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Technical Note

HEAT TREATMENT AND OPTICAL SPECTROSCOPY OF CR^{4+}:GGG FOR PASSIVELY Q-SWITCHING ND:GARNET LASERS

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Abstract: *High quality GGG:Cr,Ca crystal for passive Q-switching Nd:garnet lasers has been grown by the Czochralski method. Thermal treatment of GGG crystals co-doped with Cr^{4+} and Ca^{2+} at different temperatures is investigated. The absorption spectra were resolved into different peaks, of modified Gaussian line-shape. Transition from octahedral sites to tetrahedral ones is thermally activated. An optimal temperature interval for this transition was found to be 1200-1300 ˚C. The investigated samples were used as saturable absorbers in flash-lamp pumped Nd:YAG laser, and a pulse width of about 16 nsec was obtained.*

Keywords: *Cr,Ca:GGG; Czochralski method; Passive Q-switch; Saturable absorber.*

1. INTRODUCTION

With the development of passively Q-switched laser systems and solid state laser materials, small high power lasers have became much more practical for a variety of applications. The solid state materials that compose many modern passively Q-switched lasers are thermally and mechanically robust. These materials, combined with diode laser pump systems, enable compact passively Q-switched laser systems to be engineered. They are capable of producing high power, short pulse durations, excellent beam quality, and operate at relatively high efficiencies [1]. Solid-state laser passively Q-switching using an intracavity saturable absorber is a common approach to achieve short, high peak power laser pulses, which have wide applications in the fields of micro- machining, ranging, remote sensing, information storage, etc [1-3].

High energy laser pulses of short durations may be obtained by Q-switching techniques, where energy is stored in the gain medium through optical pumping while the quality factor of the laser resonator is decreased to prevent laser oscillation. Compared with active Q-switching, passive Q-switching is more economical and practical because of the modest requirements of optical elements inside the laser cavity. Consequently, these techniques have attracted much research regarding their design and theory. The Cr^{4+}: garnet has greater potential for useful application in passive Q-switching given their excellent opto-thermal and thermo-mechanical properties. Early studies of the Czochralski-grown Nd,Cr:GSGG crystals containing trace amounts of Mg^{2+} and Ca^{2+} impurities led to parasitic absorption at 1.06 μm [3,4]. A similar absorption in Cr^{3+}:YAG after an oxidizing anneal led to laser action at 1.35-1.45 μm [4]. The nature of the emission in oxidized Cr^{3+}:YAG was identified as Cr^{4+} ions in tetrahedral sites by careful magneto- and piezo-optic spectroscopy [5]. Gadolinium gallium garnet (GGG) is a member of the garnet family. Compared with YAG crystal, GGG can be grown easily in large sizes without optically inhomogeneous cores [6].

The GGG ($Gd_3Ga_5O_{12}$) crystal is cubic, space group Ia3d (or in Schoenflies notation), with eight formula units in a unit cell. It is schematically formulated as , where "C", "A" and "D" denote cation sites, dodecahedrally, octahedrally, and tetrahedrally coordinated, respectively. The "A" and "D" sites are occupied by Ga^{3+} ions, and "C" is occupied by the Gd^{3+} ion.

In this work, growth and the effect of annealing treatments on the absorption spectra of Cr^{4+}:GGG are analyzed and discussed. An efficiency increasing in Cr^{4+}:GGG absorber induced by the Cr^{3+} to Cr^{4+} transition has been observed making this material very effective for

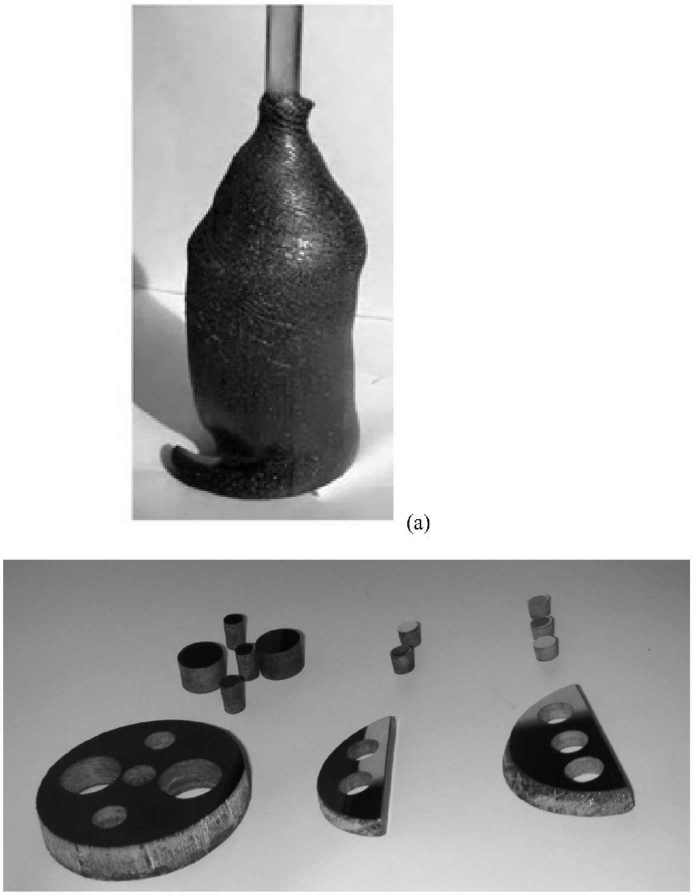
Q-switching Nd:garnet lasers. The grown and treated Cr^{4+}:GGG samples were used to passively Q-switch a Nd:YAG laser.

2. EXPERIMENTAL PROCEDURE

Cr,Ca:GGG (0.5 % at. Cr^{3+} and 0.5% at. Ca^{2+}) crystals were grown by the Czochralski technique (CZ) with an automatic diameter controlled (ADC) growth system from R.F. heated iridium crucible with the diameter of 120 mm and the depth of 120mm. The crucible loading was prepared using high purity starting materials (Gd_2O_3, Ga_2O_3 - 99.999%) for growing GGG crystals, and doping materials (Cr_2O_3, $CaCO_3$ - 99.995%) according to the formula:

$(Gd_{3-x}+zCa_x)(Ga_{5-y-z}Cr_y)O_{12}$,
with x=0.009, y=0.005-0.008 and z=0.01-0.02.

The mixture was sintered in an alumina crucible at high temperature for 30h. The obtained charge was then loaded into the iridium crucible for the crystal growth. The crucible and its lid were supported in high purity zirconia and alumina ceramics. To decrease the evaporation of Ga_2O_3 the growth atmosphere of O_2 with N_2 was adopted. An atmosphere of 2% vol. O_2 was required to suppress the evaporation of Gallium oxide from the free surface of the melt. The <111> orientation of Nd: GGG seed crystal was used in the growth process. Growth rates of 2.5-


(a)

(b)

Fig. 1. Photographs of: (a) the as-grown Cr,Ca:GGG (Ø50×110 mm) monocrystal, and (b) some of the investigated samples.

Table 1. Some characteristics of the Cr^{4+}:GGG grown and investigated samples

sample	*Diameter×Thickness mm^2*	*Cutting place*	*Cycle of heat treatment*	*$g^†$ %*	*AR coating**
S1	*6×5*	*Cone-center*	*C3*	*2.2*	√
S2	*6×5*	*Cone-edge*	*C1*	*2.2*	-
S3	*6×4*	*Cylinder-top-edge*	*C2*	*2.5*	-
S4	*6×4*	*Cylinder-top center*	*C1*	*2.5*	√
S5	*6×4*	*Cylinder-top edge*	-	*2.5*	√
S6	*6×8*	*Cylinder-bottom- edge*	*C3*	*15*	-
S7	*6×8*	*Cylinder-bottom-center*	-	*15*	√
S8	*6×8*	*Cylinder-bottom-edge*	*C3*	*15*	√
S9	*6×8*	*Cylinder-bottom-edge*	*C1-C3*	*20*	-

AR coating at 1064 nm with R=0.02%.

† g- the melt fraction that has crystallized.

Cycles of heat treatments: C1- heating to 1000 ˚C in air atmosphere,
C2- heating to 1200 ˚C in O_2 atmosphere,
C3- heating to 1400 ˚C in pure O_2 atmosphere

4 mm/h were combined with rotation rates of 15-25 rpm. The higher pull rate reduced the tendency to spiral growth which is well known in the Ga-based garnets, and can start after only about 15% of the melt has crystallized. In this study more than 25% of the Ca,Cr: GGG charge was recovered as single crystal before the spiral growth initiation. In order to prevent the crystal from cracking, it was cooled to room temperature slowly after it's pulling from the melt. The diameter of actually obtained Cr: GGG crystal was Ø50 mm and its length was 110 mm. The as-grown crystal and sliced polished pieces of Cr: GGG crystal are shown in Fig. 1.

Samples for spectroscopic measurements were cut out of the grown crystal perpendicular to the <111> growth axis with different thickness. Some characteristics of the investigated samples are presented in table 1. Some of the samples were annealed in air or pure oxygen atmosphere. The samples were held at 1100-1300°C for 10-40 h in three cycles of heat treatment. The absorption spectra were measured after each annealing, and then we proceeded to the same process, but at different temperature, once again.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The as-grown crystal was of dark brown to black colour with small colour gradient along its length. This phenomena reflects the decreasing Cr^{4+} content due to Cr segregation (kCr ≈3) [7]. The axial segregation coefficient, keff, was used to determine the dopant concentration in the investigated samples from the normal freeze equation for perfect mixing (table 1):

$$C_s = C_0 keff(1-g)^{(keff-1)} \qquad (1)$$

where C_0 and C_s are the dopant concentrations in the starting melt and solid, respectively, and g is the melt fraction that has crystallized. Moreover, an inhomogeneity of blackening was revealed in the samples cut perpendicularly to the <111> growth axis and treated in air or oxygen atmosphere. This inhomogeneity reflects the radial concentration gradient of Cr^{4+}, enhanced by the heat treatment in the presence of oxygen (explained in details later).

During the growth of Cr:GGG crystal, $CaCO_3$ was added as a charge compensator. The process is as following [8]:

$$Cr^{3+}_{oct} + 1/2(V^{2+}_0 + 2Ca^{2+}) + 1/4O_2 = (Cr^{3+}_{oct} + Ca^{2+}) \qquad (2)$$

$$Ga^{3+}_{tetr} + Cr^{4+}_{oct} = Ga^{3+}_{oct} + Cr^{4+}_{tetr} \qquad (3)$$

where "*oct*" and "*tetr*" indicate residence of each species in the octahedrally and tetrahedrally coordinated site, respectively. In the reaction described by equation (2), recombination of atmospheric oxygen with an oxygen vacancy, accompanied by electron transfer from Cr^{3+}_{oct} occurs at the crystal surface to form Cr^{4+}_{oct}. Diffusion of the oxygen vacancies to the surface enables this process. As a result, trivalent chromium ion Cr^{3+} oxidizes to form a tetravalent one Cr^{4+}. Equation (3) shows an intra-lattice cation exchange, in which tetravalent chromium ion exchanges position with an Ga^{3+} ion, thus between octahedral and tetrahedral coordination, yielding Cr^{4+}(tetr) ions. This exchange is obviously thermally activated.

4. OPTICAL CHARACTERIZATION AND CR^{4+} OPTIMIZATION

In order to calculate the absorption coefficient of investigated samples, transmission measurements were carried out using LAMBDA 2 PERKIN ELMER spectrophotometer in the spectral range of 300-1100 nm. Absorption coefficients of six different Cr:GGG samples in the range of 500-1100 at 300K are presented in Fig. 2.

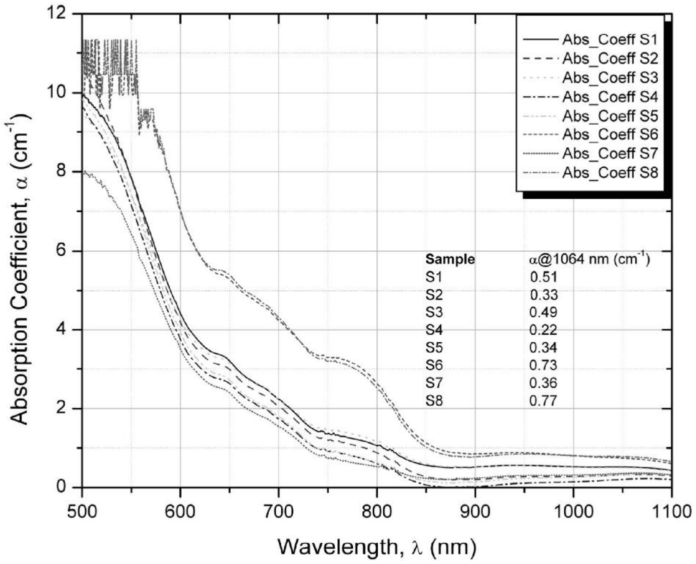


Fig. 2. 300K optical absorption spectra of eight Cr:GGG samples, sliced from different places of the GGG crystal. Inset table lists absorption coefficient at 1064 nm.

Table 2. Assignments of the optical absorption transitions at 300K for Cr,Ca:GGG crystal. For comparison, data of Cr:YAG crystal are presented.

Ion (site)	*Assignment*	*Energy (cm^{-1})*	*λ_p(nm) Cr:GGG*	*λ_p(nm) Cr:YAG [9]*
Cr^{4+}_{Tetra}	$^3B_1(^3A_2)\rightarrow {}^3E\ (^3T_1)$	15150	660	680
	$^3A_2\rightarrow {}^3T_1$	12700-13200	760-785	790
	$^3A_2\rightarrow {}^3T_2$ $^3B_1(^3A_2)\rightarrow {}^3A_2(^3T_1)$	9600-9950	1005-1040	1053
Cr^{4+}_{Octa}	$^3T_1\rightarrow {}^3T_2$	20000	500	497
Cr^{3+}_{Octa}	$^4A_{2g}\rightarrow {}^2T_{1g}$	22200-23800	420-450	406

The increase of the absorption coefficient after annealing (S6 and S8) is due to the increase of the concentration of Cr^{4+} ions at high temperature oxygen atmosphere.

In one slice, as shown in Fig. 2, the absorption coefficient around 940nm and 1060nm in the center is smaller than that in the edge (samples S4 & S^{3-} S7& S8 respectively). It is because the GGG:Cr crystal was grown by the CZ method with O_2 in the growth atmosphere. The oxygen went into the crystal body from the edge, so there are more oxygen ions in the edge than in the center and cause higher Cr^{4+} ions concentration.

An absorption spectrum of Cr,Ca:GGG crystal

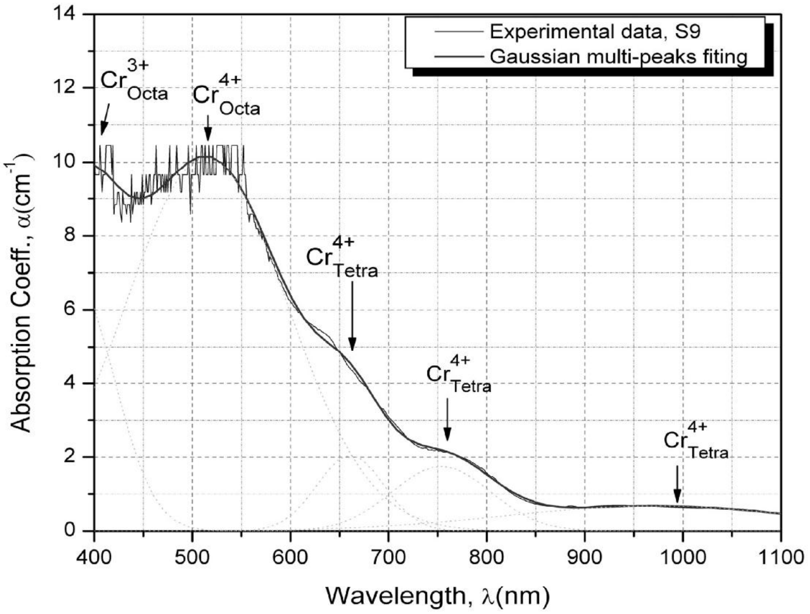
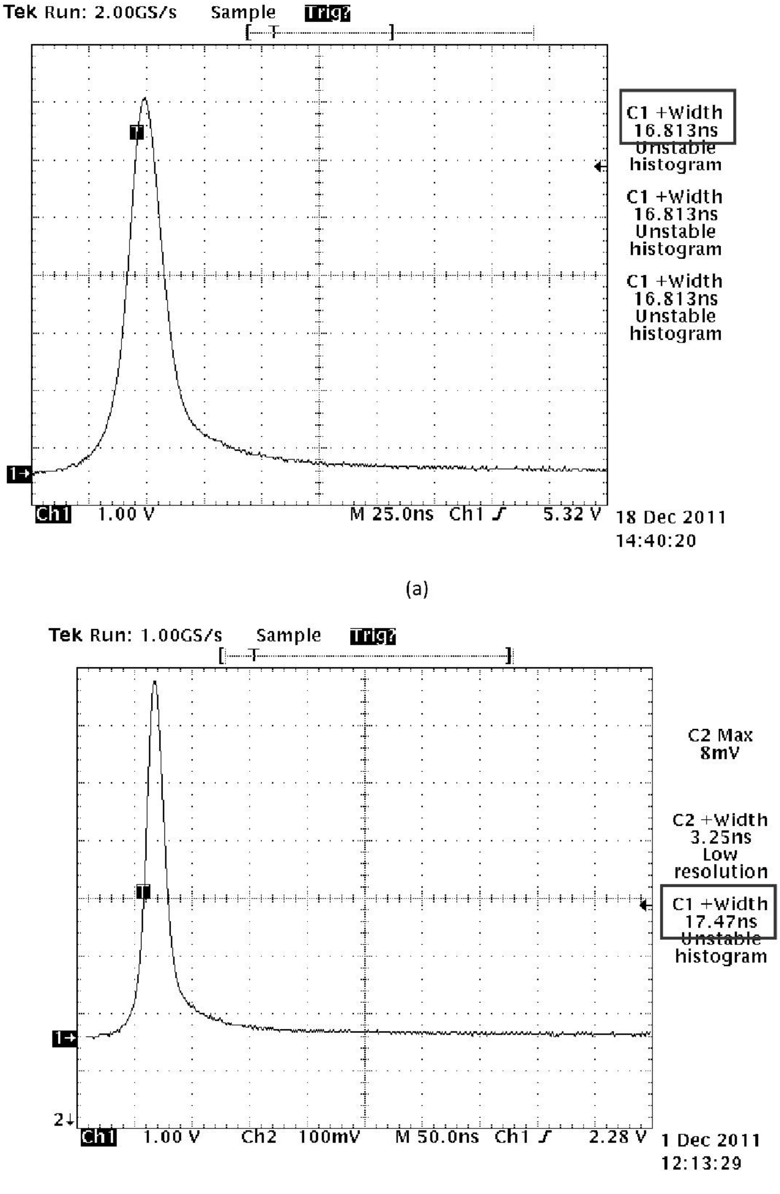


Fig. 3. Absorption spectra of Cr:GGG (sample S9), resolved into five modified Gaussian peaks. Fitted curve shown by solid line, experimental data by dashed one. The assignment of absorption bands is also indicated

exhibits at least four broad absorption bands at approximately 1.0, 0.75, 0.65, 0.5 μm (Fig. 3). To determine the assignments of absorption bands the absorption spectra was resolved into five modified Gaussian peaks (Fig. 3). Table 2 lists peak positions and the assignments of Cr-absorption transitions.

Cr^{4+}:GGG crystals exhibit effect of nonlinear absorption. Due to this effect transmission increases, affected by resonance with coherent radiation of big intensity. The investigation of single pulse generation was carried out in a plane-parallel resonator of 10 cm length with Nd:YAG laser rod (4 mm diameter, 50 mm



(a)

(b)

Fig. 4. Generation characteristics in the passive Q-switch mode for Cr^{4+}:GGG modulator with initial transmission of 70% (a) and 75% (b) respectively. (E_{pump}=3 J, laser pulse width τ_p=16- 17 nsec).

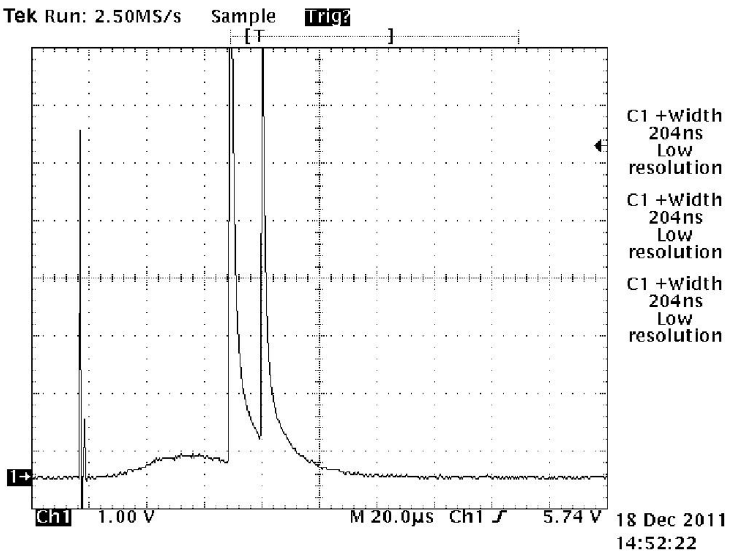


Fig. 5. Two pulses obtained for higher pumping energy Epump=6.0 J.

length). The laser head consisted of a single linear xenon flashlamp of 4 mm in diameter and a PTFE diffuser. The duration of flashlamp pulse was equal to 36 µs and the power supply energies were up to 7J. The output mirrors of 50% transmission were applied. The output laser energies were measured using Molectron Energy max 500 measuring head and the shape of giant-pulses was recorded by TDS520D Tektronix oscilloscope. Generation characteristics in the passive Q-switch mode for Cr^{4+}:GGG modulators with initial transmission 70% and 75% respectively are shown in Fig. 4. When the pumping energy increases to about 6 J we obtain two pulses in the output (Fig. 5).

Cr^{4+}:GGG is characterized by a simple construction, reliability and thermal resistance. It can be used to Q-switching of the resonator of pulse laser and to passive mode-locking. So, it can be used for the construction of the Nd:YAG pulse laser for laser range-finders, altimeters and laser systems generating giant-pulses with high frequency of operation.

CONCLUSIONS

Garnet crystal GGG doped with Cr^{4+} ions was obtained by Czochralski technique. Optimizing the amount of Cr^{4+} was achieved by the growth and post-growth annealing of samples in oxidizing atmosphere. The Cr^{4+} ions in the tetrahedral sites are the ones important for passive Q-switching of $\approx$1µm lasers. Our investigations suggest that Cr^{4+}:GGG elements, prepared for the above purposes, should be annealed under oxidizing atmosphere at elevated temperature (above 1200 °C). The broad absorption bands from 600-800 and 900-1100 nm offer potential for gain media for efficient solid-state lasers with applications in near-infrared spectroscopy, ultrafast fiber optic test systems, remote-sensing and others. Since the garnets have high damage thresholds and excellent thermal and chemical stability they also have potential for application in passive Q-switched devices at 1µm.

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