Passive Q-switching of a Tm:YLF laser with a Co\(^{2+}\) doped silver halide saturable absorber

Harel Hecht \(^a\), Zeev Burshtein \(^c\), Abraham Katzir \(^d\), Salman Noach \(^e\), Maxim Sokol \(^c\), Eugene Frumker \(^b\), Ehud Galun \(^f\), Amiel A. Ishaya \(^a,\)*

\(^a\) Department of Electrical & Computer Engineering, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel
\(^b\) Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel
\(^c\) Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel
\(^d\) Department of Physics, Tel-Aviv University, Tel-Aviv, 6996801, Israel
\(^e\) Department of Applied Physics, Jerusalem College of Technology, Jerusalem, 91160, Israel
\(^f\) DDR&D, Ministry of Defense, Israel

**Abstract**

We report a successful passive Q-switching of a Tm:YLF laser operating at \(\lambda = 1.9\) \(\mu\)m, using a Co\(^{2+}\):AgCl\(_{0.5}\)Br\(_{0.5}\) saturable absorber. Approximately 200-ns long, 150 \(\mu\)J pulses were obtained. Increase in pump energy resulted in repetitive pulsing, with a repetition rate approximately proportional to the pump pulse energy. Room-temperature optical transition saturation curves measured in \(~1\)-mm thick Co\(^{2+}\):AgCl\(_{0.5}\)Br\(_{0.5}\) plates yielded a ground state absorption cross section \(d_g = (7.8 \pm 0.5) \times 10^{-18}\) cm\(^2\), and an excited state absorption cross section \(d_{es} = (3.3 \pm 0.3) \times 10^{-18}\) cm\(^2\), at \(\lambda = 1.9\) \(\mu\)m. The lifetime of the A\(_d\)(\(^4\)I\(_{15/2}\)) second excited-state of the octahedral O symmetry was \(\tau = (0.6 \pm 0.06)\) ns.

© 2016 Elsevier B.V. All rights reserved.

**1. Introduction**

**1.1. Motivation**

In the past two decades, many types of passive laser Q-switching materials were developed, the most popular were based on transition-metal cations like Cr\(^{3+}\), Cr\(^{2+}\), V\(^{3+}\), or Co\(^{2+}\) as the active dopant [1–7]. For some important infrared lasers in the 1.3–1.7 \(\mu\)m range, especially for those exploiting the \(3_{13/2} \rightarrow 4_{15/2}\) emission of Er\(^{3+}\) ions, passive Co\(^{2+}\):Mg(Zn)Al\(_2\)O\(_4\) Q-switches represent an efficient solution [8–17]. Still, the Mg(Zn)Al\(_2\)O\(_4\) Co\(^{2+}\) host production, even in the sintered polycrystalline (ceramic) phase, requires temperatures exceeding ~1500 °C [18]. Silver halide AgCl\(_{1-x}\)Br\(_x\) crystals with \(0 < x < 1\), on the other hand, melt between 432 and 455 °C. Their single-crystal growth from melt is thus rather easy. Spectral applicability of Co\(^{2+}\) dopant ions for passive Q-switching may shift by using different hosts. Particularly, A Broad absorption band was observed in Co\(^{2+}\)-doped AgCl\(_{1-x}\)Br\(_x\) crystals between ~1.5 and 2.3 \(\mu\)m [19], rendering this spectral region applicable for passive Q-switching. Furthermore, the crystals for all those compositions are transparent between 0.4 and 30 \(\mu\)m, with a refractive index of 2.0 < n < 2.2. These properties suggest their use in a variety of applications in the said, exceptionally broad, spectral range.

In this work we investigate a Co\(^{2+}\) doped silver halide AgCl\(_{0.5}\)Br\(_{0.5}\) crystal as a passive Q-switch at the 1.885 \(\mu\)m wavelength. We performed optical bleaching experiments at 1.885 \(\mu\)m, and calculated various material parameters such as ground and excited-state absorption cross-sections, dopant densities, damage threshold, and the higher excited state lifetime. We demonstrate with this crystal, for the first time to the best of our knowledge, passive Q-switching inside a Tm:YLF laser oscillator [20] operating at \(\lambda = 1.885\) \(\mu\)m.

**1.2. Spectroscopic overview**

Basically, the AgCl\(_{0.5}\)Br\(_{0.5}\) composition forms a disordered crystal, related to the AgCl and AgBr parents. The latter each is face-centered cubic, belonging to the #225, \(O_h^2(F4/m32/c)\) space
The octahedral site, and $A^+$ ions occupy either a chlorine or a bromine ion at 50% probability. The Ag$^+$ ion still maintains its octahedral coordination, yet at a reduced symmetry; an O symmetry may be considered a fair approximation. When doped to form a Co$^{2+}$:AgCl$_{0.5}$Br$_{0.5}$ crystal, the Co$^{2+}$ ions replace two lattice Ag$^+$ ions, causing further distortion of the occupying sites. Spectroscopic studies indicate [22,23], that the majority of Co$^{2+}$ ions are octahedrally coordinated, with six halogen nearest-neighbors. A smaller portion are tetrahedrally coordinated, with four halogen nearest neighbors. For spectroscopic analyses, those different sites may be approximated as having $O$ and $T_d$ symmetries, respectively. All optical transitions in the near, and mid-IR, the region of interest in our present study, relate to the crystal field splitting of the $4\text{f}^2$ state of the free Co$^{2+}$ ion. A variety of optical properties were measured in Co$^{2+}$:AgCl$_{0.5}$Br$_{0.5}$ between 300 and 20 K. A Broad absorption band was observed between ~1.5 and 2.3 $\mu$m [19], in addition to three bands around 0.64, 0.9, and 4.25 $\mu$m. The emission lifetime of the ~4.4 $\mu$m-centered band under excitation at 1.92 $\mu$m, varied between 1.73 ms at low temperatures, and 5 $\mu$s at room temperature [24].

A Co$^{2+}$:AgCl$_{0.5}$Br$_{0.5}$ energy level diagram relevant to the said prospected application is provided in Fig. 1. The two types of possible cobalt centers, octahedral and tetrahedral [19,22,24], are addressed. In the octahedral O crystal field symmetry, the $4\text{f}^2$ state splits into $T_1(4\text{f}) + T_2(4\text{f}) + A_2(4\text{f})$ in an increasing energy order. Each state is further split by the smaller spin-orbit interaction, according to $4F_{3/2} + 4F_{7/2} + 4F_{5/2} + 4F_{3/2}$ in an increasing energy order. $T_1(4F_{9/2})$ is thus the ground state.

The spin-orbit split states energies follow the well-known relation

$$\Gamma_{\text{LSJ}} = \frac{1}{2}\xi_S[J(J + 1) - L(L + 1) - S(S + 1)].$$

where $\Gamma_{\text{LSJ}}$ is the level splitting, $\xi_S$ is the spin-orbit coupling coefficient, and $L$, $S$, and $J$ are the orbital, spin, and total angular momentum numbers, respectively. The value $\xi_S = \sim 100 \text{cm}^{-1}$ was assumed schematically for both $O$ and $T_d$ sites. In The O symmetry, $T_1(4F) \rightarrow T_2(4F)$ and $T_2(4F) \rightarrow A_2(4F)$ transitions are electric-dipole allowed. Such transitions are marked in the figure by solid arrows. The $T_1(4F) \rightarrow A_2(4F)$ transitions are electric-dipole forbidden; they are thus very weak, and marked by dashed arrows. The $T_2(4F) \rightarrow A_2(4F)$ transitions relate to the present, saturable ground-state absorption study at 1.9 $\mu$m; their cross section is thus marked $\sigma_{\text{gs}}$, and the excited $T_2(4F)$-state lifetime is marked $\tau$. The $T_2(4F) \rightarrow A_2(4F)$ transitions relate to the present, excited-state absorption study at 1.9 $\mu$m; their cross section is thus marked $\sigma_{\text{es}}$, and the higher excited $A_2(4F)$ state lifetime is marked $\tau^*$. It is assumed (and proven in our present study) that $\tau^* > \tau$.

In the tetrahedral $T_d$ crystal field symmetry, the $4\text{f}^2$ state splits into $A_1(4\text{f}) + T_1(4\text{f}) + T_2(4\text{f})$ in an increasing energy order. Each state is further split by the smaller spin-orbit interaction, same as in the octahedral site. $A_1(4F_{9/2})$ is thus the ground state, assumed to coincide with the O-symmetry one. The $A_1(4F) \rightarrow T_2(4F)$ and $T_2(4F) \rightarrow T_1(4F)$ transitions are electric-dipole allowed. Such transitions are marked in the figure by solid arrows. The $A_1(4F) \rightarrow T_1(4F)$ transitions are electric-dipole forbidden; they are thus very weak, and marked by dashed arrows. The $T_2(4F) \rightarrow T_1(4F)$ decay transitions relate to the Co$^{2+}$ measured fluorescence at ~4.4 $\mu$m [19]. The absorption spectra in the vicinity of 1.9 $\mu$m involve excitation of Co$^{2+}$ in both octahedral and tetrahedral sites; energy exchanges between the excited two type sites are also likely to occur.

Notably, Washimiya [22] erroneously presented a different assignment for the tetrahedral $T_d$ crystal-field splitting of Co$^{2+}$ ions $4\text{f}^2$-states in KCl crystal (specifically, $A_2(4F) + T_2(4F) + T_1(4F)$ in an increasing energy order). Their optical transitions assignments are correspondingly erroneous. This error has permeated into virtually all later publications by others, such as in Refs. [17,23–26].

### 1.3. Experimental setup and procedure

Bridgman-Stockbarger grown Co$^{2+}$:AgCl$_{0.5}$Br$_{0.5}$ crystalline cylindrical boules [24], ~7-cm long and approximately 8–10 mm in diameter, were used as starting material. Discs, ~1–3.5 mm thick, were cut and optically polished. To prevent bending during cutting, the sample was side mounted to an aluminium rod using bee wax. Cutting was done under a minimal load at a moderate speed of 250 rpm using a tabletop precision cut-off machine (Minitom by Struers ApS). The 0.15 mm thick cutting wheel was a low-concentration diamond-metal bonded (Struers ApS). Dual side plane grinding to the desired thickness was done sequentially from coarse (SiC grinding paper, 220 grit) to fine (SiC grinding paper, 4000 grit) using a grinding and polishing machine (LaboSystem Struers ApS) under a 10 N load at 150 rpm. Residual surface damage was removed by additional polishing by 3 and 1 $\mu$m diamond powder suspensions (DaPro Dac 3-$\mu$m/1-$\mu$m by Struers ApS) on a 20-cm aluminium wheel topped with a woven acetate fabric (MD-Dac, Struers ApS) at 5 N load. Final polishing was done by a 0.25 $\mu$m diamond powder suspension using a woven silk fabric (MD-Dur,
Optical absorption spectra of the disk-shaped samples in the 0.8–5.6 μm range were measured using an FTIR Bruker spectrometer model Vertex 80V.

Room temperature optical bleaching experiments (transmission as function of incident beam fluence) were made on discs of different thicknesses, using the 1.885 μm output of a diode-pumped, passively Q-switched lab-assembled Tm:YLF laser. The laser resonance cavity comprised a 0.8-cm long Tm:YLF crystal placed in a 28-cm long stable resonator. The rear mirror, of high reflectivity at 1.9 μm and high transmission at the 793-nm diode-laser pump wavelength, had a 10-cm radius of curvature. The front mirror had 70% reflectivity at 1.9 μm, and 20-cm radius of curvature. The Tm:YLF gain crystal was crystallographically oriented for maximal gain at vertically polarized radiation. The laser delivered transversely Gaussian, near TEM00 (M2 = 1.2) pulses, of ~1.1 mJ energy and 22 ns duration (full width at half maximum - FWHM). Different pulse energy densities (fluences) incident on the crystals were obtained by focusing the laser beam, and placing the crystal at different distances from the waist position (a modified z-scan method). Transmitted pulse energies were measured using an Ophir PE50-C energy meter. The same system was used to assess the damage threshold.

With several modifications, the same Tm:YLF laser was used for performing the Q-switching experiments. A schematic setup description is provided in Fig. 2. The commercial passive Q-switching plate (anti-reflection coated Cr2⁺:ZnSe single-crystal), was removed, then two Co2⁺:AgCl0.5Br0.5 crystalline discs, 1-mm thick, were inserted inside the resonator for passive Q switching. The two were oppositely tilted at about 40° relative to the laser axis, to decrease Fresnel losses of the vertically polarized output. The opposite tilting also served to preserve the original beam propagation axis. The diode-laser pump was operated at a quasi-CW mode of 11-ms long, 0.5–3.0 A current pulses from an SRS model DG535 pulse generator. A Thorlabs FELH1000 long-pass filter (1013–2150 nm transmitting, 200–987 nm blocking) was placed inside the resonator to filter out excess scattered pump light, thus protect the silver halide passive Q-switch.

The output pulse temporal behaviour was measured using a model ET-5000 extended InGaAs photodetector by EOT, of 28-ps rise time, and recorded with a model DDA 120 digital oscilloscope by LeCroy.

2. Results and discussion

2.1. Optical absorption spectrum

Optical absorption spectrum corrected for Fresnel reflections of a 1.3-mm thick Co2⁺:AgCl0.5Br0.5 sample is shown in Fig. 3 in the 0.8–5.6 μm range. The spectrum exhibits a broad, slightly structured absorption band between 1.4 and 2.4 μm, assigned to both A1→T2 multiplet transitions of the Td symmetry, and T1→T2 multiplet transitions of the O symmetry. A broad, much smaller transition, extending up to ~4.8 μm, is assigned to the “forbidden” A1→T1 multiplet transition of the Td symmetry (Fig. 1 above). A considerable contribution of light scattering raises the nominal calculated absorption coefficient; it is small for long wavelengths, but grows considerably with reduced wavelength, becoming rather large at ~1 μm. This scattering contribution is probably a result of the cutting and polishing process, and calls for drastic improvement in this procedure. Furthermore, a contribution (or dominance) of crystal surface and internal imperfections to the above A1→T1 assigned structure may not be ruled out.

2.2. Transmission saturation experiments

In the optical bleaching experiments, the incoming beam pulse duration was sufficiently short compared to the ~5 μs excited state relaxation time, to be addressed as a slow absorber [27]. The optical transmission $T = F(L)/F(0)$ of a disk of thickness L, where $F(0)$ is the incident pulse fluence and $F(L)$ is the transmitted one, may be given as [27,28],

$$T = T_0 + \frac{T_{FN} - T_0}{1 - T_0} (T_{max} - T_0),$$

(2)

where $T_0 = \exp(-\sigma_{es}NL)$ is the low fluence transmission limit, N is the Co2⁺ ion density, $T_{max} = \exp(-\sigma_{es}NL)$ is the high fluence transmission limit, and $T_{FN}$ is the prospected transmission of an ideal saturable absorber of $\sigma_{es} = 0$. It is given by [28]

$$T_{FN} = \frac{hv}{\sigma_{es} F(0)} \ln\left[1 + T_0 \exp\left(\frac{\sigma_{es} F(0)}{hv} - 1\right)\right],$$

(3)

where $hv$ is the photon energy. In case of a transversely Gaussian fluence distribution, 0.5$F_p(0)$ should replace $F(0)$ in the above expression, where $F_p(0)$ is the peak beam fluence incident on the
Optical transmission at $\lambda = 1.885$ $\mu$m corrected for Fresnel reflections versus the pulse fluence for a 1-mm thick disc is shown in Fig. 4 for fluences below 0.26 J/cm$^2$. A transmission rise with fluences is observed, from the low of ~57% and tendency to saturate at ~74%. The fit curve per Eqs. (2) and (3) above, yields $\sigma_{gs} = (7.8 \pm 0.5) \times 10^{-18}$ cm$^2$, $\sigma_{es} = (3.3 \pm 0.3) \times 10^{-18}$ cm$^2$, and $N = (5 \pm 0.5) \times 10^{17}$ cm$^{-3}$. Notably, the cross section values are significantly larger than previously reported values for octahedral Co$^{2+}$ in MgF$_2$ [29]. However, orders of magnitude differences in same ion cross sections among different host matrices and wavelengths are quite common. For example, the ground state absorption cross section measured value for Co$^{2+}$ in ZnSe is two orders of magnitude larger than that of Co$^{2+}$ in MgF$_2$ ($5 \times 10^{-19}$ versus $5 \times 10^{-21}$ [23,29]).

Excited state absorption is a source of loss in a laser cavity. Thus, a maximal $\sigma_{gs}/\sigma_{es}$ ratio is desirable. Average over results from four different Co$^{2+}$:AgCl$_{0.5}$Br$_{0.5}$ discs yields: $(\sigma_{gs}/\sigma_{es})_{av} = 1.8 \pm 0.1$.

For fluences exceeding about 0.26 J/cm$^2$, the transmission appeared to grow moderately with fluence above the saturation value. We interpret this growth as due to a gradual depletion of the O-symmetry excited $^4T_2(4F)$ multiplet. Assuming that $\tau^* = t_p$ (Fig. 1), where $t_p = 22$ ns is the pulse duration, an analysis on the basis of a fast saturable absorber model is appropriate [27,28], where the fully populated (saturated) excited state plays the role of a ground state. In the limit of low, sub-saturation pulse powers, the transmission is given by

$$T = T_0 \left[1 + \frac{1}{2\sqrt{2}} \left(1 - T_0 \sigma_{es} \tau^* I_p(0)/\hbar\nu\right)\right],$$

where $I_p(0)$ is the pulse peak power density.

The optical transmission versus pulse peak power density in the $1.8 \times 10^7 - 9 \times 10^7$ W/cm$^2$ range, for the same 1 mm thick disc of Fig. 4, is shown in Fig. 5. The results indeed exhibit the linear dependence predicted by Eq. (4). The linear fit yields $T_0 = 0.81$, quite close to the saturation transmission in Fig. 3, and $\tau^* = 0.6 \pm 0.06$ ns, well consistent with the $\tau^* = t_p$ assumption.

2.3. Laser Q-switching experiments

The Q-switching experiments in the system described in Fig. 2 above were performed using 11-ms long pulse pumping. Fig. 6 shows a typical Q-switched pulse from the Tm:YLF laser. The pulse duration at full width at half maximum (FWHM) was 208 ns,
and the averaged pulse energy was 150 μJ. The peak power is −0.75 kW.

In Fig. 7 we compare the output vs. input pump energy of the Tm:YLF laser (A) under free running conditions, namely without any Q-switching component present in the cavity, and (B) passively Q-switched using the commercial, anti-reflection coated Cr<sup>3+</sup>:ZnSe crystal. Dashed lines – linear fits.

2.4. Damage threshold

For incident pulse densities exceeding 2 J/cm<sup>2</sup>, persisting blackening of the disc material became evident, extending from the surface well into the bulk. We did not continue to study this effect further. We suspect that the blackening involves a photo-induced chemical reaction that changes the Ag⁺ ions into metallic Ag atoms, the latter acting as absorbing and scattering centers. A change of Co<sup>2+</sup> into Co⁺ and/or an atomic Co state may also be speculated.

2.5. Summary and conclusions

We have succeeded in fabricating, and reasonably polishing Co<sup>2+</sup>:AgCl<sub>0.5</sub>Br<sub>0.5</sub> crystalline discs that may tolerate high peak laser fluence levels of the order of 2 J/cm<sup>2</sup> (90 MW/cm<sup>2</sup> intensity) at λ ≈ 1.9 μm. We have observed saturation of the Co<sup>2+</sup> absorption bleaching, yielding a ground state absorption cross section σ<sub>gs</sub> = (7.8±0.5) × 10<sup>−18</sup> cm<sup>2</sup>, and an excited state absorption cross section σ<sub>es</sub> = (3.3±0.3) × 10<sup>−18</sup> cm<sup>2</sup> at λ = 1.9 μm. We have also demonstrated, for the first time to the best of our knowledge, passive Q-switching operation of these crystals in the cavity of a Tm:YLF laser. 208-ns long pulses of 150 μJ energy were obtained. Polishing method improvement is necessary in order to achieve better passive Q-switching performance. Since the Co<sup>2+</sup>:AgCl<sub>0.5</sub>Br<sub>0.5</sub> material is sensitive to UV-visible radiation that causes spectral changes in the material, a proper coating or radiation filtering is required.

Our results constitute a progress step towards exploiting silver halide doped crystals as optical materials in a variety of applications.

Reference


[2] T.Y. Tsai, M. Birnbaum, Q-switched 2-μm lasers by use of a Cr<sup>3+</sup>:ZnSe saturable...


