Synthesis and IR-Excited Luminescence of \((Y_{1-x}Tm_x)_2O_2S\) Solid Solutions

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Abstract—We have studied the key features of the luminescence spectra and kinetics of \((Y_{1-x}Tm_x)_2O_2S\) solid solutions in the range 400–2000 nm under laser excitation at 790 and 810 nm. The results have been used to develop a series of IR phosphors “invisible” under laser excitation in the range 790–810 nm and possessing tunable and reproducible relative intensities of three groups of IR luminescence bands in the ranges 770–840, 1360–1520, and 1650–1980 nm, respectively.

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INTRODUCTION

An important issue in the development of next-generation light conversion systems sensitive in a wide spectral range and offering a unique combination of several distinctive luminescence characteristics is to create IR phosphors possessing luminescence bands in the ranges 770–840, 1360–1520, and 1650–1980 nm under laser excitation at 790–810 nm, with visible luminescence as weak as possible. To successfully resolve this issue, one should find an activator possessing strong, narrow absorption bands in the laser emission range 790–810 nm and luminescence bands in the ranges 740–840, 1360–1520, and 1650–1980 nm, respectively, and select a host material which, when doped with a rare-earth activator, will ensure that, under laser excitation at 790 and 810 nm, the activator luminescence in the ranges 770–840, 1360–1520, and 1650–1980 nm will have an intensity sufficient for practical application and that visible anti-Stokes luminescence will be as weak as possible.

Analysis of the spectroscopic properties of rare-earth (RE) ions indicates that the most suitable rare-earth ion for this purpose is \(Tm^{3+}\). According to the diagram in Fig. 1, it absorbs in the range 790–810 nm and emits in the required spectral ranges. As shown in systematic studies of various inorganic anti-Stokes and Stokes IR phosphors under IR excitation [1–4], rare-earth-doped yttrium, lanthanum, and gadolinium oxysulfides ensure efficient conversion of the IR radiation from semiconductor lasers and light emitting diodes in the range 790–1550 nm. There is ample evidence that efficient IR phosphors emitting in the ranges 770–840, 1360–1520, and 1650–1980 nm can in principle be produced by doping yttrium, lanthanum, and gadolinium oxysulfides with \(Tm^{3+}\). In connection with this, a need has emerged to study the synthesis of \(Tm^{3+}\)-doped yttrium, lanthanum, and gadolinium oxysulfides and their luminescence spectra and kinetics under laser excitation at 790 and 810 nm.

This work forms part of such a detailed study and is concerned with the synthesis of \(Tm^{3+}\)-doped yttrium-oxysulfide-based phosphors and their luminescence under laser excitation at 790 and 810 nm.

EXPERIMENTAL

We studied \((Y_{1-x}Tm_x)_2O_2S\) samples with \(0 \leq x \leq 1 \times 10^{-1}\). Since the lighting performance of anti-Stokes and IR phosphors is extremely sensitive to RE impurities [5], we used extrapure starting materials: \(Y_2O_3, Tm_2O_3\) (99.995%), elemental sulfur, \(Na_2CO_3\) (extrapure grade), and LiF (analytical grade, for spectral analysis). The samples were prepared by a procedure described elsewhere [4].

The phase composition of the synthesized phosphors was determined by X-ray diffraction on a Siemens D-501 diffractometer (Ni-filtered \(CuK_α\) radiation). The unit-cell parameters of the samples were determined using X-ray diffraction data collected on a modified DRON-1 diffractometer.

The relative IR luminescence intensity of our samples in the range 400–2000 nm was determined from their steady-state luminescence spectra. The luminescence was excited by semiconductor lasers at 790 and 810 nm in a binder-free powder layer on a metallic substrate (0°–45° geometry). Emission spectra in the range 0.80–1.6 \(\mu\)m were measured using an MDR-204 monochromator and FPU-FS photodetector system. The IR Stokes luminescence intensity was quantified by the ratio of the maximum intensities of the spectral bands in the range 400–2000 nm for the test and reference samples.

Since the emission bands of the phosphors in the range 760–850 nm overlap with those of the lasers (790 and 810 nm), the emission spectra in this range were...
measured in kinetic mode using a Fluorolog-3 spectrofluorimeter. The measurement procedure was as follows: Using the control unit of the spectrofluorimeter, a 810-nm laser or light emitting diode was turned on for 2 ms, followed by a 0.1-ms delay and measurements over a period of 0.05 ms. This measurement cycle was repeated ten times, and the average was taken as the result. Next, the monochromator was adjusted to another wavelength with a 1-nm step, and measurements were repeated until the entire spectral range of interest was examined. The decay kinetics of IR luminescence bands in our samples were studied using the MDR-204 and an FPU-1 photodetector system. Excitation was provided by an 810-nm, 2400-mW pulsed semiconductor laser diode. The luminescence decay time was evaluated from the intensity (afterglow) decay curve as the time taken for the luminescence intensity to drop to the 1/e level after the excitation pulse was switched off.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of all the synthesized samples showed only reflections characteristic of yttrium oxysulfide, which has a uniaxial crystal structure with trigonal symmetry, usually represented in a hexagonal setting (sp. gr. \(D_{3d}\)) [6]. According to X-ray diffraction data, the unit-cell parameters of the yttrium-oxysulfide-based phosphors vary almost linearly with \(\text{Tm}^{3+}\) concentration throughout the composition range studied (0 ≤ \(x\) ≤ 1 × 10\(^{-3}\)), which points to the formation of a continuous series of solid solutions. Therefore, X-ray diffraction results indicate that all of the synthesized materials are single-phase isostructural phosphors containing no impurity phases.

At a standard incident 790-nm laser power density, ~200 mW/cm\(^2\), the discrete visible luminescence bands due to the \(^1D_4 \rightarrow ^4F_4\), \(^1G_4 \rightarrow ^3H_6\), \(^1G_4 \rightarrow ^3F_4\), and \(^3F_{2/2} \rightarrow ^3H_6\) optical transitions, characteristic of the \(\text{Tm}^{3+}\) ion, were essentially missing in the steady-state luminescence spectra of the \((\text{Y}_{1-x}\text{Tm}_x)\text{O}_2\text{S}\) solid solutions in the visible range. Similar data were obtained under 810-nm laser excitation.

In the IR spectral region (700–2000 nm), three groups of bands were observed under 790-nm laser excitation (Fig. 2). One group of IR luminescence bands was located in the range 770–840 nm (Fig. 2). We failed to completely determine the structure, number, and position of the emission bands in this group in our steady-state measurements because of the overlap with the 790- and 810-nm laser emission. To gain reliable information about the structure, number, and position of the bands and the spectral distribution of their intensity, the luminescence spectra in the range 700–850 nm were measured in kinetic mode.

Analysis of the kinetic spectrum in Fig. 3 indicates that all of the bands in the first group, between 770 and 840 nm, arise from optical transitions from the \(^3H_4\) excited state to Stark components of the \(\text{Tm}^{3+}\) ground state (Fig. 1). Comparison of the luminescence spectra of the \((\text{Y}_{1-x}\text{Tm}_x)\text{O}_2\text{S}\) solid solutions measured in a steady state and in kinetic mode provides the first evidence that, under laser excitation at 790 or 810 nm, some of the strong luminescence bands in the first group fall within the emission bands of the lasers and, accord-