



Er³⁺–Yb³⁺ doped vanadate nanocrystals: A highly sensitive thermographic phosphor and its optical nanoheater behavior



Manoj Kumar Mahata^{a,b}, Kaushal Kumar^{a,*}, Vineet Kr. Rai^a

^a Department of Applied Physics, Indian School of Mines, 826004 Dhanbad, India

^b Second Institute of Physics, University of Goettingen, 37077 Göttingen, Germany

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ABSTRACT

Optical temperature sensors play a vital role in biomedical and therapeutic applications due to their reliable and unique detection sensitivity. Internal self-heating in Er³⁺/Yb³⁺ doped yttrium vanadate particles is observed on optical excitation at 980 nm wavelength of a diode laser. Temperature sensing performance is investigated by exploiting the temperature dependent fluorescence intensity ratio (FIR) of two emission bands (²H_{11/2}/⁴S_{3/2} → ⁴I_{15/2}) of Er³⁺ ion. The calculated sensor sensitivity, 0.01169 K⁻¹ at 380 K, is found the highest among the reported results for inorganic nanosensors. The temperature of the nanocrystalline sample particles is found to increase by a large value (315–460 K) within a short interval of excitation pump power (13.18–50.45 W cm⁻²). This achievement suggests potential use of the present material as an optical nanoheater for hyper-thermal treatment.

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1. Introduction

Lanthanide ions doped upconverting (UC) nanomaterials can efficiently convert NIR light into visible or ultraviolet (UV) light through sequential multiphoton absorption processes. The upconverting nanomaterials combine many advantages over traditional two-photon imaging in biological and therapeutic applications such as low auto-fluorescence, high signal-to-noise ratio, deeper penetration depth, higher chemical stability etc. and thus promise these materials to be used in future biomedical applications [1–4].

The synthesis of inorganic nanocrystals with well defined morphologies is an interesting field of research due to strong dependence of optical properties on the structure–property relations. Therefore, many efforts have been made to replace the existing materials by particles of different geometry to improve their performance in the existing applications. Nanomaterials, whose properties are different from bulk material, often show a tendency toward agglomeration which is one of the disadvantages of practical applications of nanomaterials [5]. Therefore, it is still a challenge to synthesize chemically pure nanomaterials with controlled shape and size.

Thermographic phosphors (TGP) are those materials whose luminescence properties such as emission intensities of different

bands, emission bandwidth, lifetime, etc. are sensitive to temperature. Accurate sensing and mapping of temperature in a non-invasive way is one of the most interesting and demanding applications because of its superiority over conventional contact thermometer methods [6–8]. The temperature sensing behavior of rare earth (RE) doped phosphors is determined by two commonly used methods i.e. decay time and fluorescence intensity ratio (FIR) algorithm. Between these two methods, later one has been accepted extensively since decay lifetime method involves noise that arises due to fluctuations in the excitation light, shifting of excitation bands with temperature and non-uniform RE ions distribution [9].

From the last decade, temperature sensing has been studied using luminescent micro-crystalline compounds at the tip of scanning thermal probe, at the tip of optical fiber or on the silica-on-silicon waveguides [10–12]. These efforts seem not to be suitable because microcrystals at the tip entail a drawback that the material may act as a thermal insulator. Apart from this, the light scattering by rough surfaces of the larger particles reduces the resolution of temperature sensing. The UC nanoparticles widen the horizon of multimodal systems by sensing the cellular temperature as well as cellular image and thus possess several advantages over downconversion phosphors. By using the upconverting nanoparticles these limitations can be overcome. The most important feature of nanoscale thermometry is that UC particles can be employed inside the cells [13]. The fluorescence intensity ratio (FIR) method, in principle, uses low excitation power or short pulsed excitation in order to reduce the self-heating in

* Corresponding author. Tel.: +91 326 223 5754.

E-mail address: kumar.bhu@gmail.com (K. Kumar).

the phosphor particles. It is known to us that at high excitation pump power density, the phosphor particles undergo internal heating and the self-heating of phosphor particles is very useful in photothermal therapy [14,15]. The advantage of nanoparticles is that the self-heating is increased by many folds due to stronger electron–phonon coupling. It is reported that several RE doped particles undergo self-heating [14–17] and at the same time gives us opportunity to measure the temperature using FIR method. Precise determination of temperature in a biological media impacts on the sensibility of phosphor in pathology and physiology [18,19]. Among the luminescent thermometers proposed so far at sub-micrometer scale, only a few of them effectively illustrated the temperature sensing with a scanning microscope using $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped fluoride glass and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ nanoparticles [20,21]. Temperature sensing performance using metal-nanoparticle decorated, (Gd, Yb, Er) $_2\text{O}_3$ nanorods exploiting FIR technique and blackbody radiation is reported recently [22] but the duality of RE phosphor particles make it superior over the metal and semiconductor nanoparticles [23]. Hence, intensive efforts are required on temperature sensing by rare earth doped phosphor nanoparticles.

In this paper, we report the self-heating and temperature sensing by hydrothermally synthesized $\text{YVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ spherical particles, using near infra-red photon excitation. The temperature rise of the material is found to increase by a large value with small increment of input power.

2. Experimental

$\text{Er}^{3+}/\text{Yb}^{3+}$ doped yttrium vanadate nanocrystals were prepared by hydrothermal route using ethylene glycol (EG) as chelating agent. The composition of the material was 96.7 mol% YVO_4 + 0.3 mol% Er_2O_3 + 3 mol% Yb_2O_3 . A part of the synthesis procedure is provided in our previous report [24] where authors used citric acid instead of EG in a co-precipitation route.

The starting materials viz. V_2O_5 (Sigma–Aldrich), Y_2O_3 (Merck), Er_2O_3 (Merck), and Yb_2O_3 (Merck) were taken with 99.99% purity and their nitrates were prepared by dissolving these oxides in concentrated nitric acid. All these nitrates were mixed in a beaker with double amount of distilled water in order to remove the excess acid and placed on a magnetic stirrer whose hotplate was maintained at 80 °C for 3 h. Ethylene glycol (EG) was used as chelating agent for metal ions, keeping molar ratio of metal ions to EG at 1:2. The chelating agent prevents the agglomeration of particles at the time of reaction and thus leads to form smaller particles. After that, ammonium hydroxide (NH_4OH) was mixed drop wise under vigorous stirring. The pH of the resulting solution was kept at 8.0. Then the solution of these reagents was stirred on a magnetic stirrer whose hotplate was maintained at 80 °C. The resultant solution was transferred to a 80 ml autoclave for hydrothermal treatment at 200 °C for 24 h. The solution was cooled down to room temperature and precipitate was collected by centrifugation. After drying at room temperature, the as-synthesized powder was heated at 800 °C for 3 h in order to remove the organic impurities.

The phase structure and purity of the synthesized material were characterized by a Bruker-D8 Advanced X-ray diffractometer monochromatized with $\text{Cu-K}\alpha$ (1.5405 Å) radiation source and patterns were recorded over the angular range $10^\circ \leq 2\theta \leq 80^\circ$. The surface morphology and size of the prepared sample were inspected with a field emission scanning electron microscope (FESEM-ZEISS SUPRA 55).

A CW diode laser of 980 nm wavelength was used as excitation source for upconversion emission measurements. The laser beam was focused on the sample with a suitable spot size diameter by adjusting the collimating optics. A thermocouple was placed at very close (~2 mm) to the focal spot on the sample for the detection of

temperature. For temperature dependent measurements, the laser beam was set at 10 W cm^{-2} and chopped to avoid the direct heating of the material, though this power density produces a negligible heat to the sample.

3. Results and discussion

3.1. Structure and morphology of the synthesized material

The XRD pattern (Fig. 1a) of the resulting $\text{YVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ was indexed to tetragonal phase of YVO_4 with a zircon type structure which is exactly in agree with the standard card of tetragonal phase of yttrium vanadate (JCPDS 76-1649).

YVO_4 lattice has phonon energy of 880 cm^{-1} and it has a zircon type structure [24], described by the general formula ABO_4 , where A, B are metal ions having co-ordination number of eight and four, respectively [25]. The zircon type YVO_4 is built from the chains of alternating edge sharing VO_4 and YO_8 cages. The tetragonal YVO_4 crystal belongs to D_{4h} space group, with D_{2d} local point symmetry of Y^{3+} and is surrounded by eight O^{2-} ions at the vertices of tetragonal dodecahedron. The ionic radius of Y^{3+} (0.90 Å) ion is close to the radii of Er^{3+} (0.88 Å) and Yb^{3+} (0.86 Å). So erbium and ytterbium ions in the D_{2d} site of YVO_4 lattice can easily substitute the yttrium ions [26].

The crystallite size calculated, using Debye–Scherrer equation and Williamson–Hall equation [27] was found to be ~20 nm. The FESEM image of the same sample is shown in Fig. 1b which exhibits the spherical particles of average radius ~60 nm. The calculated crystallite size through XRD analysis much differs the size obtained from FESEM analysis. The XRD analysis gives the result for crystallite size whereas SEM image gives actual particle size. A particle is supposed to have aggregation of several crystallites. Ethylene glycol is a well-known and common solvent with high viscosity, water miscibility and co-ordination ability with metal ions which originates the (i) strong coulombic attraction between metal ion and hydroxyl groups and (ii) hydrogen bonds among the EG molecules. The proper amount of EG prohibits aggregation and further growth of the products. The possible reason for suppression of growth of YVO_4 are low ions' diffusion rate resulted from the high viscosity of the EG solvent and strong electrostatic attraction between crystal facets and EG molecules [28].

At the initial stage, the yttrium (*ortho*) vanadates are formed at acidic conditions. The ethylene glycol molecules bind to the crystal facets of these yttrium vanadates and thus make possible the isotropic crystal growth which leads to form spherical particles during hydrothermal treatment. EG molecules prevent the further aggregation and act as a protective layer for the crystals. Therefore, the main mechanism can be illustrated as: (i) Y^{3+} ions are chelated by EG molecules through the formation of EG– Y^{3+} complexes; (ii) The VO_3^- ions are transformed into VO_4^{3-} ions through OH^- ions introduction; (iii) under hydrothermal treatment, VO_4^{3-} competes with EG molecules and YVO_4 nucleation occur and (iv) the EG molecules bind onto the surface of newly formed nuclei. The pH value of the reaction system also affects the intensity of the electrostatic attraction between the crystal facets and EG molecules and thus plays an important role on the particle morphology.

3.2. Temperature sensing performance

The $\text{YVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ nanoparticles have shown strong green upconversion emission. The emission band that arises in 515–540 nm is due to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transition while the emission band in 540–560 nm is due to the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition. Fig. 2a shows the temperature dependence of intensity of two green bands. The temperature sensing measurement is based on the ratio

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