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Optically Active Material Based on Bi_2O_3@Yb^{3+}, Nd^{3+} with High Intensity of Upconversion Luminescence in the Red and Green Region

D. Artamonov, A. Tsibulnikova, I. Samusev, V. Bryukhanov, A. Kozhevnikov

***Abstract*—**The synthesis and luminescent properties of Yb_2O_3,Nd_2O_3@Bi_2O_3 complex with upconversion generation are discussed in this work. The obtained samples were measured in the visible region of the spectrum under excitation with a wavelength of 980 nm. The studies showed that the obtained complexes have a high degree of stability and intense luminescence in the wavelength range of 400-750 nm. Consideration of the time dependence of the intensity of the upconversion luminescence allowed us to conclude that the enhancement of the intensity occurs in the time interval from 5 to 30 min, followed by the appearance of a stationary mode.

***Keywords*—**Lasers, luminescence, upconversion photonics, rare earth metals.

I. Introduction

CERAMIC and glass-like materials are currently attracting particular attention due to their unique properties, including high hardness and stability at high temperatures. However, their fabrication process is a complex and multi-step. It requires the using of high temperatures and is often accompanied with the appearance of defects such as cracks and pores [1]-[3]. Therefore, research is now actively underway to develop new technologies to produce these materials. The directions of modern research are modification of glass-like ceramics in order to increase its resistance to external factors and improve its other properties.

Rare earth oxides (REOs) and their solid solutions are very important materials for optical insulators and magneto-optical materials. They provide high optical quality for information and communication technologies, data storage and processing elements, optics, magnetic and laser generation [4], [5]. However, their fabrication process is complex and requires the use of high temperatures. Research is currently underway to develop new technologies to produce these materials with improved properties and increased resistance to external factors.

Materials for optical insulators and magneto-optical materials are REOs and their solid solutions, which are used in information and communication technologies, data storage and processing elements, optics, magnetic and laser generation [6], [7]. However, their fabrication process is complex and requires the use of high temperatures. Ceramic and glass-like materials are also of interest, but the fabrication of ceramics is challenging, requiring the use of high temperatures and a multi-step process, which can lead to defects [8]-[10]. Therefore, it is important to develop new techniques to produce the materials, for example by doping with Bi_2O_3 or Y_2O_3 compounds to increase the resistance and improve other properties. Bismuth oxide can also be used to modify ceramics due to its low melting point and high reactivity [11].

The purpose of this work is the determination of luminescent features in glassy matrix Yb_2O_3,Nd_2O_3@Bi_2O_3 under excitation into the absorption band of ytterbium ions in the visible and IR ranges under conditions of stationary photoexcitation, investigating the mechanism of energy transfer between Yb^{3+} and Nd^{3+} ions.

II. Materials and Methods

Luminescence experiments were performed using a Fluorolog-3 optical system (Horiba and Jobin Yvon, France) equipped with a FL-1073 detector operating in the UV-VIS radiation ranges. An IR laser (model LSR-PS-II) with a continuously adjustable power (0.1-1.0) W and a wavelength of 980 nm was used as an excitation source. A monochromator model M266 (Solar Laser Systems, Belarus) was used to measure luminescence in the IR region.

The synthesis of this material was a multistage thermal process, the final stage of which was high-temperature sintering at T = 1250 °C (t = 3h) in a muffle furnace. Immediately before sintering, the element oxides were subjected to thorough grinding in a mortar. At T = 900 °C, the melting process of the mixture began, due to the presence of bismuth oxide, the melting point of which is T = 850 °C. The molten solution containing ytterbium oxide and neodymium oxide nanoparticles was cast on the surface. As a result of casting, the sample took the shape of a drop with a diameter of 0.5 cm. The obtained sample was investigated by optical methods in the visible and IR ranges under excitation with a wavelength of 980 nm.

III. Results and Discussion

Fig. 1 shows the upconversion luminescence of the material under excitation with wavelength of 980 nm.

As can be seen from Fig. 1, the luminescence spectrum in the visible region of Yb_2O_3,Nd_2O_3@Bi_2O_3 was measured at 0.3 W

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laser power. The maxima of the luminescence spectrum occur at 525, 545, 555, 555, 655, 665, 695 nm. The transitions between the Yb^{3+} -Nd^{3+} levels correspond with the main $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{9/2}$. Upconversion luminescence bands in the green and red bands are observed in the spectrum [12].

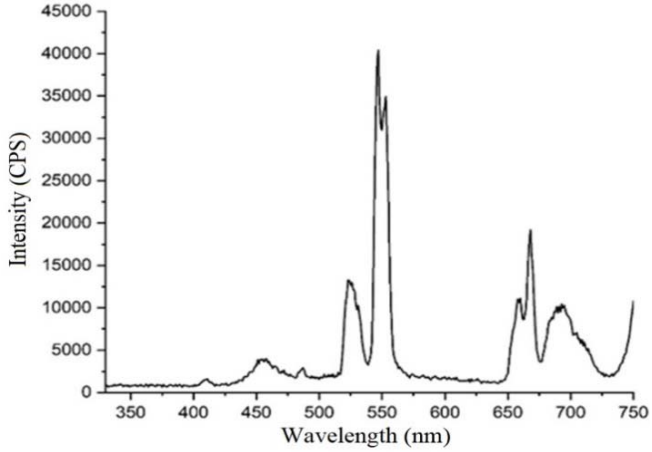

Fig. 1 Luminescence spectra in the visible region of Yb_2O_3,Nd_2O_3@Bi_2O_3 at an excitation wavelength of 980 nm

A graph of the intensity dependence vs time of laser exposure is presented in Fig. 2 for Yb_2O_3,Nd_2O_3@Bi_2O_3 system.

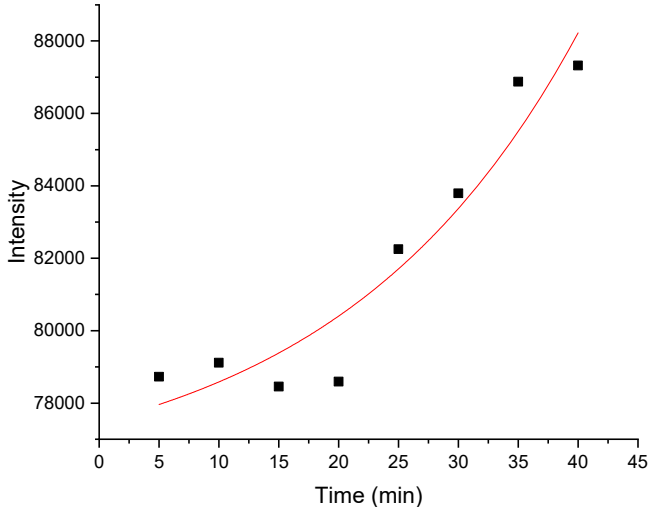

Fig. 2 Dependence of the luminescence maximum at a wavelength of 550 nm on the time of laser excitation at a wavelength of 980 nm

As can be seen from Fig. 2, the intensity enhancement occurs in the time interval from 5 min up to 30 min followed by a stationary mode. Thus, it can be seen that the luminescence intensity is a stationary process of energy accumulation at the $^2G_{9/2}$ level, since the intensity does not practically change with power. For the other wavelengths, a nonlinear dependence is observed, which is apparently due to the influence of concomitant parallel transitions on each electron transition under consideration and possible additional energy transfer from the upper levels.

The exponential growth of the high-efficiency red UCL may also indicate a sufficiently high degree of stability of the obtained material. In this context, we believe the stability is due to the Bi_2O_3 shell, which seems to delay the upconversion radiation and scatter the absorbed IR radiation in the volume of the material (drop), forming a kind of resonator, which provides irradiation of a large number of neighboring atoms.

Further, Raman spectra of Bi_2O_3@Yb^{3+}, Nd^{3+} in Yb^{3+} to Nd^{3+} concentration (m_{Yb2O3} = 0,56g;m_{Nd2O3} = 0,24g) and (m_{Yb2O3} = 0,08g;m_{Nd2O3} = 0,72g) were considered. It should be noted that the ytterbium oxide phase remains constant under the two sintering regimes (cubic lattice type Ia 3) [13].

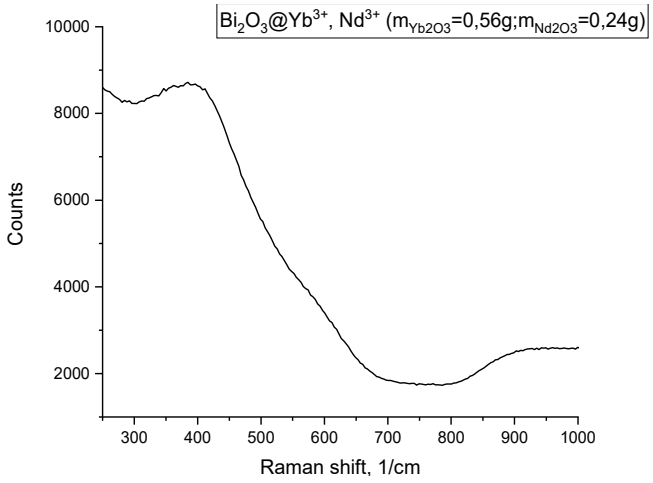

Fig. 3 Raman spectrum of Bi_2O_3@Yb^{3+}, Nd^{3+} (m_{Yb2O3} = 0,56g;m_{Nd2O3} = 0,24g)

Thus, from the spectrum presented in Fig. 3, the characteristic peaks of Nd-O bond vibrations at frequency of υ = 400 cm^{-1} corresponding to E_g Raman modes are observed [14]. The presence of this peak indicates a C-type cubic lattice with spatial symmetry Ia3 for Nd_2O_3 powder.

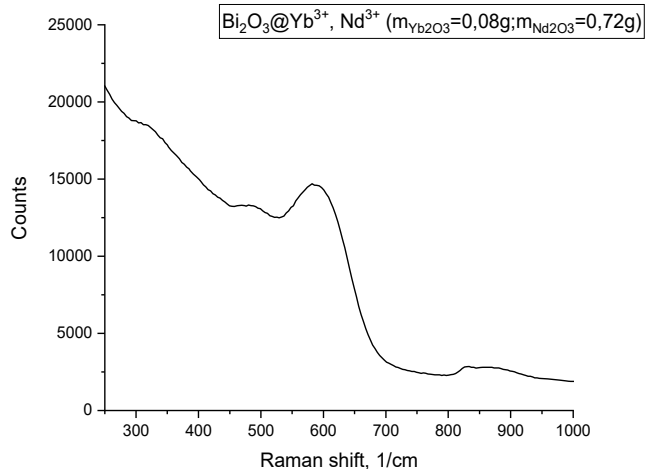

Fig. 4 Raman spectrum of Bi_2O_3@Yb^{3+}, Nd^{3+} (m_{Yb2O3} = 0.08g;m_{Nd2O3} = 0.72g)

The vibration maximum of annealed Nd_2O_3 at temperature T = 1200 °C is located at the frequency of υ = 605 cm^{-1} (e.g., mode). This neodymium oxide Nd_2O_3 is characterized by the C-

form [15]-[17].

It is important to note that in the mixture of oxides Nd_2O_3/Yb_2O_3 after annealing at T = 750 °C, there is an increase in the intensity of vibrational bands corresponding to frequencies 450 cm^{-1} and 605 cm^{-1} in the spectrum. This is due to the overlap of vibrational spectra in this region for Nd_2O_3 and Yb_2O_3 and algebraic summation of the amplitude of vibrations and oscillation strength of Nd-O_3 and Yb-O bonds [18]-[20].

Thus, based on the results of vibrational spectroscopy, it can be concluded that the phase of ytterbium oxide in Yb_2O_3,Nd_2O_3@Bi_2O_3 medium remains constant and undergoes insignificant changes, which is extremely important for the consideration of Yb^{3+} ions as an energy donor for photoactivation of Nd^{3+} ions under excitation into the electronic absorption band of Yb^{3+}. To establish the presence of luminescent properties in ytterbium oxide, the luminescence spectra of Yb_2O_3@Bi_2O_3 and Yb_2O_3,Nd_2O_3@Bi_2O_3 medium were measured.

X-ray diffraction analysis of Bi_2O_3 in powder and droplet was carried out to investigate their morphological characteristics, which affect the media values for rare earth elements. Fig. 5 shows the X-ray diffraction pattern of Bi_2O_3 powder.

Bismuth oxide has a monoclinic lattice with the space group of a P 21/c (card No. 2-498). The unit cell parameters are: a = 5.83 Å, b = 8.14 Å, c = 7.48 Å, α = 90°, β = 67.7°, γ = 90°.

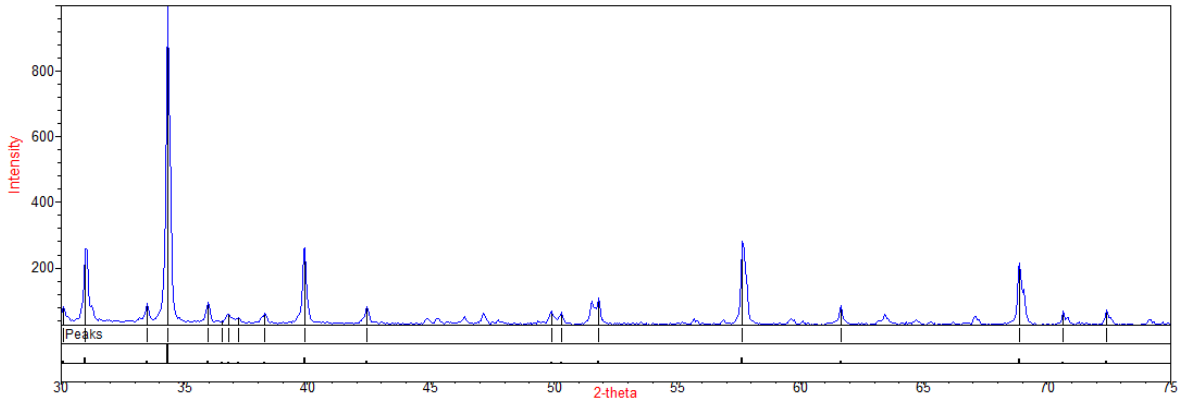

Fig. 5 X-ray diffraction pattern of the Bi_2O_3

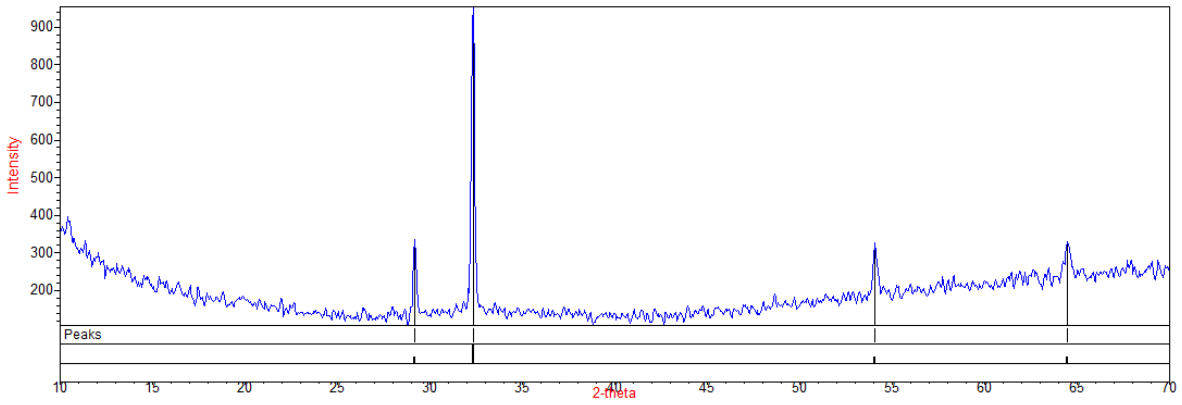

Fig. 6 X-Ray diffraction pattern of the Bi_2O_3-drop

As can be seen from Fig. 6, Bi_2O_3 in the drop at annealing temperature of 1250 °C has an amorphous state, since it has no obvious X-ray scattering peaks and therefore is a good medium for the study of upconversion processes involving ions of rare earth elements.

IV. Conclusion

Based on the results of vibrational spectroscopy, it was found that in the Raman spectrum of the mixture of oxides Nd_2O_3/Yb_2O_3 after sintering at T = 750 °C, there is an increase in the intensity of vibrational bands corresponding to frequencies 360 cm^{-1} and 605 cm^{-1}, due to the spectral overlap of bands Nd_2O_3 and Yb_2O_3. It was also found that the phase of ytterbium oxide in the medium of Yb_2O_3, Nd_2O_3@Bi_2O_3 remains constant. According to the data of luminescence analysis it was shown that the investigated material Yb_2O_3,Nd_2O_3@Bi_2O_3 has upconversion luminescence with high optical stability and has no photochemical burnout. It is proved that the upconversion transitions in the red and green regions are due to the dipole-dipole mechanism of energy transfer with simultaneous excitation of a pair of ytterbium ions in the absorption band. It is also shown that the bismuth oxide shell provides stability of the process of internal reabsorption of IR energy under conditions of constant photoexcitation of ytterbium ions.

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