Optical Materials 75 (2018) 662–665

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Structural properties of Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowders: Far-infrared spectroscopy

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ARTICLE INFO

Article history:
Received 2 October 2017
Accepted 15 November 2017

Keywords:
$Gd_2Zr_2O_7$
Eu^{3+}
Nanopowders
Phonons
Light absorption and reflection

ABSTRACT

The Solution Combustion Synthesis (SCS) method was used to prepare nanopowders of europium doped cubic $Gd_2Zr_2O_7$ nanopowders. The surface of the samples have been investigated using atomic force spectroscopy (AFM) and far-infrared spectroscopy (FIR). Far-infrared reflectivity spectra of Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowders were measured at room temperature in spectral region between 80 and 650 cm^{-1}. The Maxwell–Garnet formula was used to model dielectric function of Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowders as mixtures of homogenous spherical inclusions in air.

1. Introduction

$A_2B_2O_7$ type of pyrochlores are important class of materials because of their diverse scientific and technological applications like in nuclear waste storage [1], electro/photo catalysis [2,3], luminescence [3], CO_2 hemisorption [4], photoluminescence hosts [5], topological Mott insulator [6] etc.

Pyrochlore oxides which occur in various crystalline phases, manifest numerous interesting and important physicochemical properties which make them eligible for potential hosts for the chemical substitution [7].

Rare earth based zirconates ($Re_2Zr_2O_7$) pyrochlores have wide scientific and technological applications as: potential thermal barrier coatings (TBC), high temperature heating devices or luminescence hosts [8].

Among all rare earth based pyrochlores, $Gd_2Zr_2O_7$ stands out as a material with a distinctively low thermal conductivity and high phase stability [9]. Besides that, $Gd_2Zr_2O_7$ could be an excellent candidate for potential photoactive materials [10].

As shown through our previous work [4,11], there are two different crystal structures for $Gd_2Zr_2O_7$, pyrochlore and the fluorite type.

Rare earth ions are widely used as activators for various phosphors and other organic and inorganic luminescent materials, because they offer high color purity, high luminescence lifetime and also a narrow emission profile, thanks to its optically active 4f electrons which are strongly shielded from the rest of ions by the other 5s and 5p shells [12].

Among all lanthanides, Eu^{3+} ion is in advantage as a dopant ion for structural probing, as well as for synthesis of red light emitting phosphor [8]. The reason this ion is a useful spectroscopic probe is because of its main source of luminescence - single level, $^5D_0$ state, which prevents the convolution of overlapping emission peaks from different levels [13]. Also, doping any aliovalent ion in these oxides is not only used for structural probing, but it could also generate significant changes in photophysical behavior of those materials in such way that doping creates various kinds of defects like ion/oxygen vacancies, which can alter the band gap of materials, i.e. photophysical characteristics of one material. Particularly for $Gd_2Zr_2O_7$, it is proven that efficient doping results in tuning of thermal [14], electrical [15], optical [4] and other properties.

In this paper, we present the results obtained by using far – infrared spectroscopy (FIR) to study optical properties of the Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowders which were prepared by the Solution Combustion Synthesis (SCS) method. The dielectric function of Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowder is modeled as a mixture of

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https://doi.org/10.1016/j.optmat.2017.11.026
0925-3467/

homogenous spherical inclusions in air, by the Maxwell-Garnet formula.

2. Sample and characterization

Europium doped cubic $Gd_2Zr_2O_7$ nanopowders were prepared by Solution Combustion Synthesis (SCS) method. Starting chemicals $Gd(NO_3)\cdot 6H_2O$, $Zr(NO_3)_2\cdot H_2O$, $Eu(NO_3)\cdot 6H_2O$ with the purity of 99,99% were purchased from ABCR, Gd_2O_2 (99,9%) from the NOAH Technologies and urea $(NH_2)_2CO$ from Sigma-Aldrich.

Due to its simplicity and low cost of the synthesis procedures and possibility of tailoring the size and morphology of particles, the flame combustion process is the most frequently used. After the synthesis, the nanopowder was annealed, in order to achieve the full crystallinity, in air atmosphere at 1200 °C for 2 h. The Eu^{3+} concentration in $Gd_2Zr_2O_7$ was 2 mol%. The morphology analysis of the synthesized materials indicates the irregular crystallite size distribution and existence of agglomerated grains which are in the submicron size.

In our previous work [4,11] we performed X – ray powder diffraction (XRD) and photoluminescence measurements of the same material. XRD analysis confirmed that sample was crystallized in fluorite (F) type structure (space group Fm3m). The photoluminescence spectra showed a number of electronic transitions, among them were those at 705 nm and 713 nm ($^5D_0 - {}^7F_4$), 654 nm ($^5D_0 - {}^7F_3$), 630 and 611 nm ($^5D_0 - {}^7F_2$), 593 nm ($^5D_0 - {}^7F_1$), 584 nm ($^5D_0/^5D_1 - {}^7F_1$) and 578 nm ($^5D_0/^5D_1 - {}^7F_0$).

The Raman spectra of Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowders were measured. We registered three phonons at 177 cm^{-1}, 268 cm^{-1} and 592 cm^{-1}, as well as their overtones at 354 cm^{-1}, 445 cm^{-1}, 708 cm^{-1}, 1062 cm^{-1}, 1184 cm^{-1}, ~1530 cm^{-1} and ~1720 cm^{-1}. The phonon at 592 cm^{-1} was already known to be characteristic for $Gd_2Zr_2O_7$ fluorite – type structure, and we found that other two phonon positions to be characteristic with the observed electron – phonon observed interaction and that the registered multiphonon processes were a consequence of miniaturization that further induces changes in electronic structure of Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowders. All the above mentioned results will be useful in the far – infrared spectroscopy analysis of Eu^{3+} doped $Gd_2Zr_2O_7$ nanopowders.

3. Results and analysis

3.1. AFM

Atomic force microscopy (AFM) measurements were done using NTEGRA Prima system from NT-MDT at room temperature and ambient conditions. Imaging was done in tapping mode using NSG01 probes. Phase lag of AFM cantilever was recorded simultaneously during tapping mode imaging.

Two dimensional and three dimensional topography of the sample surface are shown in Fig. 1(a) and (b), respectively (scan size is 5 × 5 μm^2). As can be seen, the surface is rather flat with characteristic holes represented with dark color. Cross section of one characteristic hole (along dashed line in Fig. 1(a)) is given in the inset of Fig. 1(a). Hole width and depth are around 1 μm and 200 nm, respectively. Apart from this holes, the sample surface consists of small grains. They are better visualized in Fig. 1(c) and (d) showing the topography and phase contrast image of a zoomed part (scan size is 1 × 1 μm^2). Grains are clearly visible, especially

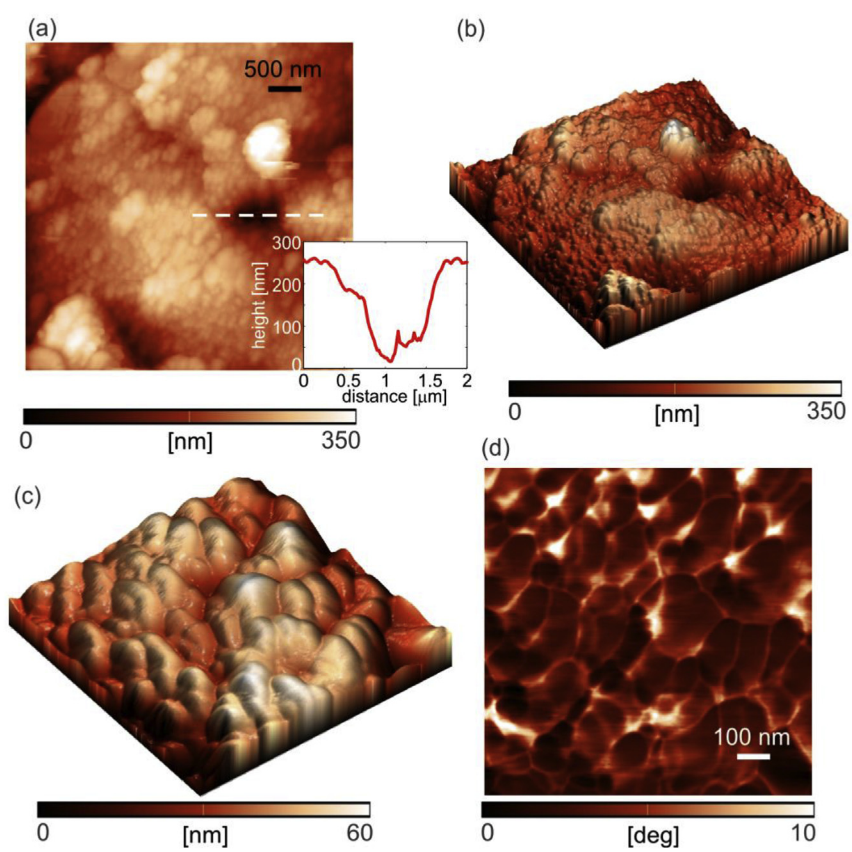

Fig. 1. (a) Two-dimensional and (b) three-dimensional topography of the sample surface. The inset in part (a) shows the cross-section along the corresponding dashed line. (c) Three-dimensional topography and (b) corresponding phase contrast image of a zoomed region from part (a).