

Photodynamic processes in $\text{LiCaAlF}_6:\text{Ce}^{3+}$ UV active medium

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Abstract. The objectives of this paper are experimental studies of pump-induced effects in $\text{LiCaAlF}_6:\text{Ce}^{3+}$ single crystals and computer model elaboration and appropriated software package engineering. The elaborated experimental technique and software allow either to calculate the nonlinear absorption/gain characteristics of the active medium on the basis of known parameters, or to find its previously unknown parameters from pump-probe experimental dependences.

1. Introduction

One of the key problems of quantum electronics is prospects estimation of using new materials as laser media. Existing methods of traditional optical spectroscopy are often cannot give a definite answer to this question, because during laser experiments the substance undergo much more intense impacts. Intense optical pumping is often accompanied by additional effects associated with the appearance of large electronic populations at the excited states of the investigated medium that may impede, impair or even completely exclude the possibility of laser action [1]. One of the effective ways to assess the real "laser potential" of new media are "pump-probe" spectroscopy methods, which suggest creation of conditions for the excitation of the material close to the conditions of the laser tests. The most informative studies are absorption/transmission coefficient investigation dependent on intensity and wavelength of exposure radiation. The specific role has interpretation methodology of the experimental data. Thus it is possible to fully characterize the active medium, quantify its prospects of realization, energetic and tunability properties of laser based on it.

2. Single-pass amplifier model

Experimental technique and samples preparations are described at our previous article [2]. By means of pump-probe spectroscopy absorption and gain coefficients of $\text{LiCaAlF}_6:\text{Ce}^{3+}$ crystals have been registered in spectral ranges correspondent to the $4f \leftrightarrow 5d$ transitions of Ce^{3+} ions versus the intensity of the pump and probe radiation. Interpretation of these dependencies is realized using a hypothetical model of photodynamic processes described in [1] and shown in Fig. 1.

The model included four level scheme of laser oscillator (levels 1-4) supplemented with transitions from excited states to the states localized in the conduction band of the crystal host (cross-sections σ_{35} at the wavelength of 266 (Pump) and 290 (Probe) nm) which result in generation of electrons and holes and photoconductivity, recombination processes (P_{51} and P_{54} probabilities) as one of the type of free charges relaxation channels and the processes of formation of color centers (P_{56} probability) as another one.



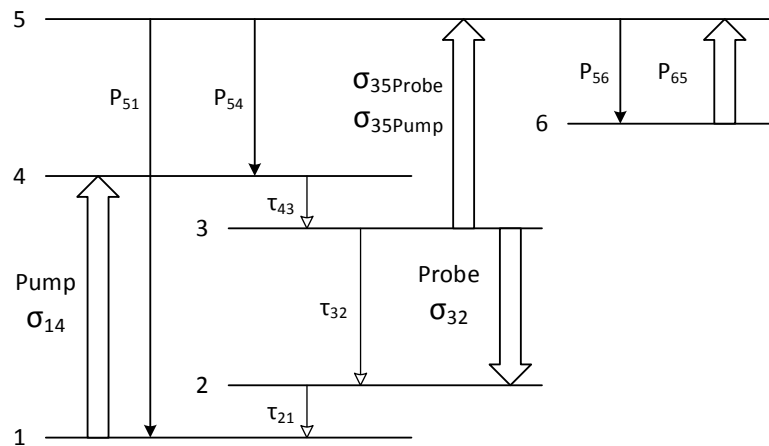


Figure 1. Stochastic model of photodynamic processes in $\text{LiCaAlF}_6:\text{Ce}^{3+}$ active media

The system also includes destruction of color centers channel both due to thermalization (P_{65} probability) and due to absorption of pump and/or laser radiations (cross-sections σ_{65} at the wavelength of 266 and 290 nm, respectively). The system of kinetic equations (1) corresponding to the model are following:

$$\begin{aligned}
 \frac{d}{dt}n_1 &= -\text{Pump}(t) \cdot \sigma_{14} \cdot n_1 + \frac{n_2}{\tau_{21}} + \text{Pump}(t) \cdot \sigma_{14} \cdot n_4 + P_{51} \cdot n_5 \\
 \frac{d}{dt}n_2 &= -\left[\text{Probe}(t) \cdot \sigma_{32} + \frac{1}{\tau_2}\right] \cdot n_2 + \left[\text{Probe}(t) \cdot \sigma_{32} + \frac{1}{\tau_3}\right] \cdot n_3 \\
 \frac{d}{dt}n_3 &= \text{Probe}(t) \cdot \sigma_{32} \cdot n_2 + \frac{n_4}{\tau_4} \\
 &\quad - \left[\text{Probe}(t) \cdot \sigma_{35\text{probe}} + \text{Probe}(t) \cdot \sigma_{32} + \text{Pump}(t) \cdot \sigma_{35\text{pump}} + \frac{1}{\tau_3}\right] \cdot n_3 \\
 \frac{d}{dt}n_4 &= \text{Pump}(t) \cdot \sigma_{14} \cdot n_1 - \left[\text{Pump}(t) \cdot \sigma_{14} + \frac{1}{\tau_4}\right] \cdot n_4 + P_{54} \cdot n_5 \\
 \frac{d}{dt}n_5 &= [\text{Probe}(t) \cdot \sigma_{35\text{probe}} + \text{Pump}(t) \cdot \sigma_{35}] \cdot n_3 - [P_{54} + P_{51} + P_{56}] \cdot n_5 \\
 &\quad + \left[\text{Probe}(t) \cdot \sigma_{65\text{probe}} + \text{Pump}(t) \cdot \sigma_{65\text{pump}} + \frac{1}{\tau_6}\right] \cdot n_6 \\
 \frac{d}{dt}n_6 &= P_{56} \cdot n_3 - \left[\text{Probe}(t) \cdot \sigma_{65\text{probe}} + \text{Pump}(t) \cdot \sigma_{65\text{pump}} + \frac{1}{\tau_6}\right] \cdot n_6
 \end{aligned} \tag{1}$$

where σ_{ij} – transition cross-sections, P_{ij} – probability of processes, τ_i – lifetime of appropriated levels, $\text{Probe}(t)$, $\text{Pump}(t)$ – probe and pump beam's photon density, n_i – appropriated level's population. The physical means of parameters of the system equations are clear from the Fig.1.

The finding solution of these equation systems are pump and probe radiations absorption or gain coefficients (2) which contents contribution of stimulated emission, ground-state, excited-state and color center absorptions:

$$\begin{aligned}
 k_{pump}(t) &= \sigma_{14} \cdot (n_1(t) - n_4(t)) + \sigma_{35pump} \cdot n_3(t) + \sigma_{65pump} \cdot n_6(t) \\
 G_{probe}(t) &= \sigma_{32} \cdot (n_3(t) - n_2(t)) - \sigma_{35probe} \cdot n_3(t) - \sigma_{65probe} \cdot n_6(t)
 \end{aligned}
 \quad (2)$$

As the solution of the kinetic equation (1) is valid for a crystal layer of infinite small thickness, the balance equations need to be integrated in the spatial coordinates along the crystal. However, similar types system of integral-differential equations arises which is unsolvable analytically, and numerical methods are time-consuming. To simplify calculation procedure, the step-by-step approach is realized – the bulk sample is considered as a stack of thin partitions which are absorbing or amplifying the pump and/or probe radiations accordingly by equations (1) and (2). Thus the beams characteristics from the output of previous partitions are using as input beams for the following ones.

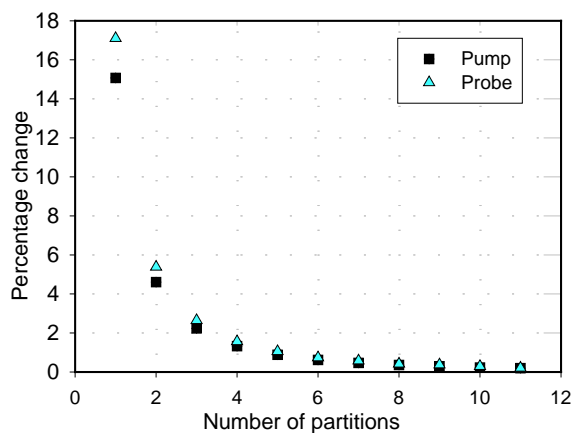


Figure 2. Determination of the optimal number of partitions.

accuracy (~1 %) in our experiments. To calculate the graphs on Fig.2 part of the model parameters were taken from the literature [3, 4] and spectral-kinetic studies of the samples. The remaining model parameters were the subject of an optimization procedure ("fitting") carried out in such a way to ensure a minimum residual between the experimentally determined and calculated data.

The number and thickness of partitions are dependent on the sample's length, parameter's values in the system equations (1), the measuring accuracy and a noise level. There is simple technique to estimate a minimal number of partitions N take into account the criteria (3) which demands that percentage change in the calculated value of the absorption or gain coefficients with the increasing N to $N+1$ should be less than experimental accuracy or noise level Δ :

$$\frac{k_{N+1}}{k_N} < \Delta \quad (3)$$

For instance, it can be seen from the Fig.2 the optimal number of partitions is 8-10 for the typical samples length (~1 cm) and measuring

3. Results and discussion

The results of optimization procedure ("fitting") are shown in Fig. 3. and it are demonstrated a good agreement between experimental data and theoretical calculations.

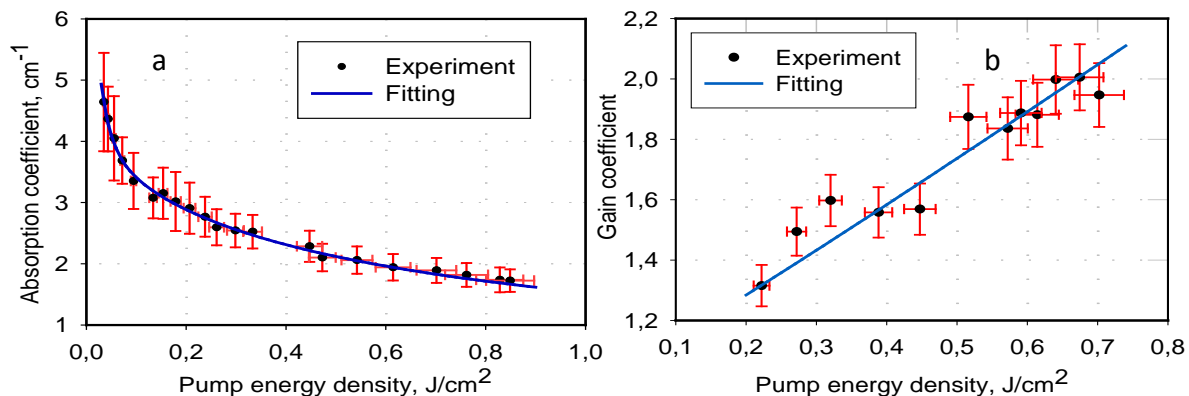


Figure 3. Absorption coefficient of pump radiation at $\lambda=266$ nm (a) and gain coefficient at $\lambda=290$ nm (b) depending on the pumping radiation energy density with the fitting results

Results are shown in the Table 1. Here are the estimated absorption cross-sections at the wavelength of 266 ($\sigma_{35\text{pump}}$) and 290 nm ($\sigma_{35\text{probe}}$) from Ce^{3+} ions 5d-excited-state and conduction band, the pump-induced color centers photoionization cross-sections at 266 ($\sigma_{65\text{pump}}$) and 290 ($\sigma_{65\text{probe}}$) nm, rates of recombination processes of free charge carriers to 5d- (P_{54}) and 4f-states (P_{51}) of Ce^{3+} ions and color center formation probabilities (P_{56}), concentration of Ce^{3+} ions and color centers.

Table 1. Parameters of photodynamic processes in $\text{LiCaAlF}_6:\text{Ce}^{3+}$ resulting from computer simulation.

Absorption cross-sections, cm^{-2}		Probabilities, s^{-1}		Concentration, cm^{-3}	
$\sigma_{35\text{pump}}$	$(1 \pm 0.3) \cdot 10^{-18}$	P_{51}	$(3 \pm 0.4) \cdot 10^8$	Ce^{3+} ions	$(7 \pm 1.2) \cdot 10^{17}$
$\sigma_{65\text{pump}}$	$(3 \pm 0.5) \cdot 10^{-17}$	P_{54}	$(9 \pm 0.4) \cdot 10^6$	Color centers	$(3 \pm 1.5) \cdot 10^{16}$
$\sigma_{35\text{probe}}$	$(3 \pm 0.5) \cdot 10^{-19}$	P_{56}	$(5 \pm 0.4) \cdot 10^8$		
$\sigma_{65\text{probe}}$	$(2 \pm 0.5) \cdot 10^{-21}$				

As it can be seen from the Table 1, concentration of Ce^{3+} ions is much more than concentration of color centers, which confirms the lack of noticeable color center formation under the pumping conditions and explains high effective laser action in $\text{Ce}:\text{LiCAF}$ active medium.

4. Conclusion

In this work for the first time the key parameters of photodynamical processes in $\text{Ce}^{3+}:\text{LiCaAlF}_6$ crystal active media were estimated. It are the 5d-excited-state photoionization cross-sections of Ce^{3+} ions and pump-induced color centers at pumping and probe beams wavelength together with rates of recombination processes of free charge carriers. Research results and developed software can be used for further design of ultrashort pulse laser based on the $\text{Ce}^{3+}:\text{LiCaAlF}_6$ single crystals, as well as for studies of photodynamic processes in other activated materials [5].

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References

- [1] Semashko V V 2005 *Physics of the Solid State* **47** 1507
- [2] Galiev A I *et al* 2013 *J. Phys.: Conf. Series* **478** 012024
- [3] Marshall C D 1994 *J. Opt. Soc. Am. B* **11** 2054
- [4] Coutts D W, McGonigle A JS 2004 *IEEE Journal of Quantum Electronics* **40** 1430-1440
- [5] Akhtyamov O R *et al* 2013 *Izv. VUZov. Fizika* **56** 39-42