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Excited-state absorption and stimulated emission of tetrahedral Co^{2+} ion in $LiGa_5O_8$

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Abstract. Differential absorption spectra measurements of tetrahedral Co^{2+}-doped $LiGa_5O_8$ have been made using a ps pump-probe technique. The stimulated emission from the $^4T_1(^4P)$ level to the $^4A_2(^4F)$ and $^4T_2(^4F)$ states is observed to be overlapped by the excited-state absorption. The excited-state absorption is tentatively assigned to transition from the $^4T_1(^4P)$ level of the Co^{2+} ion to the conduction band of $LiGa_5O_8$. For Co^{2+}:$LiGa_5O_8$, laser operation is expected to be possible in the vicinity of 720 nm and in the 860–970 nm spectral region.

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Co^{2+}-doped crystals in which the Co^{2+} ions are in a tetrahedrally coordinated lattice site have been under investigation [1–7]. This is due to the fact that crystals doped with tetrahedral Co^{2+} ions are attractive for laser applications. The tetrahedral Co^{2+} in $Y_3Sc_2Ga_3O_{12}$ (YSGG) and $Y_3Al_5O_{12}$ (YAG) has been used as saturable absorber for passive Q-switching of the Er:glass laser [8, 9]. Co^{2+}:ZnSe has been used as saturable absorber Q-switch for the Er^{3+}:Yb^{3+}:glass laser [10]. On the other hand, the tetrahedral Co^{2+} ion in a number of spinels such as $MgAl_2O_4$ [1], $LiGa_5O_8$ [2], and $ZnGa_2O_4$ [3] exhibits strong broad luminescence bands in the visible and near-infrared spectral regions with sub-μs lifetimes. This allows us to consider such crystals as possible candidates for tunable solid-state lasers in the visible and near-infrared. In this paper, excited-state absorption and stimulated emission of Co^{2+}:$LiGa_5O_8$ are studied under ps excitation in the spectral region 460–970 nm.

$LiGa_5O_8$ has an inverse spinel structure (space group O^6-$P4_332$), and contains four formula units in the cubic cell [3]. The lattice constant is $a = 0.833$ nm. One half of the Ga^{3+} ions occupy tetrahedral sites while the other half of the Ga^{3+} ions, together with the Li^+ ions, occupy octahedral sites. It has been shown [5] that the Co^{2+} ions substitute for tetrahedrally coordinated Ga^{3+} ions in the $LiGa_5O_8$ lattice and occupy sites of C_3 point-group symmetry. The thickness of the Co^{2+}:$LiGa_5O_8$ sample studied was 1.1 mm.

1 Experiment

Excited-state absorption and stimulated emission measurements were carried out by use of a ps pump-probe technique. The differential absorption spectra were measured as

$$\Delta\mathrm{OD}(\lambda) = -\lg(T/T_0)\,, \tag{1}$$

where T and T_0 are probe beam transmittance of pumped and unpumped crystal, respectively. The 15-ps-duration pulses at 0.54 μm from a frequency-doubled passively mode-locked Nd^{3+}:$YAlO_3$ laser were used as a pump beam. The ps white-light continuum, which was produced in a D_2O cell, was used as a probe beam. An optical multichannel analyzer with two photodiode arrays combined with a spectrometer was used as a recording system. All the measurements were performed at room temperature, and with a spectral resolution ≈ 1 nm. The differential absorption ΔOD of the probe beam after all the excited ions have accumulated in a level whose lifetime is much longer compared to the pulse duration, can be expressed as [11–13]

$$\Delta\mathrm{OD}(\lambda) = \Delta NL(\sigma_{\mathrm{ESA}} - \sigma_{\mathrm{GSA}} - \sigma_{\mathrm{SE}})\,, \tag{2}$$

where σ_{ESA}, σ_{GSA}, and σ_{SE} are the excited-state absorption (ESA), the ground-state absorption (GSA), and the stimulated emission (SE) cross sections, respectively, ΔN is the concentration of ions in the excited state, and L is the sample length. Notice that $\Delta\mathrm{OD} > 0$ means $\sigma_{\mathrm{ESA}} > \sigma_{\mathrm{GSA}} + \sigma_{\mathrm{SE}}$, and $\Delta\mathrm{OD} < 0$ signifies that $\sigma_{\mathrm{ESA}} < \sigma_{\mathrm{GSA}} + \sigma_{\mathrm{SE}}$. The relative shape of the $\sigma_{\mathrm{SE}}(\lambda)$ was obtained by measuring the fluorescence spectrum $I(\lambda)$ which in bulk media is related to the $\sigma_{\mathrm{SE}}(\lambda)$ by $\sigma_{\mathrm{SE}}(\lambda) \propto \lambda^5 I(\lambda)$ [14].

2 Results

The GSA spectrum of Co^{2+}:$LiGa_5O_8$ shown in Fig. 1 is similar to that of Co^{2+} ions in a tetrahedrally coordinated site in crystals with spinel, garnet, and fluorite structure [1–7]. In accordance with a Tanabe–Sugano diagram for a d^7 ion

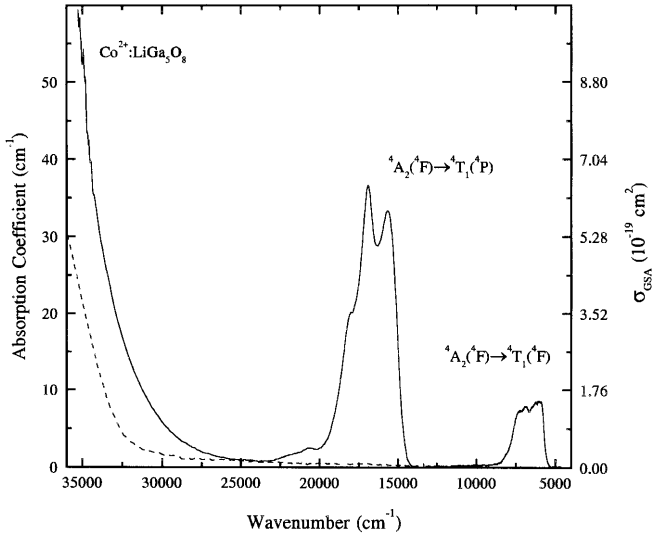

Fig. 1. The absorption spectra of the Co^{2+}:$LiGa_5O_8$ and undoped $LiGa_5O_8$ (*dashed curve*) crystals

in a tetrahedral crystal field (Fig. 2), the visible absorption band centered at 16 600 cm^{-1} ($\approx$ 600 nm) is assigned to the $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ transition, and the near-infrared band around 6700 cm^{-1} ($\approx$ 1.5 μm) to $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ transition [2]. The absorption band due to the $^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ transition expected to lie in the vicinity of 4000 cm^{-1} ($\approx$ 2.5 μm) is not observed because of its low oscillator strength. In a pure tetrahedral field this transition is electric-dipole forbidden. In a lower-symmetry crystal field (the Co^{2+} ions in $LiGa_5O_8$ occupy distorted tetrahedrally coordinated sites with C_3 point-group symmetry [2]) both the $^4T_1(^4P)$ and $^4T_1(^4F)$ energy levels split into two components, a singlet and a doublet, which are exhibited by two GSA bands with peaks at $\approx$ 16 900 cm^{-1} and $\approx$ 15 700 cm^{-1} originated from the $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ transition, and two GSA bands at $\approx$ 6150 cm^{-1} and $\approx$ 7000 cm^{-1} related to the $^4A_1(^4F) \rightarrow {}^4T_1(^4F)$ transition [2]. The absorption feature at 18 000 cm^{-1}, which is observed as a shoulder on the high-energy site of the $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ transition, is most likely due to one of the doublet levels arising from the ^2G free-ion level [2, 6]. The weak peak at $\approx$ 20 600 cm^{-1} may be assigned to the $^4A_2(^4F) \rightarrow {}^2T_1(^2P)$ transition by comparison with the spectral position of this transition observed for the tetrahedrally coordinated Co^{2+} ion in $MgAl_2O_4$ and $ZnAl_2O_4$ [1–4]. The GSA cross sections were determined from an expression $\sigma_{GSA}(\lambda) = \alpha(\lambda)/N_0$, where $\alpha(\lambda)$ is the measured ground-state absorption coefficient, N_0 is the Co^{2+} concentration in the $LiGa_5O_8$ crystal. From the known concentration of cobalt in the raw material (0.1 wt. %), the concentration N_0 was estimated to be 5.7×10^{19} cm^{-3}. The obtained values $\sigma_{GSA}(\lambda)$ are shown in Fig. 1. The band-to-band absorption of $LiGa_5O_8$ (Fig. 1) begins at $\approx$ 32 000 cm^{-1} (312 nm). The absorption edge of the Co^{2+}:$LiGa_5O_8$ crystal rising from $\approx$ 27 000 cm^{-1} (370 nm) can be assigned to the transition from die impurity level $^4A_2$ to the conduction band.

Figure 3 shows the differential absorption spectra of the Co^{2+}:$LiGa_5O_8$ crystal in the wavelength region of 460–970 nm. The sharp feature in this spectrum is a marker for the position of the pump. At this wavelength some light from the pump laser is scattered in the probe direction. GSA bleaching, ESA, and SE are observed simultaneously. Clearly observed is an ESA band in the 460–550 nm and 740–860 nm regions as well as a SE in the range of 860–970 nm (inset in Fig. 3). One can see a SE around 675 nm which is expected

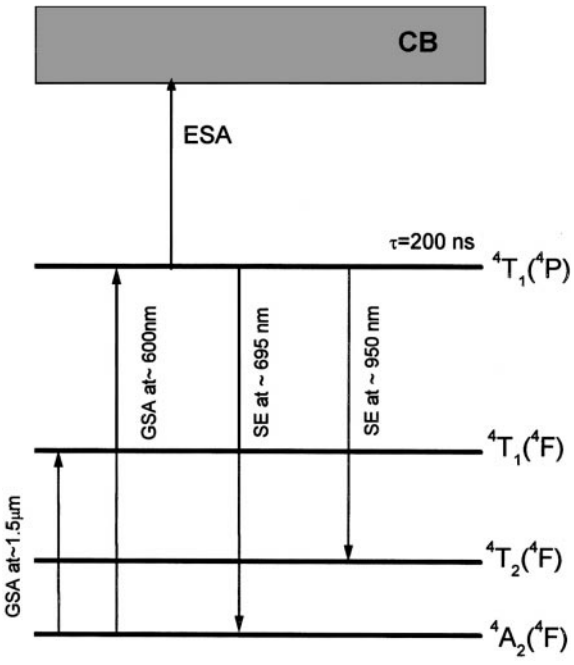

Fig. 2. Energy-level diagram of the Co^{2+} ion in $LiGa_5O_8$ in T_d symmetry. Ground-state absorption and stimulated-emission transitions are indicated by arrows. Note that doublet levels are omitted. CB, conduction band

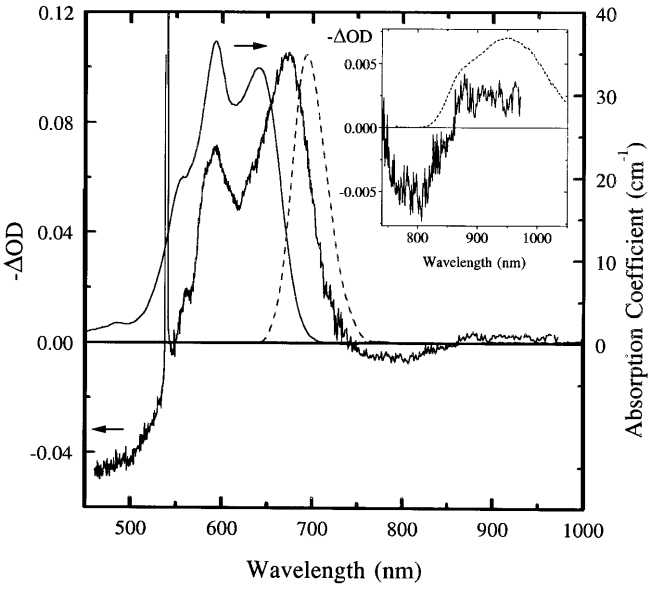

Fig. 3. The differential absorption spectrum $\Delta OD = -\lg(T/T_0)$ and corresponding ground-state absorption (*solid curve*) and stimulated-emission (*dashed curves*) spectra for Co^{2+}:$LiGa_5O_8$. The pump wavelength is 540 nm. The delay time between pump and probe pulses is 30 ps. The *inset* shows an expanded view of the ΔOD signal indicating lower values of that. The peak values of $\sigma_{SE}(\lambda)$ for the SE bands around 695 and 950 nm should not be compared

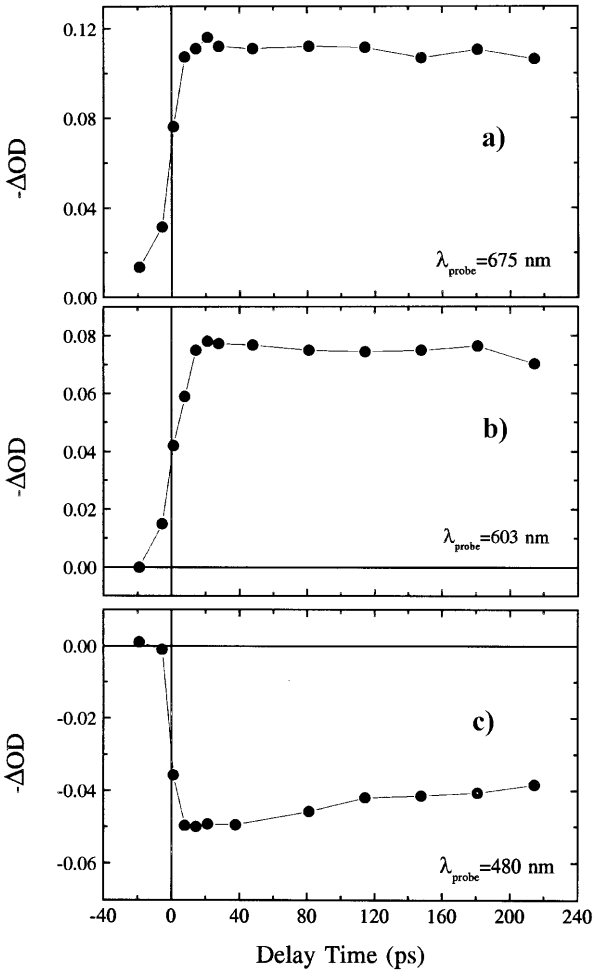

Fig. 4a–c. The differential absorption $\Delta\mathrm{OD} = -\lg(T/T_0)$ of Co^{2+}:$LiGa_5O_8$ as a function of pump-probe delay time at different wavelength of 675 nm (**a**), 603 nm (**b**), and 480 nm (**c**)

to overlap with the GSA bleaching and ESA. Figure 4 shows the temporal dependence of differential absorption ΔOD for three wavelengths from the spectral regions in which the GSA bleaching, ESA, and SE are observed. The GSA bleaching, ESA, and SE appear with an instrument-limited rise time of ≈ 20 ps, and there is its negligible decay after our maximum delay time of 230 ps.

3 Discussion

The pump wavelength at 540 nm excites the $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ transition (Fig. 2). For the $LiGa_5O_8$ crystal, the lifetime of the $^4T_1(^4P)$ level has been found to be 200 ns [2] which is much longer than the 15-ps pulse duration in our experiments. This indicates that only transitions from the $^4T_1(^4P)$ level can appear in our measured ΔOD spectra as contribution from ESA and (or) SE. The pump pulse depletes the ground-state level $^4A_2(^4F)$ resulting in the $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ transition bleaching. Since no energetically higher lying quartet levels exist (than the $^4T_1(^4P)$ one) there are no spin-allowed ESA transitions from the $^4T_1(^4P)$ level.

The ESA is tentatively assigned to the transition from the impurity energy level $^4T_1(^4P)$ to the conduction band (Fig. 2). This is supported by the relative energy position of the $^4A_2 \rightarrow$ CB absorption edge which extends from 27 000 cm^{-1} and the $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ transitions which are located at 15 700 and 16 900 cm^{-1} (Fig. 1). So the absorption related to the transition from the $^4T_1(^4P)$ excited level of the tetrahedral Co^{2+} ion to the conduction band of the $LiGa_5O_8$ crystal may be expected to rise from ≈ 11 000 cm^{-1} (≈ 900 nm). It can not be excluded that, in accordance with a Tanabe–Sugano diagram for a d^7 electronic configuration in a tetrahedral crystal field, the spin-allowed transitions from the thermally populated $^2E(^2G)$ state to doublet levels arising from the ^2F free-ion level contribute to the ESA in the 740–860 nm region. In spectral region studied here the Co^{2+}:$LiGa_5O_8$ crystal exhibits two SE bands at around 695 nm and 950 nm (Fig. 3). These SE bands are attributed to the $^4T_1(^4P) \rightarrow {}^4A_2(^4F)$ and $^4T_1(^4P) \rightarrow {}^4T_2(^4F)$ transitions, respectively (Fig. 2). The $^4T_1(^4P) \rightarrow {}^4T_2(^4F)$ SE band is affected by the ESA at the short-wavelength edge of the SE band (inset in Fig. 3). The spectral region in which σ_{SE} exceeds σ_{ESA} ranges from 860 to 970 nm. Taking into account that there is no GSA in this region we can conclude that the region 860–970 nm is promising for laser operation. The $^4T_1(^4P) \rightarrow {}^4A_2(^4F)$ SE clearly overlaps with the GSA bleaching and the ESA. The wavelength region around 720 nm in which σ_{SE} exceeds σ_{ESA}, and σ_{GSA} seems to be low compared with $\sigma_{SE} - \sigma_{ESA}$ (the reabsorption by GSA is low) appears suitable for laser operation. In order to estimate the effective stimulated-emission cross sections $\sigma_{EFF} = (\sigma_{SE} - \sigma_{ESA})$, the $\Delta\mathrm{OD}(\lambda)$ spectrum must be corrected for the GSA bleaching, see (2). The unknown constant ΔNL can be determined from (2) if a specific wavelength exists, for which the ESA and SE are negligible. Under the assumption, that the ESA and SE are small in the vicinity of 640 nm, the cross sections σ_{EFF} can be estimated to be 4.3×10^{-19} cm^2 at 700 nm and 2.2×10^{-20} cm^2 between 880 nm and 900 nm.

4 Conclusion

The differential absorption spectra measurements of tetrahedral Co^{2+}-doped $LiGa_5O_8$ crystal were carried out with a ps pump-probe technique. The stimulated emission bands due to the transitions from the $^4T_1(^4P)$ level to the $^4A_2(^4F)$ and $^4T_2(^4F)$ levels as well as the ESA in the 460–550 nm and 740–860 nm regions were clearly observed. The ESA is tentatively assigned to the transition from the $^4T_1(^4P)$ level of Co^{2+} ion to the conduction band of the $LiGa_5O_8$ crystal. For tetrahedral Co^{2+}-doped $LiGa_5O_8$ crystal, laser operation is expected in the 860–970 nm spectral region and in the vicinity of 720 nm.

References

1. N.V. Kuleshov, V.P. Mikhailov, V.G. Scherbitsky, P.V. Prokoshin, K.V. Yumashev: J. Lumin. **55**, 265 (1993)
2. J.F. Donegan, F.G. Anderson, F.J. Bergin, T.J. Glynn, G.F. Imbusch: Phys. Rev. B **45**, 563 (1992)
3. T. Abritta, F.H. Blak: J. Lumin. **48**/**49**, 558 (1991)
4. J. Ferguson, D.L. Wood, L.G. Van Uitert: J. Chem. Phys. **51**, 2904 (1969)

5. R. Pappalardo, D.L. Wood, R.C. Linares: J. Chem. Phys. **35**, 2041 (1961)
6. D.L. Wood, J.P. Remeika: J. Chem. Phys. **46**, 3595 (1967)
7. V.M. Orera, R. Merino, R. Cases, R. Alcala: J. Phys. Condens. Matter. **5**, 3717 (1993)
8. M.B. Camargo, R.D. Stultz, M. Birnbaum, M. Kokta: Opt. Lett. **20**, 339 (1995)
9. R.D. Stultz, M.B. Camargo, M. Birnbaum, M. Kokta: OSA Proc. on Advanced Solid-State Lasers, Vol. 24, 1995, ed. by B.H.T. Chai, S. Payne, pp. 460–464
10. M. Birnbaum, M.B. Camargo, S. Lee, F.Unlu. R.D. Stultz: OSA TOPS on Advanced Solid-State Lasers, Vol. 10, 1997, ed. by C.R. Pollock, W.R. Bosenberg, pp 148–151
11. N.T. Melamed, F. de S.Barros, P.J. Viecaro, J.O. Artman: Phys. Rev. B **5**, 3377 (1972)
12. R.M. MacFarlane, J.C. Vial: Phys. Rev. B **34**, 1 (1986)
13. H. Manaa, C. Pedrini, R. Moncorge: OSA Proc. on Advanced Solid-State Lasers, Vol. 10, 1991, ed. by G. Dube, L. Chase, pp. 371–375
14. B.F. Aull, H.P. Jensen: IEEE J. Qauntum Electron. **QE-18**, 925 (1982)