PAPER

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To cite this article: V S Gorelik and M G Burdanova 2014 *Laser Phys.* **24** 125001

IOP Publishing | Astro Ltd Laser Physics
Laser Phys. **24** (2014) 125001 (6pp) doi:10.1088/1054-660X/24/12/125001

Photoluminescence and polariton dispersion in erbium nitrate hydrate

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Received 6 May 2014
Accepted for publication 4 September 2014
Published 7 October 2014

Abstract
The photoluminescence spectrum of erbium nitrate hydrate is analyzed. The dispersion dependencies of polaritonic waves in erbium nitrate hydrate are established by means of a model of the interaction between electromagnetic waves and resonance electronic states of Er^{3+} ions. The positions of unitary polaritons, for which the refraction index is unity, are established. Velocity and effective mass of unitary polaritons are calculated. Our research allows construction of a liquid-core laser. The calculations show an increase of pump efficiency in such a laser.

Keywords: erbium, erbium nitrate hydrate, photoluminescence spectrum, dispersion relations, polaritons, liquid-core fibre, laser

(Some figures may appear in colour only in the online journal)

1. Introduction

In material media such as dielectrics, a wave, called the polariton wave, is generated as a result of the interaction between electromagnetic wave and charged particle oscillation. Moreover, quasi-particles, which correspond to the polariton waves, are called polaritons [1].

Material media interact with electromagnetic waves by means of high-frequency transverse oscillations. These interactions are most efficient when frequencies and wave vectors of electromagnetic wave and phonon waves are equal, that is, when resonance occurs. Therefore, in such conditions, hybrid (polariton) waves, for which dispersion relation is typical, are formed.

The term ‘polariton’ was first introduced by Hopfield [1]. Polariton dispersion was first observed in cubic GaP crystals by Henry and Hopfield in 1965 [2] and in hexagonal ZnO crystals by Porto, Tell and Darner in 1966 [3]. Since then, many materials have been investigated.

Polariton dispersion has found numerous applications in many diverse fields of science and engineering. Nevertheless, they are all based on the theory that allows calculation of the refractive index and polariton characteristics such as velocity, effective mass and spectral density of light radiation energy, among others.

The examination of erbium ions Er^{3+} is particularly important as it is necessary to develop laser models with high efficiency and high power of laser emission together with good spatial characteristics. There is a tendency in laser technology to focus strongly on research on the near infrared range. This can be explained by the fact that the main laser transition for erbium Er^{3+} is a resonant transition with the wavelength 1.53 microns. Radiation at this wavelength accords with the ‘window’ of atmospheric transparency and the area of minimum optical losses of quartz fibres.

This paper presents a method for assessing the optical properties of erbium nitrate hydrate. The refractive index dispersion and dispersion characteristics of erbium nitrate hydrate were obtained for a wide frequency range. In particular, we calculated velocity and effective mass of unitary polaritons, for which the refractive index is unity.

2. Experimental procedures

Samples of erbium nitrate hydrate with the concentration Er^{3+} 1% were used in the research. It should be noted that nitrate hydrate is readily soluble in water even at room temperature.

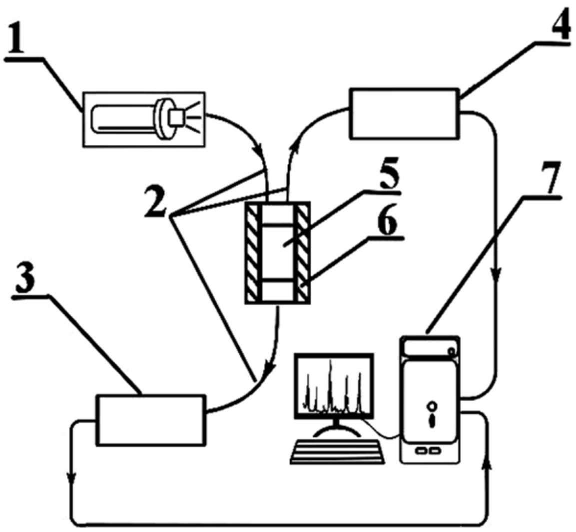

Figure 1. The schematic of the experimental setup for observing photoluminescence spectrum of erbium nitrate hydrate: 1—light-emitting diodes; 2—fibre; 3,4—spectrometers; 5—sample; 6—cuvette and 7—computer.

The scheme of the experimental setup for observing photoluminescence spectra is illustrated in figure 1. Here, the light-emitting diodes (1) have the wavelength of $\lambda = 368, 386, 410, 463, 522, 593$ and 641 nm. This radiation was directed with the help of fibre (2) into a cuvette (6) with samples (5). The absorption and photoluminescence spectrums were registered on the spectrometers (3) and (4). The experimental data was input to an analogue-to-digital converter of a computer (7) for final processing.

In figure 1, the photoluminescence spectrum of erbium nitrate hydrate for different pump radiation is given. It should be noted that these relationships are normalized according to the maximum experimentally obtained date (curve 1—pump radiation, curve 2—photoluminescence spectrum).

Based on these results, we determined that photoluminescence in erbium nitrate hydrate observed on five resonant frequencies is visible. Free ions of erbium Er^{3+} have 13 electrons in a 4f shell. The ground-state manifold for erbium ions is $^4I_{15/2}$. After excitation, a transition between another manifold and ground-state manifold is realized, which can be nonradiative or fluorescent.

The empirical energy level scheme that emerged from this was then compared with the free energy levels calculated by Wybourne (1960) and Carlson and Crosswhite (1960) [4, 5]. This showed that for energies up to about 25 000 cm^{-1}, there is excellent agreement. For each of the theoretically expected levels, there is an empirical level and all the observed levels are accounted for (table 1).

3. Theoretical analysis

Theoretical modelling of the propagation of electromagnetic waves in erbium nitrate hydrate relies on Maxwell's equation:

Table 1. Calculated and experimentally observed $4f^{11}$ energy levels for erbium nitrate hydrate.

	Free ions [6]		Erbium nitrate hydrate	
	Er^{3+}		$Er(NO_3)_3 \cdot nH_2O$	
Energy level	E, cm^{-1}	λ, nm	E, cm^{-1}	λ, nm
$^4I_{15/2}$	0	∞	0	∞
$^4I_{13/2}$	6485	1542	6464	1548
$^4I_{11/2}$	10123	988	10123	988
$^4F_{9/2}$	15182	659	15348	652
$^4S_{3/2}$	18299	547	18532	540
$^2H_{11/2}$	19010	526	19062	525
$^4F_{7/2}$	20494	488	20634	485
$^2H_{9/2}$	24475	408	24649	406

The work [7] shows that transition $^4I_{11/2} \to {}^4I_{15/2}$ with a wavelength around 1548 μm and transition $^4I_{13/2} \to {}^4I_{15/2}$ with a wavelength around 0.988 μm are also possible (table 1).

$$\begin{cases} \mathrm{rot}\vec{E} = -\dfrac{\partial \vec{B}}{\partial t}; \\ \mathrm{div}\vec{B} = 0; \\ \mathrm{rot}\vec{H} = \dfrac{\partial \vec{B}}{\partial t}; \\ \mathrm{div}\vec{D} = 0. \end{cases} \tag{1}$$

Material equations are needed to close Maxwell's equations. The material equations in the cases of liner and isotropic materials link the electromagnetic quantities with each other:

$$\begin{cases} \vec{D} = \varepsilon_0 \varepsilon \vec{E} = \varepsilon_0 \vec{E} + \vec{P}; \\ \vec{B} = \mu_0 \mu \vec{H} = \mu_0 \vec{H} + \mu_0 \vec{M}\,. \end{cases} \tag{2}$$

If we want to solve (1), we have the following conditions and material:

$$\rho(r) = 0, j(r) = 0.$$

Here, the electric charge density and electric current density are assumed to be zero.

After applying a few vector operations, the wave equation for the electromagnetic field E is

$$\mathrm{rot}\,\mathrm{rot}\,\vec{E} - \mathrm{grad}\,\mathrm{div}\,\vec{E} = -\mu_0\,\mu \frac{\partial}{\partial t}\mathrm{rot}\,\vec{H} = -\mu_0\,\mu\,\varepsilon_0 \varepsilon\,\frac{\partial^2 \vec{E}}{\partial t^2}\,. \tag{3}$$

The simplest possible solution to Maxwell's equation is the plane wave. For monochromatic plane waves in a dielectric medium,

$$\left(\nabla^2 - \frac{\varepsilon \mu}{c_0^2}\right)\vec{E} = 0. \tag{4}$$

Finally, the dispersion law for polaritons waves has the form:

$$\omega^2 = \frac{c_0^2 k^2}{\varepsilon(\omega)\,\mu(\omega)};\ \mu(\omega) = 1;\ \omega^2 = \frac{c_0^2 k^2}{\varepsilon(\omega)}; \tag{5}$$

$$i\varepsilon\varepsilon_0\vec{k}\vec{E}_0\exp\left[i\vec{k}\vec{r}-\omega t\right]=0. \tag{6}$$

For dipole moment and the polarization vector, we obtain:

$$\vec{p}_0=\frac{e^2F}{m\left(\omega_0^2-\omega^2\right)}\vec{E}_0; \tag{7}$$

$$\vec{p}_0=\frac{e^2F}{mV_0\left(\omega_0^2-\omega^2\right)}\vec{E}_0. \tag{8}$$

The equation of motion for the polarization vector is represented as:

$$\dot{\vec{P}}=-\omega_0^2\vec{P}+\frac{e^2F}{mV_0}\vec{E};\quad \vec{P}=\frac{e\sqrt{F}\vec{u}}{V_0}\vec{P}_0\exp i\left(\vec{k}\vec{r}-\omega t\right). \tag{9}$$

Introducing the plasma frequency ω_p from equation (9), we obtain the relation:

$$\dot{\vec{P}}=-\omega_0^2\vec{P}+\omega_p^2\vec{E};\ \omega_p^2=\frac{e^2F}{mV_0}. \tag{10}$$

For electric displacement we have:

$$\vec{D}_0=\varepsilon_0\vec{E}_0+\vec{P}_0=\varepsilon_0\left[1+\frac{e^2F}{mV_0\left(\omega_0^2-\omega^2\right)}\right]\vec{E}_0=\varepsilon_0\varepsilon\ (\omega)\,\vec{E}_0. \tag{11}$$

Therefore, the dispersion of electromagnetic waves can be described as:

$$\begin{cases}\varepsilon(\omega)=1+\dfrac{e^2F}{mV_0\left(\omega_0^2-\omega^2\right)}=1+\dfrac{\omega_p^2}{\omega_0^2-\omega^2}=\dfrac{\omega_l^2-\omega^2}{\omega_0^2-\omega^2};\\ \omega_l^2=\omega_0^2+\omega_p^2;\\ \omega_p^2=\dfrac{e^2F}{mV_0}.\end{cases} \tag{12}$$

The permittivity description can be represented as:

$$\varepsilon(\omega)=\varepsilon_\infty\frac{\omega_l^2-\omega^2}{\omega_0^2-\omega^2};\ \varepsilon_\infty=n_\infty^2. \tag{13}$$

Here, epsilon infinity is high-frequency permittivity and omega i and omega zero are the frequencies of the corresponding longitudinal and transverse waves.

Accordingly, the dispersion law of polaritons in dielectric media is given by:

$$\omega^2=\frac{c_0^2k^2}{\varepsilon(\omega)\mu(\omega)}=\frac{c_0^2k^2\left(\omega_0^2-\omega^2\right)}{\varepsilon_\infty\left(\omega_l^2-\omega^2\right)}=\frac{c^2k^2\left(\omega_0^2-\omega^2\right)}{\left(\omega_l^2-\omega^2\right)};$$
$$c^2=\frac{c_0^2}{\varepsilon_\infty}. \tag{14}$$

Solving (14) gives two frequency-dependent solutions for the wave vector k as a function of ω since the left-hand side is quadratic in k. Close to absorption, two solutions exist. This means that near resonance, the dispersion of light cannot be considered independent from the dispersion of excitations in the material. They both form a composite new entity propagating in the medium. This is called the polariton.

The general form of the dielectric function is given as:

$$\varepsilon(\omega)=\varepsilon_\infty+\sum_{j=1}^{j=n}\frac{q_jN}{m_j\varepsilon_0\left(\omega_{0j}^2-\omega^2\right)}. \tag{15}$$

Finally we obtain the permittivity description as the well-known Kurasawa relation:

$$\varepsilon(\omega)=\varepsilon_\infty\prod_{j-1}^{j=n}\frac{\omega^2_{lj}-\omega^2}{\omega^2_{0j}-\omega^2}. \tag{16}$$

Similarly, we obtain results expression by plugging (16) into (14):

$$\omega^2=\frac{?_0^2k^2}{\varepsilon_\infty\prod\limits_{j-1}^{j=n}\dfrac{\omega^2_{lj}-\omega^2}{\omega^2_{0j}-\omega^2}}. \tag{17}$$

Here, we proved that magnetic permeability is unity.

For unitary polaritons for which the refraction index is unity, we thus obtain the following expressions:

$$n^2=\varepsilon\mu=\frac{c_0^2k^2}{\omega^2}=1 \tag{18}$$

$$\frac{c_0^2k^2}{\omega^2}=\frac{\varepsilon_\infty c_0^2k^2\prod\limits_{j-1}^{j=n}\dfrac{\omega^2_{lj}-\omega^2}{\omega^2_{0j}-\omega^2}}{?_0^2k^2}=\varepsilon_\infty\prod_{j-1}^{j=n}\frac{\omega^2_{lj}-\omega^2}{\omega^2_{0j}-\omega^2}=1. \tag{19}$$

The group velocity of quasi-particles (in this case, polaritons velocity) in a material can be found from the known relation:

$$V(\omega)=\frac{d\omega}{dk}=\left(\frac{dk}{d\omega}\right)^{-1}. \tag{20}$$

For the effective mass of quasi-particles in an isotropic media, we use the formula:

$$m(\omega)=\left(\frac{d^2E}{dp^2}\right)^{-1}=\hbar^2\left(\frac{d^2\varepsilon}{dk^2}\right)^{-1}=\hbar\left(V(\omega)\frac{dV(\omega)}{d\omega}\right)^{-1}. \tag{21}$$

4. Calculations

Applying the above formulas, we establish the dispersion dependencies of polaritonic waves in erbium nitrate hydrate. To determine this in the infrared range, the following formula was used:

$$\varepsilon(\omega)=\varepsilon_\infty\frac{\left(\omega^2_{l1}-\omega^2\right)\left(\omega^2_{l2}-\omega^2\right)}{\left(\omega^2_{01}-\omega^2\right)\left(\omega^2_{02}-\omega^2\right)}. \tag{22}$$

Similarly, we can obtain results for the dependencies of visible polaritonic waves with:

$$\varepsilon(\omega)=\varepsilon_\infty\prod_{j-1}^{j=5}\frac{\omega^2_{lj}-\omega^2}{\omega^2_{0j}-\omega^2}. \tag{23}$$

For distilled water this is assumed to be $\varepsilon_\infty=(n_{\mathrm{H_2O}})^2=(1,33)^2$.

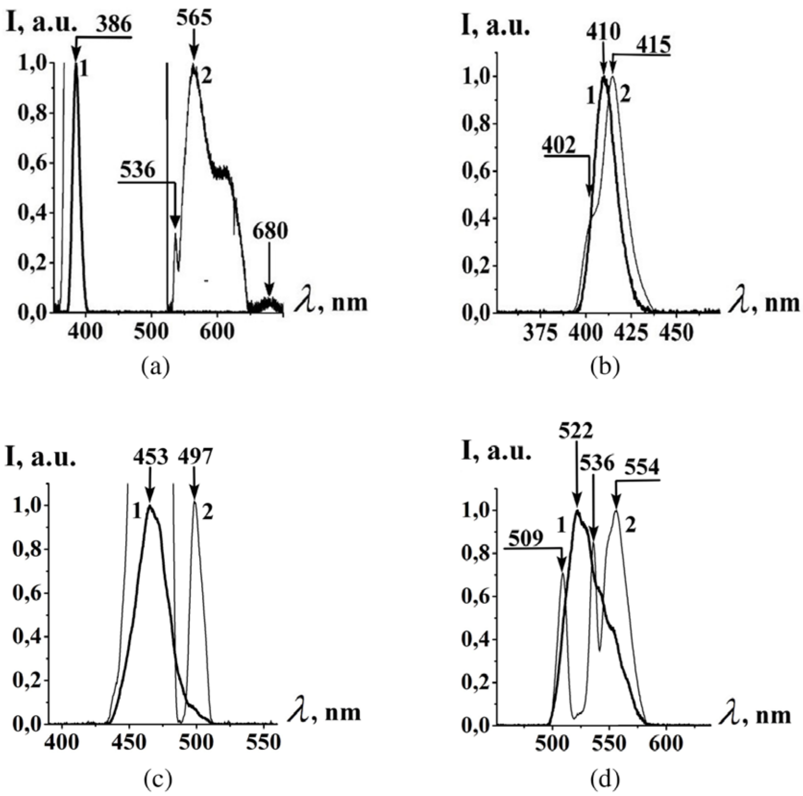

Figure 2. The spectra of the experimental setup for observing photoluminescence spectrum of erbium nitrate hydrate with various wavelengths of pump radiation: (*a*) 386 nm, (*b*) 410 nm, (*c*) 453 nm and (*d*) 522 nm.

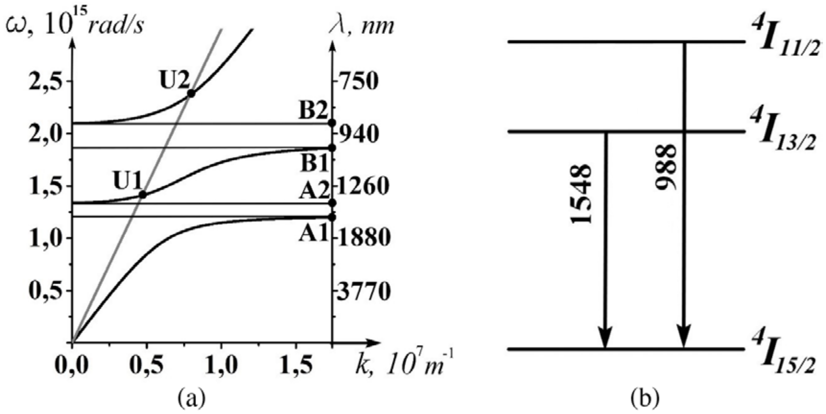

Figure 3. (*a*) The dispersion curves $\omega(k)$ for the erbium nitrate hydrate in infrared range. The corresponding wavelength: A1—1548 nm, A2—1407 nm, B1—988 nm, B2—897 нм, U1—1327 nm and U2—792 nm; (*b*) The corresponding transition between energy levels.

Previous work [8] has shown that longitudinal frequencies are of the same order as transverse frequencies. To make a more exact calculation that will agree more closely with the results of the experiment, we must consider $\omega_{\mathrm{LO}} \approx (1,1 \div 1,2)\,\omega_{\mathrm{TO}}$ for high frequency and $\omega_{\mathrm{LO}} \approx (1,01 \div 1,02)\,\omega_{\mathrm{TO}}$ for low frequency.

Figures 3 and 4 illustrate the calculation dispersion law $\omega(k)$ for electromagnetic waves in near infrared and visible ranges.

The parameters of electromagnetic waves at the points corresponding unitary polaritons, for which the refractive index is unity, are shown in tables 2 and 3. In those points, the reflection coefficient at normal incidence is zero, i.e. the material is characterized by high transparency for the incident radiation.

As shown in the next section, the calculated parameters can be used to increase the efficiency in active media for lasers.

5. Liquid-core laser

A liquid-core waveguide can be made from tubing in which the wall material has a lower refractive index than the liquid-core material. Water has a refractive index of 1.33. Until the late 1980s, no coating or tubing materials were available with

Table 2. Parameters of electromagnetic waves at singular points in infrared range.

Singular points	ω, 10^{15} rad s^{-1}	λ, nm	ν, 10^{18} m^{-1}	k, 10^7 m^{-1}	n	R	v, 10^8 m s^{-1}	m, 10^{-36} kg
U1	1,41	1337	0,75	0,47	1,0	0,0	0,42	6,28
U2	2,36	799	1,25	0,78	1,0	0,0	1,03	3,73
A1	1,21	1548	0,64	–	∞	1,0	0,0	–
A2	1,34	1407	0,71	–	$-\infty$	1,0	0,0	–
B1	1,90	988	1,01	–	∞	1,0	0,0	–
B2	2,10	897	1,11	–	$-\infty$	1,0	0,0	–

Table 3. Parameters of electromagnetic waves at singular points in visible range.

Singular points	ω, 10^{15} rad s^{-1}	λ, nm	ν, 10^6m^{-1}	k, 10^7 m^{-1}	N	R	v, 10^8 m s^{-1}	m, 10^{-36} kg
U1	2,93	643	1,56	0,977	1,0	0,0	0,29	155
U2	3,52	535	1,87	1,171	1,0	0,0	0,62	4384
U3	3,63	519	1,92	1,211	1,0	0,0	0,01	709
U4	4,37	431	2,32	1,458	1,0	0,0	0,13	288
U5	5,99	315	3,18	1,994	1,0	0,0	1,21	11
A1	2,89	652	1,53	–	∞	1,0	0,0	–
A2	2,91	645	1,55	–	$-\infty$	1,0	0,0	–
B1	3,49	540	1,85	–	∞	1,0	0,0	–
B2	3,52	534	1,87	–	$-\infty$	1,0	0,0	–
C1	3,59	525	1,91	–	∞	1,0	0,0	–
C2	3,62	520	1,92	–	$-\infty$	1,0	0,0	–
D1	3,88	485	2,06	–	∞	1,0	0,0	–
D2	4,27	441	2,27	–	$-\infty$	1,0	0,0	–
E1	4,64	406	2,46	–	∞	1,0	0,0	–
E2	5,11	369	2,71	–	$-\infty$	1,0	0,0	–

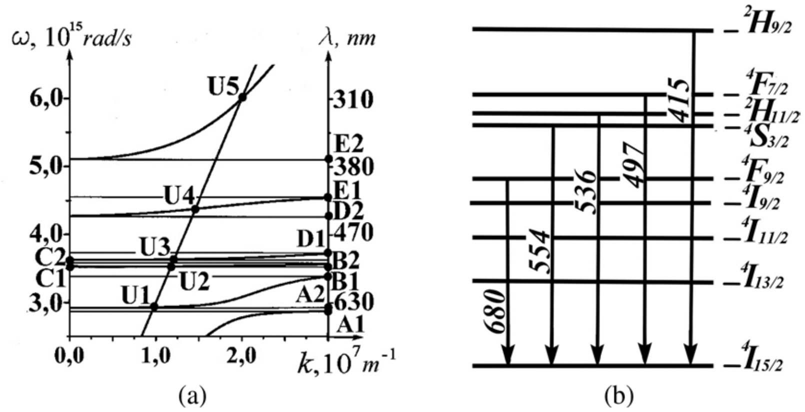

Figure 4. (*a*) The dispersion curves $\omega(k)$ for the erbium nitrate hydrate in visible range. The corresponding wavelength: A1—652 nm, A2—645 nm, B1—540 nm, B2—534 nm, C1—525 nm, C2—520 nm, D1—485 nm, D2—441 nm, E1—406 nm, E2—369 nm, U1—643 nm, U2—535 nm, U3—519 nm, U4—431 nm and U5—315 nm; (*b*) the corresponding transition between energy levels.

a lower refractive index. The use of glass or polymer tubing meant that either nonaqueous liquids with even higher refractive had to be used as the core or a cladding-air interface was required.

These problems were eliminated when DuPont introduced a fluoropolymer (Teflon AF) with a refractive index less than 1.33 [9]. Teflon AF is fluoropolymer (2,2-bistrifluoromethyl-4,5-difluoro-1,3,-dioxole) and has a refractive index in the range 1.31–1.29. It is important that in infrared and visible ranges, the refractive index is about 1.29.

In addition to its lower refractive index, Teflon AF has exceptional preventive capacities such as flexibility and hydrophobicity. In some cases, Teflon AF has higher optical losses than a traditional waveguide but is easier and cheaper to produce. This product appears promising.

A principal scheme of the liquid-core laser based on erbium nitrate hydrate is presented in figure 5.

Optical fibres are necessary for input and output focusing ((3) and (7), respectively) and directing the pump radiation. The connection between the fibres and the liquid-core waveguide (5) is realized through input and output clutches ((4) and (6), respectively). The above mentioned scheme provides a number of advantages over other known schemes, including other optical focusing elements absent from the scheme, high

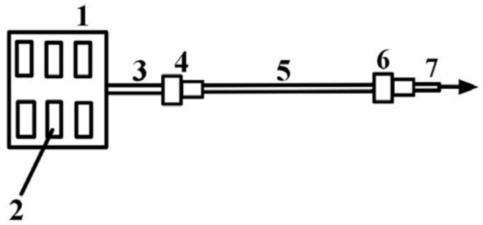

Figure 5. A principal scheme of the liquid-core laser based on erbium nitrate hydrate: 1—source of optical radiation, 2—light-emitting diodes, 3—input fibre, 4—input clutch, 5—liquid-core waveguide 6—output clutch, and 7—output fibre.

quality of connection and reduction of materials needed for production. This scheme has face pumping.

It should be emphasized that, under such conditions, when unitary polaritons are formed, efficiency of energy light density in this laser increases. This means that, for example, at the wavelength of 519 nm, the efficiency of energy light density increases by a factor of 100 because group velocity decreases by a factor of 100.

6. Conclusions

In summary, in this paper, we presented and analyzed the photoluminescence spectrum of erbium nitrate hydrate. The study compared both theoretical and experimental results for energy levels of free ions of Er^{3+} and erbium nitrate hydrate and was based on the analysis of empirical research provided in energy level diagrams.

The dispersion dependencies of polaritonic waves in erbium nitrate hydrate were established. The positions of unitary polaritons for which the refraction index is unity were determined. As a result, the group velocities of unitary polaritons were shown to be significantly decreased. The effective mass of unitary polaritons has low magnitude, comparable to the mass of electrons. The increase of efficiency of energy light density in this laser at such point was also demonstrated.

We have shown that it is possible to develop a liquid-core laser. In summary, the principle scheme of the laser such kind was presented. The possibility of a laser generating at wavelengths 1548, 988, 652, 540, 525, 485, and 406 nm was shown. The conditions for pumping optimizing operation of lasers based on erbium nitrate hydrate were established.

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