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Homogeneously precipitated Lu_2O_3:Eu nanocrystalline phosphor for X-ray detection

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Abstract

Nanocrystalline Lu_2O_3 doped with 1 at.% of Eu was obtained precipitating hydroxide of lutetium with urea at 80 °C from water solution and decomposing the hydroxide to oxide at 500 °C. Polyvinyl alcohol was used to hinder the particles growth during precipitation. The average size of the fabricated particles was 2–5 nm. Although at 500 °C the hydroxide decomposed to Eu-doped Lu_2O_3 traces of OH impurities were present in the material unless heated at 1200 °C. Radioluminescence was very poor for samples heated at 800 °C or lower temperature. After heating the precipitated powder at or above 1200 °C the efficiency jumped 45 times reaching 75% of the output from commercial microcrystalline Gd_2O_2S:Eu. The properties make nanocrystalline Lu_2O_3:Eu prepared in the described way a promising X-ray phosphor for planar digital medical imaging.

Keywords: Nanocrystalline phosphor; Lu_2O_3; Radioluminescence; Medical imaging

1. Introduction

During the last decade lutetium oxide activated with other lanthanides became a widely investigated material [1–8]. Lutetia is considered one of the most attractive host lattices for novel X-ray detectors. What makes the material especially attractive for such applications is its exceptionally high density of 9.42 g/cm^3 and the high atomic number of Lu ($Z = 71$). The combination of the two parameters makes Lu_2O_3 very efficient in absorbing any kind of ionizing radiation [9]. What is more, the absorption of photons of ionizing radiation occurs preferentially through so called photoelectric absorption process, and not through Compton scattering [10]. This is strongly preferred situation as it significantly reduces blurring of images [1,9,10]. Indeed, Nagarkar et al. [11] and Farman et al. [12] showed that a Lu_2O_3:Eu screen can produce images, whose quality may surpass those obtained using the standard X-ray Gd_2O_2S:Tb phosphor. Furthermore, the Eu^{3+} emission from lutetia host appears in the region of the highest quantum efficiency of CCD cameras, which falls within 550–800 nm. This makes lutetia-based materials especially promising for planar digital real-time imaging with a CCD detector. For such a purpose either sintered transparent ceramics or powdered Lu_2O_3:Eu could be of great interests [1,9,11].

Lempicki et al. [1] proved that sintered ceramics need to be pixilated to be able to create good quality images. Unfortunately, fabrication of large plates of such ceramics is not an easy task and right now such ceramics are considered more appropriate for dental application, where the size of the imaging tool is obviously small. For imaging of larger objects, screens made using nanocrystalline non-agglomerated powders could be a better solution. Comparing to the presently used in the film-screen technique microcrystalline Gd_2O_2S:Tb, nanocrystalline Lu_2O_3 doped with appropriate activator could bring at least two important advantages. Firstly, since the absorption coefficient for X-ray radiation of lutetia is higher than for Gd_2O_2S the screen thickness could be reduced accordingly. This would directly translate into reduction of images blurring since the overall scattering would

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be reduced. Secondly, nano-sized grains scatter light to much lesser degree than their micron-sized counterparts since the emitted light wavelength is much longer than the size of crystallites within which the luminescence is created. Thus if only appropriately activated Lu_2O_3 could be produced in the form of nanocrystalline material of high light output under X-ray stimulation such a phosphor could be of interests for CCD-based digital planar real-time imaging systems [11]. In this paper we shall present results of our efforts in making of such a phosphor material.

2. Materials and experiments

Fabrication of investigated Lu_2O_3:Eu phosphors was based on precipitation of lutetia hydroxides with urea from water solutions heated up to about 80 °C. In such conditions urea, $CO(NH_2)_2$ decomposes to ammonia and carbon dioxide. As a result the solution pH steadily increases and metals hydroxides continuously precipitates. To hinder the particles growth some polyvinyl alcohol (PVA) together with toluene were added to the water solution containing $Lu(NO_3)_3$, $Eu(NO_3)_3$ and urea. The amount of Eu was set at 1 at.% with respect to Lu. PVA works here as a surfactant. Small addition of Li_2SO_4 was routinely used as it was found to increase the amount of formed precipitate noticeably. The process was carried on for 24 h under continuous stirring. After cooling the product was separated by vacuum filtering and washed thoroughly with warm water and finally with acetone. Then the powder was dried using ultrasonic baths and finally the product was dried for a few hours at 150 °C. Afterwards, the produced powder was a subject of thermal treatment at various temperatures in the range of 500–1400 °C. For comparative measurements of X-ray excited emissions we used Gd_2O_2S:Eu commercial phosphor kindly supplied by G. Sorce from Phosphor Technology, GB. The average size of crystallites of this material was 3 μm.

The thermal analysis was performed in the range of 20–900 °C under nitrogen atmosphere using the SETSYS 16/18 system manufactured by SETARAM. The heating rate was 10 °C/min. X-ray analysis were performed with a DRON-1 diffractometer, using Cu Kα radiation (λ = 1.5418 Å) filtered with Ni. The diffractograms were recorded with a step of $2\theta = 0.1^\circ$ for the range of $2\theta = 10$–120°. The Scherrer's relation, Eq. (1), was used to estimate the crystallites size [13].

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

In this equation D is an average crystallite size, λ denotes the X-ray radiation wavelength, β a full-width at half maximum of a diffraction line located at θ and β_0 represents a scan aperture of the diffractometer. High resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were taken with the Philips CM20 Super Twin microscope operating at 200 kV and providing 0.25 nm resolution.

Photoluminescence and excitation spectra were recorded using a SPF 500 Spectrofluorimeter equipped with a 300 W Xe-lamp with a sapphire window and an Al-coated parabolic reflector. The emission monochromator was equipped with a 1200 line/mm ruled grating blazed at 500 nm. The excitation monochromator used a 1200 line/mm holographic grating optimized for 250–300 nm. Emission spectra were taken with 0.25 nm resolution. Emission spectra were not corrected for the setup characteristics, and the sensitivity of the detection system (PMT-grating) was highest in the range of 400–750 nm. For selected samples high-resolution luminescence spectra in the range of 570–605 nm were recorded at liquid nitrogen temperature using a SpectraPro-750 analyzing monochromator.

X-ray excited emissions were recorded using the white X-ray radiation from a Cu lamp of a DRON-1 diffractometer, the same one which was used for XRD measurements. A lab-made sample holder was used and the spectra were recorded in a reflection geometry using an OceanOptics HR2000CG-UV-NIR spectrometer equipped with a 600 μm fiber optic and a 25 μm slit. The spectrometer resolution was about 1.3 nm.

3. Results and discussion

The fabricated powders are very fine and fluffy. Heating at various temperatures, even at the highest 1400 °C, do not stimulate the material particles to sinter and the powder stays very loose. This is a very important property, highly advantageous for making uniform screens.

The thermogravimetric analysis presented in Fig. 1 proves that the material looses a significant amount of mass in the 20–450 °C range of temperature. A detailed analysis indicates that the raw material is hydrated lutetium hydroxide containing 3–4 molecules of water. The uncertain number of water molecules cannot surprise since the extremely high surface of

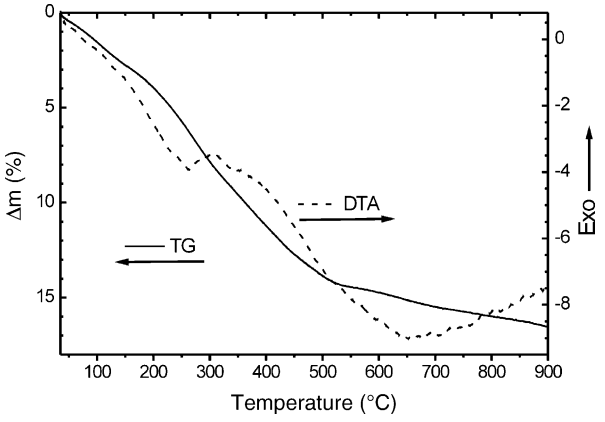

Fig. 1. Thermogravimetric analysis of the raw material dried at 150 °C. Although the main decomposition finishes around 500 °C leading to the formation of Lu_2O_3, still some loss of mass occurs up to 900 °C.