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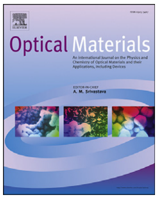

Synthesis, structure and spectroscopic properties of luminescent $GdVO_4:Dy^{3+}$ and $DyVO_4$ particles

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ABSTRACT

In this work, we focused on the syntheses, structure and spectroscopic properties of $GdVO_4:Dy^{3+}$ and $DyVO_4$ (nano)particles of different sizes and shapes (spherical nanoparticles of 2 nm, 4 nm, and 20 nm in size, nanorods with a few nanometers in diameter and up to 10–20 nm in length and microparticles of 1–8 μm) obtained by four synthetic methods. The size effect on the structure, Raman active modes, and photoluminescence emission intensities was analyzed by X-ray diffraction, Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and diffuse reflection spectroscopy. All X-ray diffraction patterns clearly indicated presence of a single tetragonal zircon-type phase; absence of impurity phases indicate that the dopant Dy^{3+} ions were successfully and uniformly incorporated into the $GdVO_4$ host lattice due to the equal valence and similar ionic radii. Micro-Raman measurements support the XRD measurements and showed Raman-active modes of the $REVO_4$ systems (RE = Gd, Dy). The difference between the two hosts in the diffuse reflectance spectra was observed and it could be attributed to more effective Gd^{3+} ions on the charge transfer bands and different polarization (compared to bulk material) in smaller nanoparticles. Photoluminescence spectroscopy showed several bands in the visible and near-infrared regions which can be exclusively attributed to the f–f transitions of Dy^{3+} ions.

1. Introduction

Lanthanide (Ln)-doped luminescent inorganic materials play an important role in everyday life due to their unique structural and physicochemical properties, in particular, optical properties which make them potentially useful in a wide range of applications. These materials, both microcrystalline and nanocrystalline, can exhibit down-conversion or up-conversion luminescence under ultraviolet (UV) or near-infrared (NIR) excitation, depending on the selected dopant ions and crystal structure of the host material. Ln-doped phosphors are primarily used in conventional, novel, and emerging display and lighting technologies and their advantages include high energy conversion efficiency, purity in spectral colors, strong emission and high thermal stability and conductivity [1–4].

Rare-earth orthovanadates with general formula $REVO_4$ (where RE is a rare-earth element, including lanthanoids from La to Lu as well as Y and Sc) have proved to be good host lattices for optically-active trivalent Ln ions. Due to the same valence, similar ionic radii, ectronegativities and electronic structures between RE ions in a host and dopant ions, doping is possible in a wide range of concentrations without much affecting the lattice structure. Such materials exhibit intense luminescence emission caused by an efficient energy transfer from the vanadate groups to Ln ions, and

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wide colour tuning is easily made by selection of dopant ions. Both undoped and Ln-doped $REVO_4$ nanostructures have been extensively studied as an important class of multifunctional materials which are very attractive for different applications such as phosphors, optical polarizers, laser host materials, scintillators, and photocatalysts [5–8].

By appropriate selection of a matrix, Dy^{3+}-doped materials show excellent luminescent properties due to a large number of closely spaced energy levels in the visible (Vis), NIR and mid-infrared (Mid-IR) spectral regions. In the Vis region, Dy^{3+} generally have two dominant emission bands. One is the blue band due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition, while another is the yellowish band due to the hypersensitive $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. Since Dy^{3+} ions are among several the NIR and Mid-IR emitting Ln ions, Dy^{3+} -based materials have been studied as potentially useful in the NIR and Mid-IR region, in particular, in construction of Mid-IR lasers and amplifiers [9,10].

It is well known that all physical, chemical, mechanical and optical properties are size-dependent in nano-scale range. The nanomaterials generally are showing reduced quantum efficiency of emission in small-size particles. Up to now, the size effect on photoluminescent properties of several different materials has been studied [11–13].

Herein, our focus was mainly on the syntheses, structure and spectroscopic properties of luminescent $GdVO_4:Dy^{3+}$ and $DyVO_4$ (nano)particles of different sizes and shapes. In particular, with a view to incorporating Dy^{3+}- containing nanoparticles in silica waveguides, it was interesting to assess their luminescence performance in the NIR region. $GdVO_4$ was used as a host for Dy^{3+} ions because of several reasons: an easy doping, high absorption cross section, low phonon energy, efficient energy transfer from VO_4^{3-} group to the Dy^{3+} ions, low sensitivity to humidity, high melting point (~1800 °C), and high potential for multi-functional applications [7,8]. Unlike $GdVO_4$, $DyVO_4$ is relatively less studied and only dozen or so reports on it are available in the recent literature [14].

2. Experimental

2.1. Materials and methods

Two different series of powdered samples, S1 and S2, respectively, of $GdVO_4:Dy^{3+}$ and $DyVO_4$ with different particle sizes were synthesized by four different methods: the high-temperature solid-state, co-precipitation, reverse micelle and colloidal techniques. All chemicals: gadolinium(III) oxide, Gd_2O_3 (99.99%, Alfa Aesar), dysprosium (III) oxide, Dy_2O_3 (99.99%, Alfa Aesar), gadolinium (III) nitrate hexahydrate $Gd(NO_3)_3 \times 6H_2O$ (99.99%, Alfa Aesar), dysprosium (III) nitrate hexahydrate, $Dy(NO_3)_3 \times 6H_2O$ (99.9%, Alfa Aesar), ammonium vanadate, NH_4VO_3 (Alfa Aesar, 99.999%), $Na_3C_6H_5O_7x2H_2O$, trisodium citrate dihydrate (≥99%, Sigma Aldrich), NaOH, cyclohexane, Triton X-100, and n-pentanol were of the highest purity commercially available and were used without further purification. Milli-Q deionized water (electrical resistivity = 18.2 MΩ cm^{-1}) was used as a solvent.

Using different techniques of synthesis, the series S1 and S2 were prepared similarly to our previously reported syntheses of Ln - doped $GdVO_4$ materials [8,15–17]. Throughout the manuscript, the samples are denoted as in Table 1 (See below). For the $GdVO_4:Dy^{3+}$ samples concentration of Dy^{3+} ions was 2 mol% with respect to Gd^{3+} ions. Here, procedures used for preparation of $GdVO_4:Dy^{3+}$ are given in more detail, while the $DyVO_4$ samples were produced analogously.

2.1.1. The high-temperature solid-state method

In a typical synthesis, the Gd_2O_3, Dy_2O_3 and NH_4VO_3, were homogeneously mixed by dry grinding and heated for 1 h in open crucibles at 800 °C. The products were removed from the furnace, cooled down to room temperature, ground, and reheated at 1100 °C for 3 h to complete the reaction. Then, the powder was homogeneously ground, washed with 2 M NaOH solution water and methanol and finally calcined at 1150 °C for 90 min to improve the crystallinity of material and to remove ligands attached to particle surfaces during the washing step.

2.1.2. The co-precipitation method

Typically, an appropriate amount of NH_4VO_3 was dissolved in aqueous solutions of NaOH. A mixture of aqueous solutions of Gd^{3+} and Dy^{3+} ions was added drop-wise to a NH_4VO_3 solution. A formed milk-white opalescent precipitate of $GdVO_4:Dy^{3+}$ was additionally heated and stirred at 70 °C for 1 h. The precipitate was separated from the suspension by centrifugation, and washed several times with distilled water. Finally, the collected powder of $GdVO_4:Dy^{3+}$ was dried at 70 °C in the air for 20 h. To improve their crystallinity and to get particles of different size and morphology, the as-prepared powder was additionally annealed at 600 °C for 2 h.

2.1.3. Reverse micelles method

A typical synthesis was performed at room temperature by using three separately prepared solutions: 1) An oil phase mixture of cyclohexane, Triton X-100, and n-pentanol in a corresponding volume ratio; 2) a mixture of aqueous solutions of $Gd(NO_3)_3 \times 6H_2O$ and $Dy(NO_3)_3 \times 6H_2O$ and, 3) an aqueous solution of NH_4VO_3. The solution 3) was drop-wise added into mixture of the solutions 1) and 2) under continuous magnetic stirring. After stirring and aging for 24 h, methanol was added to destabilize the solution and resulting precipitate was separated by centrifugation and washed several times by methanol and water. The collected precipitate of $GdVO_4:Dy^{3+}$ was dried at 70 °C in the air for 20 h.

2.1.4. Colloidal synthesis

It is noteworthy that, to the best of our knowledge, both, $GdVO_4$:Dy and $DyVO_4$ nanoparticles were obtained, for the first time, in the colloidal form with the lowest diameter ever reported. In brief, solution of trisodium citrate dihydrate was added drop by drop to the mixture of $Gd(NO_3)_3 \times 6H_2O$ and $Dy(NO_3)_3 \times 6H_2O$ solution,

Table 1
Sample names, method of synthesis, preparation temperature and obtained morphology and size.

Samples name	Method of synthesis	Preparation temperature T (°C)	Morphology and size
S1-1 ($GdVO_4$:Dy) S2-1 ($DyVO_4$)	High-temperature solid-state	1150	Irregular spheres 1-8 μm
S1-2 ($GdVO_4$:Dy) S2-2($DyVO_4$)	Co-precipitation with annealing	600	Nanospheres 20 nm
S1-3 ($GdVO_4$:Dy) S2-3 ($DyVO_4$)	Co-precipitation without annealing	70	Nanorods 2 nm × 10 nm
S1-4 ($GdVO_4$:Dy) S2-4 ($DyVO_4$)	Reverse micelle	70	Nanospheres 4 nm
S1-5 ($GdVO_4$:Dy) S2-5 ($DyVO_4$)	Colloidal	70	Nanospheres 2 nm