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Emission properties of nanostructured Eu^{3+} doped zinc aluminate spinels

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Abstract

The preparation of nanostructured $ZnAl_2O_4$ spinel powders doped with Eu^{3+} ions obtained by a hydrothermal method is described. XRD analyses demonstrated that the powders were single-phase spinel nanopowders with high crystallite dispersion. The averaged spinel particle size was determined to be 6 nm as prepared and it increased up to 8 nm for calcination at 500°C. The emission spectra of Eu^{3+} ions measured for the samples calcinated at 500°C demonstrated inhomogeneous shapes characteristic for disordered material which after heating at 1500°C changed shape into an ordered shape characteristic of the crystalline form.

Keywords: Eu^{3+} doping; $ZnAl_2O_4$ spinel powders

1. Introduction

Since the discovery by Bhagrava and Galagher [1] that nanosize semiconductors doped with lanthanides demonstrate significant enhancement of radiative transitions, one observes an increasing interest in studies of lanthanide-doped nanocrystalline materials with particle diameters less than 100 nm. Such an effect may find potential applications in designing optoelectronical materials and also as efficient phosphor materials for flat-panel displays. It was found that decreasing nanoparticle sizes increases their emission efficiency in contrast to the microscale powders.

The emission properties of the Eu^{3+}-doped γ-Al_2O_3 were reported by Felofilov et al. [2]. The effect of the shape of nanocrystalline particles on emission properties of Eu^{3+} in Al_2O_3 was reported by us [3].

Zinc aluminate $ZnAl_2O_4$ spinels are widely used as catalytic, ceramic (or glass ceramic) and electronic materials [4–6]. The optical properties of pure zinc aluminate spinels prepared by the solid state route were reported by Sampath et al. [7], however to our knowledge only the transition metal ion-doped $ZnAl_2O_4$ spinels were investigated. For instance the optical properties of the Cr^{3+}-doped $ZnAl_2O_4$ spinel obtained by traditional ceramic processing followed by calcination at relatively high temperatures were studied by Nie et al. [8]. No rare-earth-doped zinc aluminate spinels were reported.

Recently, a new method of synthesis of the zinc aluminate spinel has been developed which seems to be very useful for obtaining a nanosize and nanoporous material of a spinel structure with a high surface area [9–11]. Those properties make them interesting as a host lattice for active systems like rare earth ions.

In this paper we report the emission properties of Eu^{3+} in nanostructured zinc aluminate spinel $ZnAl_2O_4$ powders.

2. Experimental

2.1. Synthesis

A nanocrystalline and nanoporous zinc aluminate matrix with high specific surface area and narrow pore size distribution was obtained under hydrothermal conditions. The starting materials for the synthesis were basic aluminium nitrate and hydrated zinc acetate. Basic aluminium nitrate (empirical formula: $Al_2(OH)_{6-x}(NO_3)_x$ where x was close to 1) was obtained by hydrolysis of powdered aluminium metal in aqueous solution of aluminium nitrate at elevated temperature for some days.

The mixture which was used for the synthesis was prepared in the following manner: an appropriate amount of zinc acetate was gradually added to the aqueous solution of basic aluminium nitrate to form a homogeneous mixture in which the molar ratio of Al:Zn was close or equal to 2:1. After that, a steel autoclave of 300 ml capacity was filled with the mixture up to 80% of the total volume. The autoclave was sealed and maintained, with continuous stirring of the reaction mixture, at 430 K for 4 h. After

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quenching the autoclave in cold water, the obtained sol was used as a precursor for the zinc aluminate matrix.

Europium was introduced into the zinc aluminate matrix in two ways. First, CH_3COOH solutions of europium oxide with concentration calculated to obtain the desired amount of Eu in the zinc aluminate matrix were prepared.

In the first way, the europium solution was added into the zinc aluminate sol. The sol was then air dried and calcined at 773 K and 1273 K to obtain the well crystallised $ZnAl_2O_4$ matrix containing 1 wt.% Eu.

In the other way, the zinc aluminate matrix was first formed from a previously dried and heated sol. Europium was introduced by the impregnation method – the matrix was immersed in europium solution, then dried and heated again at the same temperatures.

2.2. Characterization

An XRD analysis showed that samples prepared through the hydrothermal process were a single-phase material – the $ZnAl_2O_4$ spinel. The broadening of the diffraction peaks indicates the nanocrystalline size of the samples. Calculated from the half-width of diffraction peaks using Schererr's formula, they were 8 and 15 nm for samples heated at 500°C and 1000°C, respectively.

The presence of europium in the zinc aluminate matrix was confirmed by an EDAX analysis.

The size and shape of the prepared and calcined spinel sample particles were investigated by TEM. It was found that the morphology of hydrothermally prepared samples is homogeneous, and that the spinel particles consist of uniform quasi-spherical crystallites of an average size, consistent with whose obtained from the XRD patterns.

The textural properties of zinc aluminate matrixes obtained from nitrogen adsorption/desorption isotherms are collected in Table 1.

2.3. Emission measurements

Emission spectra were measured at room temperature on a Jobin-Yvon spectrophotometer using as the excitation source a Lambda Physics excimer laser operating at 308 nm. The spectra were measured at room and liquid nitrogen temperatures.

Emission lifetimes were measured using a Jobin-Yvon THR 1000 spectrophotometer, a Hamamatsu R928 photomultiplier as a detector and a digital oscilloscope Tektronix TDS 380 for data collection. The decay curve deconvolution was done with PSIPLOT software.

Table 1
Surface area (S_{BET}), pore size (r_p) and volume (V_p) of the $ZnAl_2O_4$ matrix heated at different temperatures

Heating temperature (K)	S_{BET} (m^2/g)	V_p (cm^3/g)	r_p (nm)
773	240	0.18	1.9
1273	32	0.06	3.1

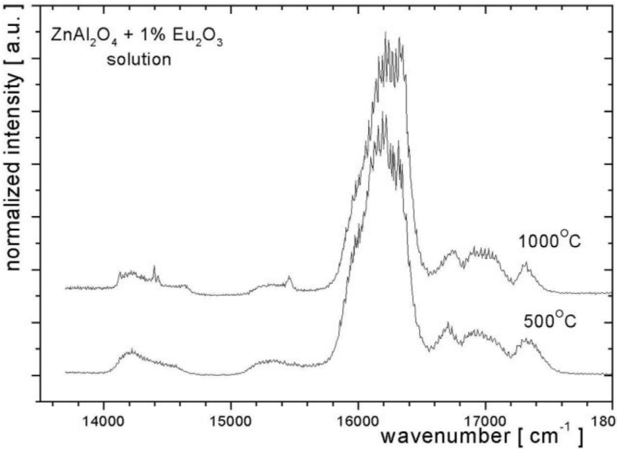

Fig. 1. Emission spectra of nanostructured $ZnAl_2O_4$ spinels doped with Eu^{3+} ions obtained from solution. The samples were calcined at 500°C and 1000°C and the spectra were measured at room temperature.

3. Results and discussion

The emission spectra of nanoparticle $ZnAl_2O_4$ spinels were measured for samples heated at 500°C. The emission spectra of the powders were measured at room temperature and are shown in Figs. 1 and 2. The assignment of the transition bands is given in the figures.

The spectra of samples heated at 500°C have demonstrated broad bands. A band broadening is typical for disordered systems and is due to multisite distribution. The intensity ratios of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition band to the $^5D_0 \rightarrow {}^7F_1$ transition band were determined and are listed in Table 2. One can note that the intensity

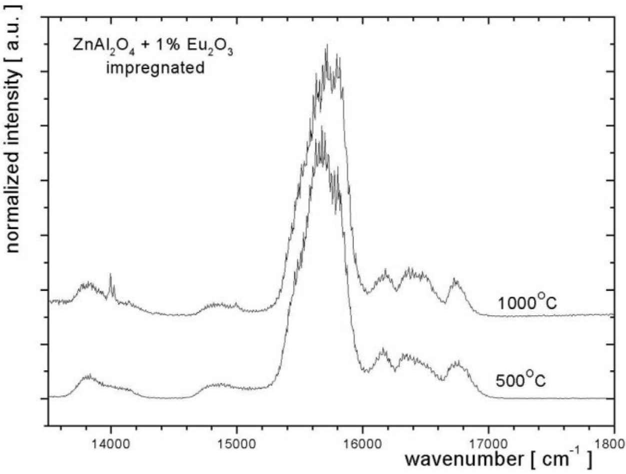

Fig. 2. Emission spectra of nanostructured $ZnAl_2O_4$ spinels doped with Eu^{3+} ions obtained by impregnation. The samples were calcined at 500°C and 1000°C and the spectra were measured at room temperature.

Table 2
Fluorescence branching ratios and fluorescence lifetimes of $ZnAl_2O_4$ spinels doped with Eu^{3+} obtained by different preparation methods

Material		Temperature of preparation	Branching ratio I_{0-2}/I_{total}	Lifetime (ms)
		500°C	68.1	0.90
$ZnAl_2O_4$ + 1% Eu_2O_3	Gel	1000°C 3 h	68.9	1.10
		500°C	70.3	0.88
	Impregnated	1000°C	70.4	1.25

branching ratios were somewhat higher for the impregnated samples and they did not change very much with increasing up to 1000°C calcination temperature.

The spectra measured for the powders obtained after heating at 1000°C were substantially different. We could note some additional sharp and well resolved lines characteristic to the ordered crystalline systems.

We have measured also the emission decay times (see Table 2). We have observed a significant enhancement of the decay times for the samples obtained from gels (by almost 20%) as well as for the impregnated ones (by almost 40%).

The nature of the Eu^{3+} ions which are doping the nanoparticle $ZnAl_2O_4$ spinels seems to be complex. They may substitute the trivalent Al^{3+} ions or divalent Zn^{2+} ions. As one knows the RE^{3+} and Al^{3+} ionic radii demonstrate significant differences. Moreover the Eu^{3+} ions can be occluded on surfaces of the nanoparticles due to the porosity of the spinel. It seems that the second possibility is the most probable one, because we have noted that the structure of the emission spectra was almost the same for the nanoparticles synthesised in the gel process and prepared by impregnation.

4. Conclusions

Nanocrystalline $ZnAl_2O_4$ spinels doped with Eu^{3+} ions were prepared by two different doping techniques. The morphology of the obtained nanostructural matrices was studied. The size of the nanocrystallites was determined to be 8 and 15 nm for crystallites heated at 500°C and 1000°C, respectively. It was found that the emission properties of Eu^{3+} were not dependent on the doping techniques. It means that the Eu^{3+} ions are occluded in pores on surfaces of the spinel particles. However a significant prolongation of emission lifetimes for samples heated at higher temperature was noted. Such behaviour can be explained by size effect of nanocrystallites or reduction of nonradiative decay channel. Further spectroscopic investigations of the emission nature of Eu^{3+} ions in nanocrystallites observed in the annealed samples are in progress.

Acknowledgements

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