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Synthesis and characterization of Y_2O_3:Nd^{3+} nanocrystalline powders and ceramics

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ABSTRACT

In this work, we report on Nd^{3+}-doped Y_2O_3 nanocrystalline powders synthesized by standard Pechini and combined Pechini-foaming method. The structural and luminescence properties of nanocrystalline powders were studied using XRD, SEM, Raman and photoluminescence spectroscopy. Doping concentration effect on the luminescence intensity and lifetime of Y_2O_3:Nd^{3+} nanophosphors was investigated in detail. The optimum doping concentration of Nd^{3+} ions in yttria host was determined to be 1 at.%. Steady-state and kinetics photoluminescence properties of starting nanocrystalline powder and ceramics obtained with hot pressing were measured and discussed.

1. Introduction

Transparent ceramics have been attracting much attention in the fields of scintillators and solid-state lasers for the past decade. Compared with single crystals, ceramic materials have many advantages including wider range of compositions, improved mechanical properties and processability, lower cost of fabrication, etc. [1–4]. Moreover, ceramic materials have possibility of fabricating large size samples with multi-layer and multi-functional ceramic structure [5].

Ultra-disperse systems with particles sizes of 1–100 nm are the most promising precursors to form optical ceramics. However, due to highly developed surface, the obtaining of disperse materials is complicated by several factors. One of them is a spontaneous enlargement of particles in such an unstable system, which decreases surface energy. It is well known that aggregation process takes place during synthesis, storage and usage of the disperse material. Synthesis of separate crystalline oxide compounds is supposed to be one of the most difficult tasks.

Yttrium sesquioxide Y_2O_3 is an excellent optical material that has been extensively used for functional applications in photonics, optoelectronics, laser and scintillation techniques [6]. This material possesses unique properties such as high melting point (2430 °C), broad range of transparency (0.17–8 μm), high corrosion resistance, thermal stability and high isomorphic capacity for introduction of luminescent ions [7].

This work is devoted to the synthesis and study of the Nd^{3+}-doped nanocrystalline yttrium oxide powders, which was used as a precursor for laser ceramics. For effective process of material hardening the precursor should consist of agglomerates, which can be easily deformed. The agglomerates represent a great number of crystalline nanoparticles with different adhesion between each other. During the ceramics formation the crystalline structure undergoes changes in surroundings of a rare earth ion of short and long range orders. It leads to the changes of luminescent properties which is a matter of interest and considered in this work.

2. Experimental

Nd^{3+}-doped Y_2O_3 nanocrystalline powders were synthesized by

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the standard Pechini and combined Pechini-foaming method. Sol-gel techniques were chosen due to the uniform distribution of metal ions in the sample (at the molecular level), which prevents coarsening of the particles during heat treatment. Studying of the yttrium oxide synthesis by Pechini method allowed to modify the technique for obtaining the weakly-agglomerated precursors for the optical ceramics [8,9]. In Pechini method the product is obtained after the thermal treatment of the polymer gel which can be defined as a structured colloid system. Boundaries between particles are destroyed during the gel annealing, which leads to the strong agglomeration of derived samples. To prevent particles agglomeration, combined Pechini-foaming method includes phase of intense gas release. For this purpose, before the polymer formation a foaming agent was introduced into the system to fill the structural net of the gel. The mixture of aluminum nitrate and potassium chloride was chosen as a foaming agent in Y_2O_3 synthesis. Briefly, combined Pechini-foaming method can be described as follows. $Y(NO_3)_3$ and $Nd(NO_3)_3$ prepared by dissolving of Y_2O_3 and Nd_2O_3 in nitric acid were used as initial salts for the synthesis process. Then $Al(NO_3)_3$, saturated solution of citric acid in distilled water (volume ratio 1:1), and the potassium chloride powder were added. This mixture was heated up to 150–200 °C and as a result the chelate complexes were formed. The solution was transformed into polymer gel after the etherification reaction, and then the gel was annealed at 1000°C during 90 min to remove organic components. Y_2O_3 nanoparticles with homogeneously distributed Nd^{3+} ions were obtained; the reaction byproducts were removed by washing in weak NaOH solution. The resulting washed samples were dried naturally.

Y_2O_3:Nd^{3+} 1 at.% powders were synthesized using both the standard Pechini and combined Pechini-foaming method, whereas the concentration series of Y_2O_3:Nd^{3+} particles (0.01–2 at.%) was prepared using the combined Pechini-foaming technique. The synthesized powder samples (5 mg) and potassium bromide (300 mg) were pressed into pellets (diameter 13 mm) for luminescence studies.

In this work the uniaxial hot pressing was carried out. The pressing is first stage of ceramics samples formation. The formation is necessary to set the material density, shape, size, mechanical strength. The hot pressing process was carried out in a vacuum chamber with a molybdenum press form. The temperature and pressure were 1450 °C and 100 MPa, respectively, the sample density ratio was obtained to be 98–99%.

X-ray diffraction patterns were measured with the powder diffractometer UltimaIV (Rigaku) in Bregg-Bretano geometry with CuKα1 radiation (λ = 1.54059 Å) in the 2θ range from 10° to 70°. Phase identification was carried out using a powder diffraction database Powder Diffraction File (PDF-2, 2011). Electron micrograph images were obtained with Zeiss Supra 40VP scanning electron microscope (resolution 4 nm). Raman spectra were collected with Bruker SENTERRA Raman Microscope with semiconductor laser 488 nm as an excitation source. Steady-state luminescence spectra were recorded with a fluorescence spectrometer Fluorolog-3 equipped with a Xe-arc lamp (450 W power). Luminescence decay curves were obtained using Xe-flash lamp (150 W power, 3 μs pulse width) as an excitation source. All structural and luminescence measurements were performed at the room temperature.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD patterns of Y_2O_3:Nd^{3+} 1at.% nanocrystalline phosphors synthesized by standard Pechini and combined Pechini-foaming methods. As it can be seen, all the peaks in diffraction patterns coincide with cubic phase of Y_2O_3 (JCPDS 41-1105). No impurity phase was detected. It should be noted that diffraction lines of sample prepared by combined Pechini-foaming technique are narrower comparing with sample synthesized by standard Pechini method. The average size of coherent scattering region (crystallite size) can be calculated using the Scherer's approach [10]:

$$D = \frac{0.9\lambda}{cos\theta\sqrt{\beta^2 - \beta_0^2}} \quad (1)$$

where D is an average size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; λ is the X-ray wavelength; β is the full width at half-maximum (FWHM) of a diffraction line located at θ in radians; θ is the Bragg angle; β_0 is the scan aperture of the diffractometer. Calculated average crystallite size (coherent-scattering region) of Y_2O_3:Nd^{3+} 1 at.% samples was determined to be about 24 and 37 nm for standard Pechini and combined Pechini-foaming method, respectively. Larger coherent-scattering region in case of combined Pechini-foaming method can be explained by faster crystalline structure formation of oxides in molten salt [11]. Thus, we obtained two different disperse structures: the powder consisting of small particles with strong connections and forming big agglomerates, and the powder formed of well-defined single nanoparticles with weak connections. Big agglomerates have smaller coherent-scattering region while nanoparticles have more perfect crystalline structure.

Fig. 2 presents SEM image of Y_2O_3:Nd^{3+} 1 at.% powders synthesized by different methods. Nanocrystalline powder prepared using standard Pechini technique consists of stable agglomerates of several microns (Fig. 2a). Calcination with foaming agent into polymer gel matrix prevents strong agglomeration of synthesized particles. Therefore, nanophosphors synthesized by combined Pechini-foaming technique consist of weakly agglomerated small spherical nanoparticles with average size about 40 nm (Fig. 2b). Weak agglomeration can be confirmed by precise contours of the particles on the surface of agglomerates and possibility of such nanoparticles to form colloidal solutions [8].

Fig. 3 presents normalized Raman spectra of Y_2O_3:Nd^{3+} 1 at.%

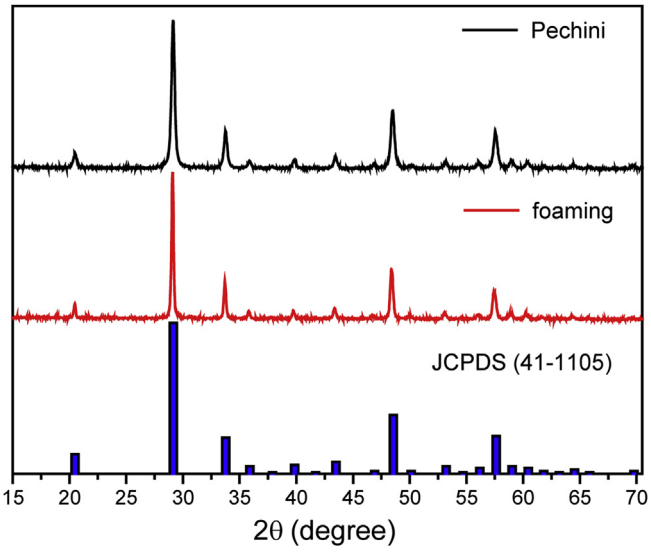

Fig. 1. XRD patterns of Y_2O_3:Nd^{3+} 1 at.% nanocrystalline powders synthesized via standard Pechini and combined Pechini-foaming methods and Y_2O_3 standard card.