Journal of Luminescence 173 (2016) 11–18

Contents lists available at ScienceDirect

Journal of Luminescence

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

Full Length Article

Optical and structural investigation of dysprosium doped-$Y_2Te_4O_{11}$

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ARTICLE INFO

Article history:
Received 7 October 2015
Received in revised form
11 December 2015
Accepted 14 December 2015
Available online 21 December 2015

Keywords:
Oxotellurates
Dy^{3+} ion
Luminescence
Emission-cross section
Laser materials

ABSTRACT

In this paper, the optical properties of $Y_2Te_4O_{11}$ microcrystalline powders doped with Dy^{3+} ions, ranging between 0.01 and 5.0 at%, are reported. The powders were successfully synthesized by the solid state reaction method. Absorption (300 K), excitation (300 K) and fluorescence spectra (at 11.6 and 300 K) as well as fluorescence decay curves recorded at room temperature are presented and analyzed in details. Oscillator strengths, phenomenological Ω_λ (λ=2, 4, 6) Judd-Ofelt parameters, radiative transition probabilities, branching ratios, the radiative lifetime of the $^4F_{9/2}$ level as well as the stimulated emission cross-section for the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition have been determined. The observed non-exponential decay nature and concentration quenching of the $^4F_{9/2}$ emitting level of the Dy^{3+} ion, have been attributed to cross-relaxation processes. The high value of the stimulated emission cross-section for the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at 576.6 nm, equal to 0.756×10^{-20} cm^2, indicates that $Y_2Te_4O_{11}$ activated by trivalent dysprosium ions is an attractive candidate for a solid-sate laser.

1. Introduction

Materials doped with rare earth ions play an important role in various of scientific and technological fields. Especially promising materials for application in modern optoelectronic technology are those, activated with trivalent dysprosium ions [1–3]. In recent times, more attention was paid on the MIR emission of Dy^{3+} ions. The observed in low phonon materials infrared emissions from Dy^{3+} ions at 1.3 μm (corresponds to the $^6F_{11/2}+{}^6H_{9/2} \rightarrow {}^6H_{15/2}$ transition), 2.8–3.2 μm ($^6H_{13/2} \rightarrow {}^6H_{15/2}$), 4.0–4.7 μm ($^6H_{11/2} \rightarrow {}^6H_{13/2}$) and 5.4–6.0 μm ($^6F_{11/2}+{}^6H_{9/2} \rightarrow {}^6H_{11/2}$) have found application in optical fiber communication, medicine and for military aims, respectively [4–7]. However, with new possibilities of optical pumping offered by increased availability of different laser sources, investigations on luminescence properties of Dy^{3+}-doped materials are currently focusing on the emission in the visible range. In that region the Dy^{3+} ion exhibit three well separated emission bands. The blue emission at 480 nm, the yellow at 580 nm and the weak red at about 660 nm have been attributed to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, the hypersensitive $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and the $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition, respectively. Earlier investigation on the unique spectral and emission properties of Dy^{3+} ions in the visible region suggest that Dy^{3+}-doped materials can be considered as excellent candidates for application in laser technology in the 560–590 nm region [8,9]. Besides, the hypersensitive transition ($\Delta L=2$, $\Delta J=2$) is strongly influenced by the local site symmetry of the Dy^{3+} ion. For this reason, the ion will give rise to a white light emission when emitting a suitable yellow to blue intensity ratio. Hence, materials doped with Dy^{3+} or co-doped with other RE^{3+} ions are considered as promising candidates for white LED-s applications [10,11].

The research carried out by Redman, Parada and other authors shows that oxotellurates(IV) of the general formula $RE_2Te_nO_{2n+3}$ (where n=4 or 5), doped with trivalent lanthanides ions are very attractive host matrixes [12,13]. Crystallographic studies on RE_2O_3-$(TeO_2)_n$ indicate, that oxotellurates(V) are isostructural through the entire series of RE=Y, La-Nd, Sm-Lu and crystallize in the monoclinic and triclinic space system for n equal to 4 and 5, respectively [14,15]. One crystallographic site of the RE^{3+} ions $RE_2Te_4O_{11}$ and a lone pair of electrons in Te(IV) suggest that this type of oxotellurates(IV) possesses interesting properties as luminescent activators. Spectroscopic investigations of oxotellurates (IV) activated Pr^{3+}, Nd^{3+} [16], Sm^{3+} [17], Eu^{3+} [18,19] and Tb^{3+} [20] confirm that these compounds are good candidates also for phosphors and laser materials. Additionally, oxotellurates(IV) are characterized by a relatively low temperature of synthesis (below 800 °C), chemical stability and exhibit good mechanical properties.

To the best of our knowledge, the luminescence properties of Dy^{3+}-doped $Y_2Te_4O_{11}$ have not been hitherto studied and reported. In this paper, the spectroscopic properties of microcrystalline powder samples of Dy^{3+}:$Y_2Te_4O_{11}$ are presented and discussed in details. The luminescence properties of these samples were analyzed by means of optical absorption (300 K), fluorescence (11.6 K and 300 K), photoluminescence excitation (300 K) spectra as well

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http://dx.doi.org/10.1016/j.jlumin.2015.12.023
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as fluorescence decay curves (300 K). The Judd-Ofelt theory has been applied in order to determine the radiative properties arising from the $^4F_{9/2}$ level of the Dy^{3+} ion. The influence of the concentration of Dy^{3+} ions on the decay time and energy transfer mechanism between the Dy^{3+}-Dy^{3+} ions is also discussed.

2. Experimental

2.1. Solid-state synthesis

As starting materials, high purity Y_2O_3 (99.999%, Stanford Materials), Dy_2O_3 (99.999%, Stanford Materials) and TeO_2 (99.95%, Sigma Aldrich) oxides were used. The $Y_{2-x}Dy_xTe_4O_{11}$ (where x=0.01, 0.02, 0.1, 0.5, 1.0, 2.0 and 5.0 at%) microcrystalline powders were obtained according to the procedure reported for $Y_2Te_4O_{11}$ in Ref. [21]. The starting oxides were mixed in stoichiometric proportions, thoroughly homogenized over 12 h and finally pressed into pellets of 15 mm in diameter at 0.5 GPa. In the next step, the obtained pellets were placed in a platinum-iridium crucibles (20 mm in diameter and 60 mm height) and heated in an electric furnace at 770 °C (1043 K) for 24 h in order to obtain a microcrystalline Dy^{3+}:$Y_2Te_4O_{11}$ powder.

2.2. Characterization

X-ray powder diffraction (XRD) measurements were recorded on a Bruker D8 Advance X-ray Diffractometer, using Ni-filtered Cu $K\alpha_1$ radiation ($\lambda=1.5418$ Å). The measurements were performed in the $2\theta=10-100°$ range with the step of $2\theta=0.008°$. The morphology of the $Y_2Te_4O_{11}$ microcrystalline powder was examined by a Hitachi S-3400N scanning electron microscope equipped with an EDS Thermo Scientific Ultra Dry detector. SEM and EDS measurements were carried out using an accelerating voltage of 30 kV. Analyzed samples of $Y_2Te_4O_{11}$, without and with 5.0 at% of an activator, were coated with a ultra thin layer of gold (~20 nm in thickness).

The concentration of the Dy, Y and Te elements in the $Y_2Te_4O_{11}$ samples with different concentration of dysprosium ions, were determined by inductively coupled plasma (ICP), using an ARL spectrometer, Model 3410 ICP (Fisons Instruments). Approximately 30 mg of the sample was transferred into a Teflon beaker, followed by 30 cm^3 2 M HCl. The mixture was thoroughly stirred until a clear greenish solution has been obtained. The solution was next transferred to a 100 cm^3 volumetric flask and brought up to the volume with a 2 M HCl. Single component standards of Dy, Y and Te (each one with the content of 1.000 mg/cm^3) were used.

The optical absorption spectra were recorded at 300 K on a Cary 5000 UV–vis-NIR spectrophotometer (Agilent Technologies). High-quality absorption spectra have been obtained from transmittance measurements of a microcrystalline sample of Dy^{3+}:$Y_2Te_4O_{11}$, in the form of a compressed transparent pellet. The diameter (equal to 12.63 mm) and thickness (0.260 mm) of the obtained pellet were measured by using a digital micrometer screw. Before measurements of the absorption spectra the samples have been heated for 1 h at 500 °C, in order to remove water from the surface of the pellets.

The fluorescence spectra (at 11.6 and 300 K) were recorded using an Ocean-Optics high-resolution spectrometer (model HR-4000) upon excitation of a 445 nm laser diode. For measurements of the fluorescence spectra at low temperature (11.6 K) a closed cycle helium refrigerator (APD-Criogenic ARS-2HW) equipped with a temperature controller was used. The fluorescence excitation spectra (300 K) and fluorescence decay curves (300 K) were recorded on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) equipped with a pulsed xenon lamp as an excitation source.

3. Results and discussion

3.1. X-ray diffraction patterns

C_{2h}^6 In Fig. 1 is shown the X-ray powder diffraction pattern of Dy^{3+} (5.0 at%) doped-$Y_2Te_4O_{11}$ together with the indexed theoretical simulation pattern (ICSD#418854) [19]. One may notice that the diffraction peaks of the sample may be assigned to the pure $Y_2Te_4O_1$ phase. Yttrium oxotellurate(IV) crystallizes in the monoclinic space group C2/c C_{2h}^6 (No. 15) with Z=4 and is isostructural with $Ln_2Te_4O_{11}$ (Ln=La-Nd, Sm-Lu). The unit-cell parameters are: a=12.3876, b=5.1068, c=16.0193 Å, $\beta=106.154°$ and V=973.38 $Å^3$ [19]. No other phase could be detected. It indicates that the Dy^{3+} ions replace Y^{3+} ions on the single crystallographic position of the C_1 site symmetry, due to a similar ionic radius r:(Y^{3+})=1.075 Å, r:(Dy^{3+})=1.027 Å for the coordination number equal to 8 [22].

3.2. SEM and EDS analyses

Fig. 2a–c show the representative SEM images of the un-doped $Y_2Te_4O_{11}$ (Fig. 2a) and Dy^{3+} (5.0 at.%)-doped $Y_2Te_4O_{11}$ (Fig. 2b–c). The presented SEM images indicate that the grains, of various shapes and sizes (between 10 to 25 µm), are randomly distributed and the morphology is independent of the activator concentration. Fig. 2d presents the EDS spectrum of the Dy^{3+} (5.0 at%):$Y_2Te_4O_{11}$ sample, which shows the presence of Te, O, Y and Dy elements. The molar percentage of the elements in the Dy^{3+} (5.0 at%)-doped $Y_2Te_4O_{11}$ sample was calculated on the basis of a quantitative EDS microanalysis. The received similar theoretical (Y=11.47%, Dy=0.30%, Te=23.53% and O=64.70%) and experimental (Y=12.48 ± 0.18%, Dy=0.33 ± 0.03%, Te=22.35 ± 0.18% and O=64.89 ± 0.71%) values indicate, that the Y:Dy:Te:O molar percentage ratio of the elements is in good agreement with the structural formula.

3.3. Absorption spectra, Judd-Ofelt analysis and radiative properties

The room-temperature optical absorption spectrum of Dy^{3+} (2.0 at%):$Y_2Te_4O_{11}$ (1.53×10^{19}ions per cm^3) in the 5450–14000 cm^{-1} spectral range, is shown on Fig. 3. The spectrum was calibrated in absorption cross-section units (in cm^2). In the 5430–14280 cm^{-1} (1842–700 nm) range, relatively intense and well

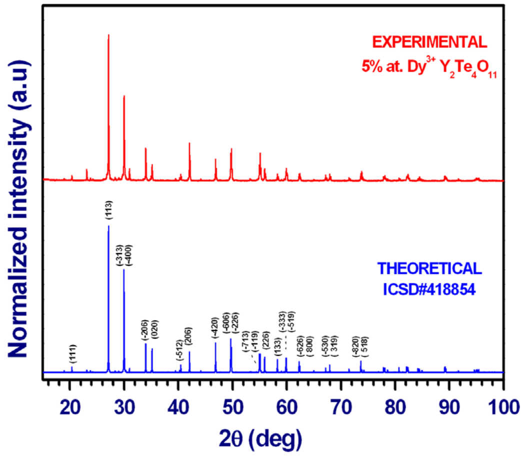

Fig. 1. Theoretical [19] and experimental XRD pattern of the $Y_2Te_4O_{11}$ powder.