecylamine hydrochloride in ethanol. The solutions formed micelles containing the \(YAG:Ce\) precursor composites, and they were reduced in volume by boiling until they became viscous. The viscous precursor materials were fired in alumina crucibles at a minimum temperature of \(1200\)\(^o\)C over a range of annealing times. The micelles were eliminated during the initial combustion of the precursor solution, this occurs after ca. 15 seconds of introducing the crucible into the furnace at the minimum temperature of \(1200\)\(^o\)C or above. The combustion process is completed after ca. 1 minute when the micelles and ethanol that constitutes the fuel driving the process have been consumed. During the combustion process, the precursor phosphor materials are converted to \(YAG:Ce\); further annealing then increases the emission intensities of the materials. Longer annealing times and higher annealing temperatures can lead to improved luminescence, but may cause sintering of the networked particles forming the sheets.

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The photoluminescence spectra of the nanophosphors were measured by means of a Bentham spectrometer equipped with an integrating sphere for luminous efficacy determinations. Luminous efficacies were measured on the Bentham spectrometer equipped with a M300 monochromator and a 100 W quartz halogen source and silicon detector, both of which were NPL calibrated. The CL luminescence spectra of all \(Y_2O_3:Eu\) samples were collected using a Bentham excitation/emission spectrometer connected by fibre optic cable to a Photometer Telescope (TEL 301).

Scanning electron micrographs (SEMs) of the phosphor samples were collected in order to determine the particle sizes. Transmission electron microscopy (TEM) was used to determine the crystallinity of the samples on a Jeol
2000CX instrument. The samples were mounted on carbon film that was settled onto copper grids.

3. RESULTS AND DISCUSSION

A SEM of a Y₂O₃:Eu nanophosphor sample fired at 650°C is shown in Figure 1. The material is composed of a sheet of Y₂O₃:Eu fibres between 100 to 200 nm in length, which appear to be held together by much smaller fibres. The texture of the matrix is caused by escaping gases, which keep the particles apart as they form and grow rapidly during the combustion process.

![Fig. 1. SEM image of a sheet composed entirely of the Y₂O₃:Eu fibres (the scale bar is 200 nm).](image)

CL luminance measurements of Y₂O₃:Eu nanoparticle samples annealed at 650, 750, 850 and 950°C are shown in Figure 2. It can be seen that the samples fired at 850 and 950°C display the highest emission intensities, which can be correlated with larger crystallite sizes.

![Fig. 2. Plot of CL luminance vs. electron beam accelerating voltage for Y₂O₃:Eu nanoparticle samples annealed between 650 to 950°C.](image)

Figure 3 shows an SEM micrograph of a YAG:Ce phosphor sample prepared by our novel micelle method and fired at 1500°C. The average particle size is ca. 200 nm.

![Fig. 3. SEM of nanoparticulate YAG:Ce phosphor prepared by the novel micelle method (the scale bar is 1 μm).](image)

The particles show some evidence of sintering, and the single layer network is composed of branched particles that may be evidence of a relic branched micelle architecture. The luminous efficacy of this sample was determined to be 211 lm/W under 470 nm excitation, which is lower than the values of > 300 lm/W that we have measured from particles that are > 1 μm in size. Although the particle size is small, the luminous efficacy for this sample agrees quite well with those of the samples fired at the same temperature but made by the urea gel method [2].

4. SUMMARY

The novel synthesis is based on the rare ability of alkylammonium chloride chains to form a range of self-assembled structures in solution such as micelles, planar multilayers and multilamellar vesicles under different physico-chemical conditions. The general approach used for the synthesis of REE-doped oxide nanophosphor systems in this work was to exploit the ability of the alkylammonium chloride chains to form various organic-inorganic self-assembled architectures containing nanophosphor host lattice ions and REE activator ions. The resulting compounds could then be converted to the luminescent oxides by a combustion synthesis.

5. ACKNOWLEDGEMENTS

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6. REFERENCES