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Studies of the spectroscopic behavior of Cr^{+3}:LiCAF pumped by a solid-state dye laser

Raz Gvishi [a,*], Ehud Gonen [a], Yehoshua Kalisky [a], Stanley Rotman [b]

[a] *Arava Laser Laboratory, Ben-Gurion University, Temed Industrial Park, Mishor Yamin, D.N. Arava, 86800 Beer Sheva, Israel*

[b] *Electrical Engineering Department, Ben-Gurion University, Temed Industrial Park, Mishor Yamin, D.N. Arava, 86800 Beer Sheva, Israel*

Abstract

In this work we present spectroscopic studies of a laser system which combines transition metal-doped crystal pumped by a dye-doped solid-state laser. A dye-doped solid state laser emitting at ~610 nm was chosen to allow a better fit into the absorption peak of the LiCAF crystal, peaking at ~625 nm, in order to increase the efficiency of the light absorption of the Cr^{+3} ions. The pump laser is a dye-doped solid state laser Red Perylimide Dye (RPD)-doped in a composite-glass. This lasing maximum is at ~608 nm with a threshold energy of ~0.3 mJ/pulse, and a lasing slope efficiency of ~2.5% under excitation of 532 nm Nd:YAG laser. With the excitation of dye-doped solid state laser the Cr^{+3}:LiCAF emission centered at ~740 nm (due to the $^4T_2 \rightarrow {}^4A_2$ transition) with lifetime of 170 μs and emission cross-section, σ_f, of 1.4×10^{-20} cm^{-2}. The observed data allow us to plan a tunable Cr-crystal laser pumped by a solid-state dye laser.

1. Introduction

Solid-state lasers today are actively developing commercial field. Solid-state lasers encompass four different families of lasers: rare earth-doped solid-state lasers which are currently used for research and industry; diode laser arrays or bars which are becoming a growing commercial market; transition metal-doped solid-state lasers (such as Ti:sapphire) which exhibit some attractive laser properties; and dye-doped solid-state lasers which combine the unique features of dye lasers and the merits of solid-state matrix. The important feature of both transition metal-doped solid-state lasers and dye-doped solid-state lasers is the extremely large emission bandwidth, which provides two important laser characteristics: tunability and short pulse lasers. In this work we present a spectroscopic study of a laser system, which consists of a transition metal-doped crystal pumped by a dye-doped solid-state laser.

One of the most promising transition metal-doped crystals as laser media is Cr^{+3}:$LiCaAlF_6$ (Cr:LiCAF) [1–6]. Cr^{+3} ion has been reported to lase in more than 15 material hosts [1], including ruby (Cr^{+3}:Al_2O_3) lasers, which is a three-level laser, and one of the most successful tunable solid-state lasers, alexandrite, (Cr^{+3}:$BeAl_2O_4$) which is a four-level laser [1]. A tunable four-level laser operation of Cr^{+3} is obtained if the crystal field at the Cr^{+3} site is small enough resulting that the lowest excited state is the $^4T_2$ level, instead of the ^2E level. The difference in the electronic configuration

* Corresponding author.

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between the excited state ($^4T_2$) and the ground state ($^4A_2$) leads to a broadband emission. Cr^{+3}:LiCAF, as well as emerald and alexandrite yield laser efficiencies greater than 50% [1], which implies that excited-state absorption losses are low in these crystals. An additional advantage of the Cr^{+3}:LiCAF crystal is the relatively long excited-state lifetime, 170 μs [2]. In previous works, the Cr^{+3}:LiCAF crystal was pumped with Nd:YAG lasers, flash-lamps [2] and diode-lasers [3,4]. In order to increase the absorption of the Cr^{+3} ions, we chose a pump laser which emits at the red region (~610 nm), where there is a maximum in the absorption cross-section. The pump laser is a dye-doped solid state laser, which allows fitting the output pump wavelength to the maximum absorption wavelength of the crystal, at about 610 nm.

The details of the sol–gel dye doped lasers have been reported in the past by several authors [7–15]. The advantages of solid-state dye lasers over liquid dye lasers are that they are non-volatile, non-flammable, non-toxic, compact and mechanically stable. The problem of heat dissipation; however, poses a serious impediment for their utilization in applications that require high powers under either cw or pulsed high repetition rate operation. In liquid dyes, on the other hand, a fluid solution or a jet is a practical means of solving the heat problem. In both cases photostability is a property of prime importance for selecting a laser dye.

Sol–gel derived from composite glass is found to be a promising matrix due to its high photostability, optical quality, and mechanical stability compared to the other discussed matrices [12–15]. From extended studies of several groups [12–15], the perylimide red dye doped in composite glass was found to be one of the most photostable dyes in solid media. Therefore, in this paper we built a laser based on this media to use it as a pump source for study the spectroscopy properties of Cr^{+3}:LiCAF.

2. Experimental

2.1. Sample preparation

Gvishi et al. [7] described the procedure used to prepare the solid sample of dye-doped composite glasses previously. It is based on the composite glass preparation method of Pope et al. [11]. Briefly, the sol–gel process prepared highly porous silica-gel bulk glasses. It is followed by impregnation of bulk glasses with methylmethacrylate (MMA), which diffuses into the bulk glass pores and polymerizes in situ. The final glass was cleaned and polished. The result is a nanostructure composite glass of high optical quality. It can be doped with two (or more) different dyes, each of them residing in different phases of the matrix (the silica phase, the PMMA phase and the interfacial phase), to make multifunctional bulk materials for photonics.

Red perylimide dye (RPD) was doped in the PMMA phase by impregnation through the monomer MMA solution. This procedure resulted in a concentration of $\sim 3 \times 10^{-3}$ M RPD (this concentration represents the volume of the pores of the glass, ~70%, assuming that no chromophore evaporate ion occurred).

The commercial laser crystal of Cr^{+3}:LiCAF was supplied by VLOC (Fl, USA). The concentration of the Cr ions in the crystal was 0.8%.

2.2. Measurements

The absorption spectra of Cr^{+3}:LiCAF sample were obtained using a Jasco V-570 UV-VIS computerized spectrophotometer with a resolution of 1 nm.

Excitation and emission spectra of the dye-doped glass were collected on a Hitachi F-2000 spectrofluorometer, with a 10 nm resolution, and the emission was collected at 90° geometry.

The excitation of the Cr^{+3}:LiCAF crystal was measured using a Xenon flash lamp as a light source. The light excitation was passed through a monochromator (PTI 1200 g/mm) to select the relevant wavelengths. The chopped beam was focused on the crystal, while the emission of the crystal was collected by a second monochromator and furthermore filtered by a high pass filter attached on the inlet slit. The observed signal was detected with a photomultiplier (Hamamatsu R636) coupled to a lock-in-amplifier (SR 510).

The fluorescence spectra and lifetime of Cr^{+3}:LiCAF were measured by a sol–gel dye laser pumped by a 532 nm frequency-doubled (Quanta

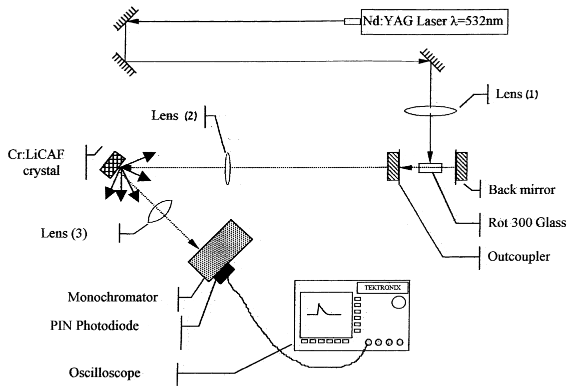

Fig. 1. Experimental set-up – Fluorescence an lifetime measurements of Cr^{+3}:LiCAF pumped by a solid-state dye laser.

International) Nd:YAG laser. The experimental set-up is presented in Fig. 1. The excitation source, Nd:YAG laser, was producing about 3 mJ per pulse at repetition rate of 2 Hz. The beam was passed through a set of mirrors and cylindrical lens and focused on the dye doped sol–gel sample. The sample was placed in a transverse pump configuration, which consist of a ~100% reflecting flat mirror and a ~35% reflecting flat output coupler in the red region. The performance of our home built dye laser, namely lasing output vs. wavelength of the dye-doped composite glasses was measured by passing the lasing output through a monochromator (Jerrall Ash, 1 nm resoltuion), which was scanned manually. Then, the beam detected by a fast PIN Photodiode (Model SGA 100A, 0.5 μs response) attached to Tektronics oscilloscope (model TDS 724A).

An output lasing of few tens of μJ was enough to achieve significant emission from the Cr^{+3}:LiCAF crystal. This emission was passed through a monochromator (Jerrall Ash, 1 nm resolution), that was manually scanned. Then, the beam was detected by a fast PIN Photodiode (Model SGA 100A, 0.5 μs response) which was attached to Tektronics oscilloscope (model TDS 724A).

3. Results and discussion

The wavelength dependence of the RPD:composite glass (~0.003 M) laser output is presented in Fig. 2 (dashed line). The output peak is centered at ~608 nm with a full width at half maximum (FWHM) of 9 nm. The dye laser output at 608 nm is an optimal pump source to excite the Cr^{+3}:LiCAF crystal which can absorb at the red region. An excitation spectrum of Cr^{+3}:LiCAF crystal emitted at 750 nm is presented in Fig. 2 (continuous line). The excitation spectrum exhibits two major peaks centered at ~440 nm (22 700 cm^{-1}) and ~625 nm (16 000 cm^{-1}). The peaks are attributed to the $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ transitions, respectively. The red excitation band ($^4A_2 \rightarrow {}^4T_2$ transition) exhibits two shoulders, one blue shifted (~610 nm (16 400 cm^{-1})) and one red shifted (~650 nm (15 400 cm^{-1})). These shoulders were previously attributed [6] to the influence of $^2T_1$ and ^2E energy levels on the $^4T_2$ energy level, respectively. From this phenomena we obtain that for LiCAF the value of D_q/B is equal to 2.15, the energy value where level $^4T_2$ crosses levels $^2T_1$ and ^2E [6]. From Fig. 2 it is clearly seen that the RPD:composite glass (608 nm) is much more appropriate than a frequency-doubled Nd:YAG laser ($\lambda = 532$ nm) for exciting the Cr^{+3}:LiCAF crystal.

A typical data of the fluorescence of Cr^{+3}:LiCAF crystal is presented in Fig. 3. The fluorescence spectrum is centered at ~740 nm (13 500 cm^{-1}) with a full width at half maxima (FWHM) of 70 nm (1300 cm^{-1}). This emission band is attributed to the $^4T_2 \rightarrow {}^4A_2$ transition. The shape of the observed spectrum is far from gaussian shape and it exhibits a shoulder at ~770 nm (13 000 cm^{-1}). The phenomena not discussed in previous

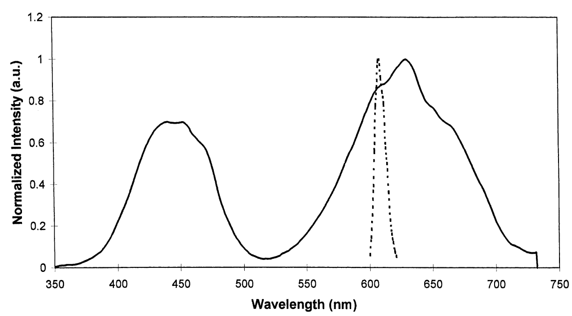

Fig. 2. An excitation spectrum of Cr^{+3}:LiCAF crystal emitted at 750 nm (continuous line). Wavelength dependence of the RPD: composite glass (~0.003M) laser output (dashed line).

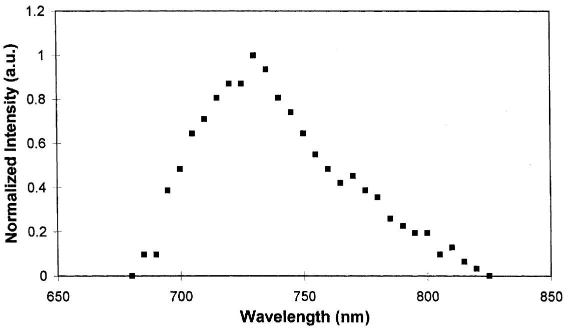

Fig. 3. A wavelength dependence spectrum of Cr^{+3}:LiCAF crystal fluorescence under excitation of RPD:composite glass laser (608 nm).

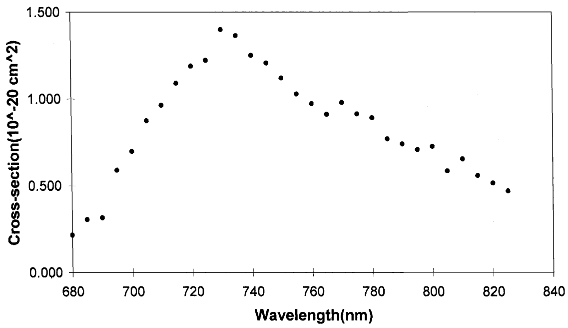

Fig. 5. A wavelength dependence of the emission cross-section spectrum of Cr^{+3}:LiCAF crystal under excitation of dye laser (608 nm).

works are attributed to the contribution of $^2E \rightarrow {}^4A_2$ transition.

From preliminary results it is found that the lifetime decay plots are of exponential nature. Fig. 4 presents the lifetime decay curve measured at room temperature (295 K) with excitation of 608 nm RPD-doped glass laser. The decay curve is fitted to an exponential decay with a lifetime equal to 170 μs at 295 K. Payne et al. [1] report a little variation in the measured lifetimes as a function of temperature. For a temperature of 295 K, a 175 μs lifetime was observed and for a temperature of 20 K the observed lifetime increase to 200 μs. This effect is typical of a centrosymmetric environment without non-radiative decay.

The emission cross-section was calculated with the following formula:

$$\sigma_f = \lambda_0^4(\tau\pi n^2 c)^* g(\lambda), \tag{1}$$

where τ is the radiative emission lifetime, λ the lasing wavelength, n the refractive index, c the speed of light, and $g(\lambda) = F(\lambda)/fF(\lambda)$ where $F(\lambda)$ is the measured emission intensity. By inserting the experimental values for the emission peak at the wavelength $\lambda_{max} = 730$ nm, obtained by exciting with RPD-doped glass laser, we obtain a value for $\sigma_f = 1.4 \times 10^{-20}$ cm^2 (presented in Fig. 5). Payne et al. [1] reported a value for $\sigma_f =\sim 0.9 \times 10^{-20}$ cm^2 for the parallel polarization excitation. Payne et al. results give us only a reference point. We cannot compare our undefined polarization experiments to that of Payne et al., but we can note that our results are close to the results mention above.

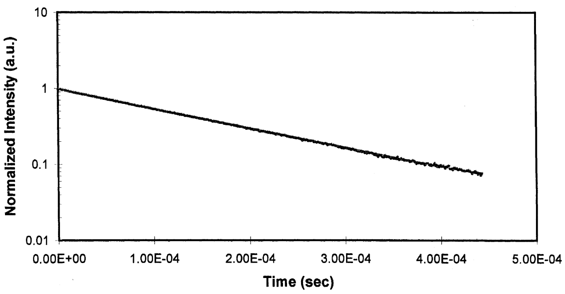

Fig. 4. A fluorescence lifetime decay plot of Cr^{+3}:LiCAF crystal measured with excitation of 608 nm RPD-doped glass laser.

In order to achieve efficient lasing, σ_{eff}, the effective stimulated emission cross-section, should be large [6]. The effective stimulated emission cross-section is related to the emission cross-section, σ_f, the ground-state absorption cross-section, σ_a, and to the excited-state absorption (ESA) by the following equation:

$$\sigma_{eff} = \sigma_f + \sigma_a - \sigma_{ESA}. \tag{2}$$

Therefore we intend to measure the excited-state absorption of the crystal. The observed data which will obtained from this work will allows us to plan and achieve a tunable Cr-crystal laser pumped by a solid-state dye laser. The final goal is to achieve a compact system pumped by a diode-pumped Nd:YAG laser.

4. Conclusions

In this work we study the spectroscopic behavior of Cr^{+3}:LiCAF pumped by a solid-state dye laser. Cr^{+3}:LiCAF is one of the most promising transition metal-doped crystals with laser efficiency greater than 50%. The high efficiency implies that excited-state absorption losses are low in these crystals. In previous works, the Cr:LiCAF crystal was pumped with Nd:YAG laser, flash-lamp and diode-laser. In order to increase the absorption of the Cr^{+3} ions we chose a pump laser which emits at the red region (~610 nm), where there is a maximum in the absorption cross-section. The pump dye-doped solid state laser was a red perylimide dye (RPD)-doped in a composite-glass, which is found to be a very photostable dye. This laser showed a output lasing at ~608 nm with a threshold of ~0.3 mJ/pulse. The lasing slopes efficiencies of ~2.5% under excitation of Nd:YAG laser. With the excitation of dye-doped solid state laser the Cr^{+3}:LiCAF crystal observed centered at ~740 nm of the $^4T_2 \rightarrow {}^4A_2$ transition with lifetime of 170 μs and $\sigma_f = 1.4 \times 10^{-20}$ cm^{-2}. The observed data allow us to contract a tunable Cr-crystal laser pumped by a solid-state dye laser.

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