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Crystal size dependence of the persistent phosphorescence in $Sr_2ZnSi_2O_7$: Eu^{2+}, Dy^{3+}

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Abstract

There has been considerable interest recently in materials which show prolonged persistent phosphorescence following short periods of excitation; the persistence has been reported in a large variety of phosphor materials including sulfides, oxides, and complex silicates and aluminates. The phosphorescence has generally been attributed to the presence of traps in most instances produced by a co-dopant ion. In this paper, we investigate the behavior of the persistent phosphorescence as a function of phosphor particle size and find that the persistence time increases as a function of decreasing particle size. The increase in time is attributable to an increase in surface trapping levels commensurate with changes in the surface to volume ratio in the phosphor particles.
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Keywords: Persistence phosphors; Size effects; Nanoparticle; Eu^{2+}

1. Introduction

There has been a revival of interest in materials which evince a long persistent luminescence or phosphorescence [1–6]. This phenomenon has been reported in a large variety of insulating materials and has most recently focused on doubly activated complex silicates and aluminates. For example, a commercially available material, Luminova, is an aluminate activated by Eu^{2+} and Dy^{3+}; it is generally thought that the Dy^{3+} ion in this material creates hole traps which are ultimately responsible for the excitation of the Eu^{2+} phosphorescence observed. Rare earth doped nano-phosphors have been also prepared and their optical properties have been investigated in recent years, such as Gd_2O_3:Yb,Er and Gd_2O_3S:Yb,Er [7], ZnS:Eu [8], and Y_2O_3:Eu [9]. Spectral shifts have been observed due to the surface/size effects [1,10]. In this paper, we have studied the behavior of the persistent phosphorescence decay as a function of particle size and find a functionality which is consistent with increase of traps as the surface to volume ratio increases with decreasing size. We report on this as well as the synthesis and optical properties of $Sr_2ZnSi_2O_7$:Eu^{2+}, Dy^{3+}.

2. Experimental

The samples were prepared using a sol-gel procedure similar to that described by Jiang and coworkers [4]. In this procedure strontium and zinc acetates and tetraethoxysilane were used as starting materials and water and methanol were selected as solvents for all the salts. Europium and dysprosium chloride were obtained by reacting stoichiometric amounts of lanthanide oxides with hydrochloric acid. The dissolved salt solutions were stirred into the tetraethoxysilane solution and the mixture was stirred vigorously at 50 °C for 2 h until a transparent solution resulted. The sol was heated at 100 °C for 24 h to form the gel; the resulting gel was crushed and heated under hydrogen atmosphere at various temperatures above 700 °C to form $Sr_2ZnSi_2O_7$: 1.0%Eu^{2+}, 1.5%Dy^{3+} of varying dimensions. Emission and excitation spectra were measured using a FluoroMax III spectrometer with Xe excitation source.

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Bulk samples were prepared by mixing the doping compounds (Eu_2O_3 and Eu_2O_3) with host ingredients ($SrCO_3$, SiO_2, and ZnO) and sintering. Powder materials of 99.99% purity were used throughout.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the resulting gel powders for different annealing temperatures. This results show that the samples possess good crystallinity and that the material synthesized has the structure of the compounded $Sr_2ZnSi_2O_7$ rather than the simpler Sr_2SiO_4. Through increased thermal mobility, the average phosphor particle size is found to increase with increased annealing temperature. The particle size dependence on temperature is illustrated in Fig. 2; as can be seen from there, we were able to synthesize particles with sizes ranging from 35 to approximately 60 nm in diameter. Particle sizes were determined using a variety of microscopes.

The emission and the excitation spectra and the room temperature afterglow decay were measured using standard spectroscopic methods. The excitation and emission spectra of $Sr_2ZnSi_2O_7$:Eu^{2+}, Dy^{3+} as a function of particle size are shown in Fig. 3. The emission spectra are largely comprised d to f transitions of the Eu^{2+} roughly peaking at 480 and 560 nm, respectively. The intensity ratio of the two peaks varies as the particle size changes, as observed in other system [10]. Time resolved spectra were also collected and detailed investigation is underway. The spectra observed is, however, in overall agreement to that observed in the bulk sample (Fig. 3(d)) and to that reported in the literature [4].

The samples were exposed to UV radiation from a xenon lamp for approximately 10 min and the decay of the resulting afterglow or persistence was recorded. The afterglow of all samples is visible to the dark adapted eye for several minutes again consistent with the literature.

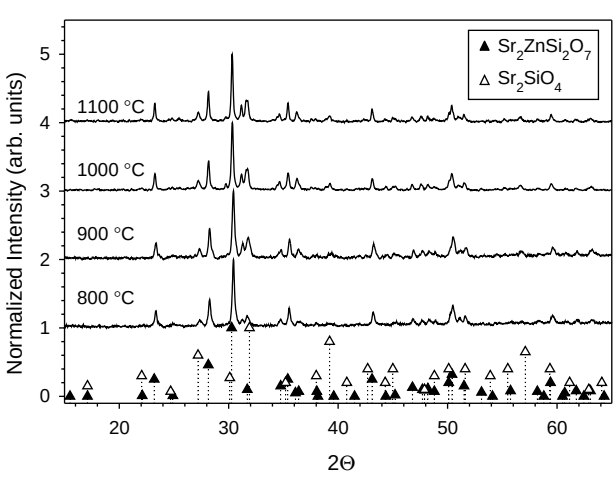

Fig. 1. X-ray diffraction patterns of the resulting gel nano-powders for different annealing temperatures (solid triangles: $Sr_2ZnSi_2O_7$; open triangles: Sr_2SiO_4).

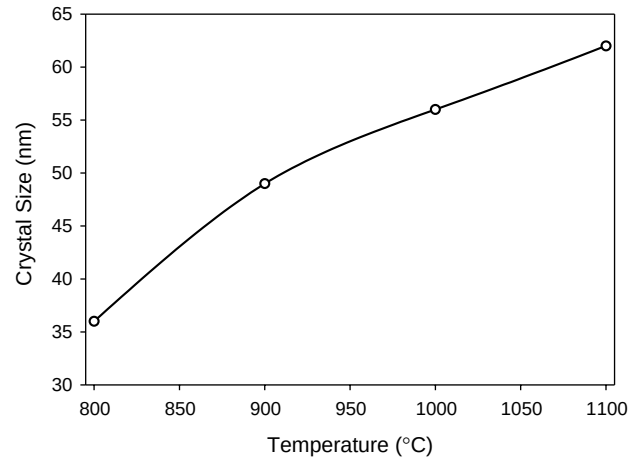

Fig. 2. The particle size dependence as a function of annealing temperature.

The decay dynamics, however, are found to be dependent on the phosphor size as can be seen from Fig. 4. It is apparent that the decay time of the persistent phosphorescence varies inversely to the sample size with the smaller sample producing both a brighter and a longer persistent decay. The bulk sample shows the shortest persistent time.

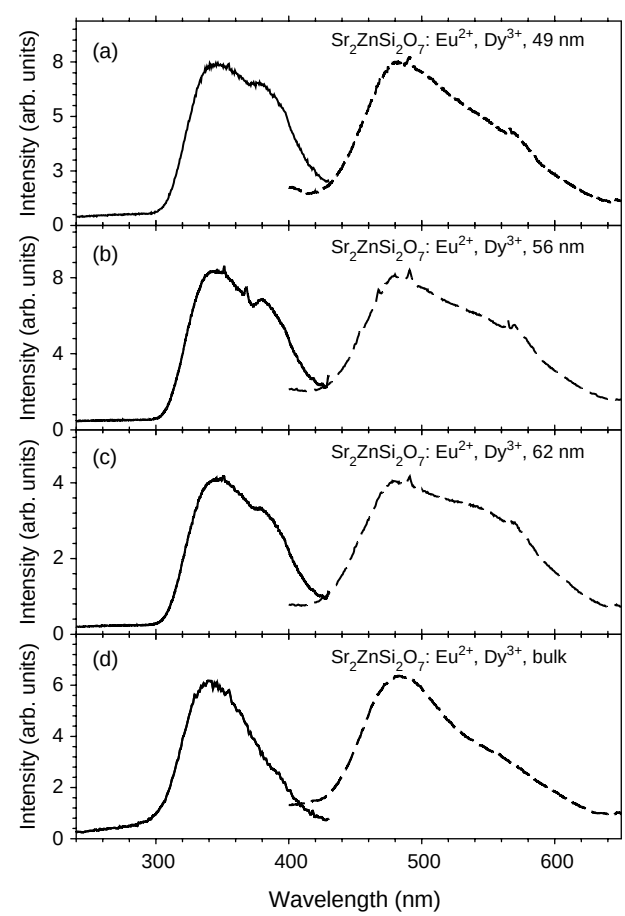

Fig. 3. The excitation (solid lines, monitoring 482 nm) and emission (dashed lines, exciting at 344 nm) spectra of $Sr_2ZnSi_2O_7$:Eu^{2+}, Dy^{3+} for different particle sizes.

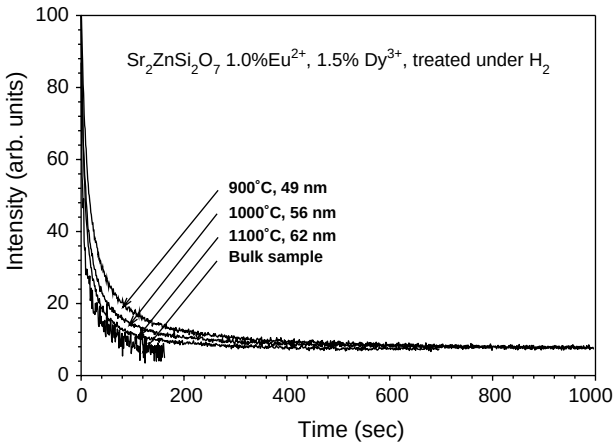

Fig. 4. The persistence time of phosphorescence for nano-particles with different sizes and for bulk samples.

This result allows us to conclude that since the persistence is directly related to the existence of trapping sites, higher brightness and longer decays are consistent with an increased number of such sites in the smaller particle materials. The surface trapping levels increase commensurate with changes in the surface to volume ratio in the phosphor particles.

4. Conclusions

In summary, we believe that this is the first study, though preliminary, of the dependence of persistent phosphorescence or afterglow properties of this class of phosphors to be carried out in nano-materials as a function of particle size. We have shown that it is possible to synthesize phosphor materials in a controllable way through the sol-gel technique and that materials grown in by this technique largely retain the optical properties of the bulk materials. The principal result from our study is that the persistence of the afterglow is visible dependent on the particle size.

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