



OPTICAL ABSORPTION, ABSORPTION SATURATION AND A USEFUL FIGURE OF MERIT FOR CHROMIUM DOPED GLASSES

EGBERTO MUNIN*, A. BALBIN VILLAYERDE*, MICHAEL BASS†
and K. CERQUA-RICHARDSON†

*Instituto de Física Gleb Wataghin, IFGW, Universidade Estadual de Campinas, UNICAMP,
13083-970 Campinas, SP, Brazil

†Center for Research and Education in Optics and Lasers, CREOL University of Central Florida,
UCF, Orlando, FL 32826, U.S.A.

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Abstract—Chromium-doped aluminate and silicate glasses have been prepared in both inert and oxidizing atmospheres. Spectroscopic measurements indicate that some of the glasses incorporated the chromium ion in the +4 valence state. These Cr⁴⁺ doped glasses exhibit a broad spectral emission covering the communication window and the eye safe region around 1.5 μm. Ten glass samples and two crystalline materials, were used to study the phenomenon of saturable absorption in the Cr⁴⁺ ion. A figure of merit was defined to compare the performance of different materials as saturable absorbers. The preparing conditions that lead to a glass saturable absorber with better figure of merit have been investigated. A Q-switched Cr:LiSAF laser was used for the saturable absorption measurements. Copyright © 1996 Elsevier Science Ltd

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INTRODUCTION

In this work, we report on a research effort toward the development of an adequate glass host for the Cr⁴⁺ ion. Two base glass compositions were investigated. Chromium doped aluminate and silicate glasses were prepared under various melting environments, yielding materials with different properties. Such materials were studied by using spectroscopic tools as well as intensity dependent absorption. Emphasis is given to the study of saturable absorption in those samples in which the spectroscopic measurements revealed the presence of the chromium ion in the 4+ valence state. Two crystalline samples were included for comparison. The present work makes an important contribution to understanding the behavior of the Cr⁴⁺ ion in glasses; a difficult task because of the presence of Cr ions in other valences in the glasses studied.

The recent demonstration of near infrared laser action in several tetravalent chromium doped crystals [1-3] has promoted considerable interest in the optical properties of such an impurity ion in different hosts. In a previous work [4] we demonstrated intensity dependent absorption in such Cr⁴⁺ doped crystals as Y₂SiO₅ (YSO) and Ca₂Al₂SiO₇ (CAS). When we placed these solid state saturable absorbers inside the resonator of a tunable Cr:LiSAF laser we successfully obtained passive Q-switching action in the spectral range between 800 and 900 nm. Other Cr⁴⁺-doped

crystalline materials like Cr⁴⁺:YAG, Cr⁴⁺:GSGG, Cr⁴⁺:YSGG, Cr⁴⁺:Mg₂SiO₄ have been employed recently to obtain Q-switching of neodymium lasers near 1.06 μm [5-9]. The variety of scientific investigations on this subject reflects strong interest in development of solid state saturable absorbers. Such devices can support an all-solid-state laser technology, overcoming the disadvantages of liquid dye solution Q-switches. Cr⁴⁺ ions doped in solid state hosts have made possible the construction of passively switched, microchip lasers operating in the picosecond regime [10]. Because glasses may be manufactured in large sizes with excellent optical quality and at a lower price than most crystals, they may be a very attractive choice for a Cr⁴⁺ based solid state saturable absorber. Initial studies to evaluate suitable host glass systems and the optical performance of Cr doped glass materials was reported earlier [11]. Although one can find many published works reporting on the properties of the Cr³⁺ ion doped in both crystals and glasses, the same does not hold for the Cr⁴⁺ ion, whose properties have been studied almost exclusively in crystalline systems. The scarcity of experimental data about Cr⁴⁺:glass system results from the difficulty of obtaining glasses doped with chromium ions predominantly in the tetravalent state. To date, chromium containing glasses prepared under reducing and oxidizing conditions have yielded materials

Table 1. Batch compositions in atomic % of the base glasses prepared for this work

	Aluminate glass Series AC _x , x = 1–4	Aluminate glass Series A2CO _x , x = 1–15	Silicate glass
AlO _{1.5}	48	45.6	4.8
SiO ₂			49.8
CaO	36	33.7	
BaO + MgO	16	18.6	
NaO _{0.5}		2.1	
LiO _{0.5} + NaO _{0.5}			36
SrO			9.4

containing Cr in the 3+ and 6+ valence, respectively [12]. In pioneer work, Lunkin and co-workers [13] obtained Cr⁴⁺ ions in an aluminum–lime glass and studied the absorption spectrum.

EXPERIMENTAL

Several glass samples were prepared for this study including material melted in inert (oxygen free) atmospheres of argon or nitrogen and others melted in oxidizing atmospheres containing a mixture of argon with various amounts of oxygen. A platinum crucible heated in a RF furnace was used. The batch compositions of the base glasses that we used are given in

Table 1. The references to the samples in all tables in this paper follow the nomenclature in Table 1. The two Czochralski grown single crystals included in our study have been considered in the literature as pure Cr⁴⁺ systems as the host structures contain no octahedral sites capable of incorporating Cr³⁺. In these crystals, the Cr⁴⁺ ion substitutes the Si⁴⁺ in tetrahedrally coordinated sites and no codoping for the sake of charge compensation is needed.

The linear absorption spectra were taken with a Perkin Elmer, model 330 spectrophotometer with a slit resolution of 2 nm. Saturable absorption measurements were performed by using an electro-optically Q-switched Cr:LiSAF laser. A large area silicon detector (UV444 from EG&G) calibrated with a energy meter was used to detect the laser pulses transmitted through the samples. The signal from this detector could be viewed on a digital oscilloscope. Additional details of the experimental setup for the measurements of the intensity dependent absorption may be found elsewhere [4, 14].

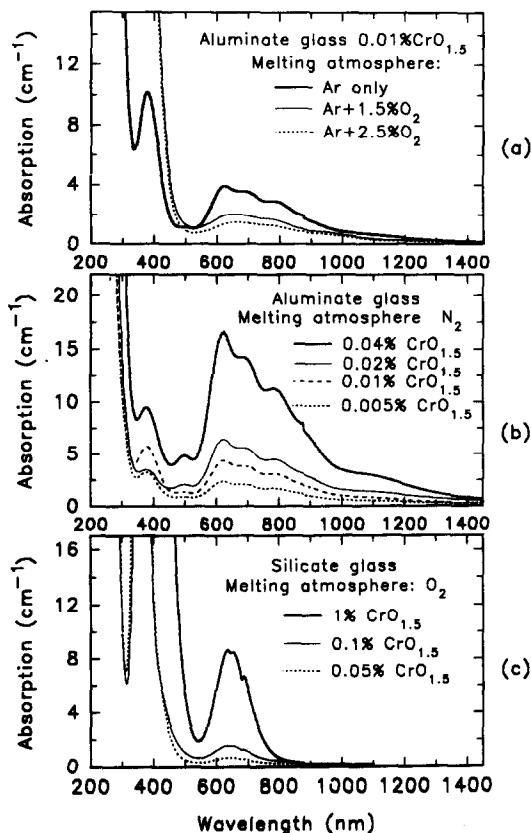


Fig. 1. Absorption spectra for: (a) aluminate glasses melted in atmospheres containing different fractions of O₂; (b) aluminate glasses melted in a nitrogen atmosphere; (c) silicate glasses melted in an oxygen atmosphere.

SPECTROSCOPIC MEASUREMENTS

The low intensity absorption spectra are shown in Fig. 1. It is expected that increasing the amount of oxygen present in the melting atmosphere should favor the higher valence states of the chromium ion. One can verify this by looking at Figs 1(a) and 1(b), which show the absorption spectra for aluminate glasses. It can be seen that increased oxygen in the melting atmosphere reduces the absorption in the 600–1000 nm range while strengthening the absorption band around 450 nm, which is due to a Cr⁶⁺ charge transfer transition [15, 16]. The aluminate glasses exhibit an absorption tail extending beyond 1000 nm, a feature commonly observed in Cr⁴⁺ doped crystals. The absence of this absorption tail in the silicate glass composition suggests that, in this type of glass, the occurrence of the Cr⁴⁺ valence state is negligible or this species is not present at all [17]. This finding is supported by the emission spectra observed from these glasses. Emission spectra are shown in Fig. 2 and were taken with an InGaAs

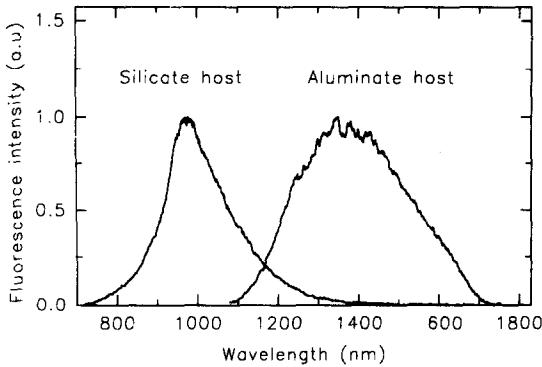


Fig. 2. Emission spectra for chromium-doped aluminate and silicate glasses. The excitation was at 532 nm.

photodetector. The spectra were not corrected with respect to the detector sensitivity curve. Excitation was at 532 nm. In the case of the aluminate glass melted in inert atmosphere, the emission band occurred in the same characteristic range as that observed in Cr^{4+} doped in crystals. Such emission from chromium ions in aluminate glass ranges from 1100 to 1700 nm, with the peak located around 1340 nm. The aluminate glass samples melted in an atmosphere containing oxygen showed a decreasing emission strength in the 1100–1700 nm range when the amount of oxygen in the melting atmosphere was increased from 0 to 2.5%. For the sample melted in 2.5% oxygen atmosphere, the emission signal detected was very noisy and was not recorded. This decrease in the emission strength can be attributed to the reduction in the number of Cr^{4+} ions that are incorporated into the glass matrix when an oxidizing atmosphere is employed in the melting process. Evidence for this

comes from electron spin resonance analysis which showed that glass samples melted in an oxygen containing atmosphere contained +3, +5 and +6 species in addition to Cr^{4+} [11]. Cr^{3+} emission from such samples was not observed and is likely the result of reabsorption of the Cr^{3+} light by other ionic species present. For the silicate glass, the observed emission spectrum is similar to that typically observed from Cr^{3+} ion occupying low field octahedrally coordinated sites [15, 16] and may be assigned to the vibronically broadened Cr^{3+} transition ${}^4T_2 \rightarrow {}^4A_2$.

The relaxation time τ of a saturable absorber, when compared to the duration of the propagating light pulse τ_p , defines a slow absorber if $\tau \gg \tau_p$ and a fast absorber if $\tau \ll \tau_p$. The fluorescence kinetics of the chromium ion doped in aluminate and silicate glasses were examined after excitation with the second harmonic of a Q-switched Nd:YAG laser. Both glass types exhibited a fast non-exponential decay. A double exponential model was observed to fit well to the experimental decay curves captured with a digitizing oscilloscope. From this fitting we obtained for the aluminate glass the characteristic value of 0.65 μs for the slow component of the decay curve and the value of 0.13 μs for the fast component which dominates the beginning of the decay curve. For the silicate glass we obtained 6.63 μs and 0.703 μs for the slow and the fast components, respectively, of the decay curve. These values were measured in each case at the peak wavelength of the emission bands shown in Fig. 2 (i.e. 1340 nm and 980 nm for the aluminate and silicate glasses, respectively). The temperature dependence of the decay time measured at 980 nm for the silicate glass is shown in Fig. 3. It is observed that when the temperature is lowered from ~ 325 K to cryogenic temperatures the decay time increases by a factor of ~ 4 . When probed in different points within the broad luminescence band of the chromium in the glass, we observe a reduction in the decay rate with wavelength (i.e. the lifetime increases) towards the short wavelength side of the emission band. This behavior is shown for silicate glass samples in Fig. 4 at three different temperatures. The effect is more prominent at low temperatures. Because of this variation in the relaxation rate, one should be able to detect a blue shift of the emission band with time. Andrews and co-workers [16] have performed time resolved measurements of the emission spectra in Cr^{3+} doped potassium aluminum borate glass. They observed such a blue shift of the emission band with time, consistent with our data. They attributed a strong dependence of the decay time with the wavelength to the variety of sites available for the chromium ion in the glass matrix; sites possessing different ligand fields and therefore yielding different spectra and

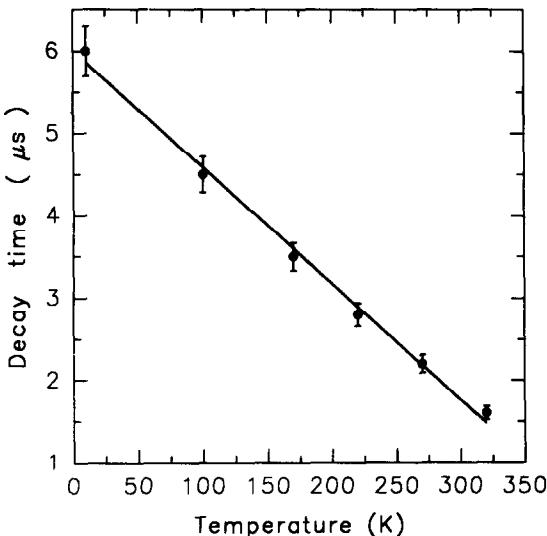


Fig. 3. Temperature dependence of the decay time measured at the $1/e$ point for the silicate glass doped at 1%. Probe wavelength was 980 nm. The excitation was at 532 nm. The solid line is merely a straight line fit to the experimental data.

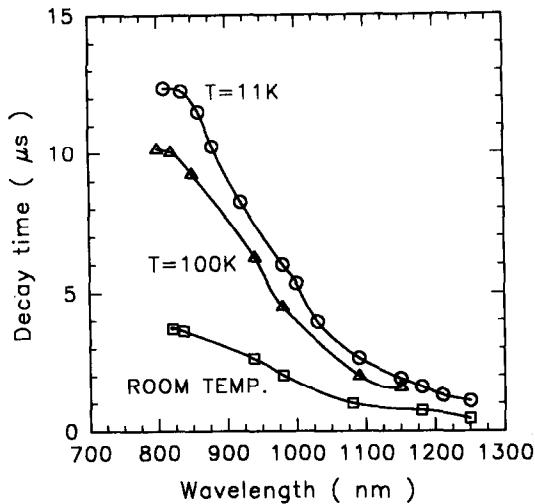


Fig. 4. Time for the emission intensity to fall to $1/e$ within the broad emission band of chromium in silicate glass doped at 1%. The excitation was at 532 nm. The experimental points were joined by spline curves.

different relaxation rates. The slower relaxation rates would originate from the higher field sites.

SATURABLE ABSORPTION

Saturable absorption measurements were performed on 10 aluminate glass samples and two crystalline samples. The saturable absorption in the silicate glasses were not measured because they have no appreciable absorption in the wavelengths range of interest. We measured for each sample the low signal transmission T_0 and the transmission in the bleached regime T_b . The results, together with some relevant information for each sample, are listed in Table 2. The

glass samples were sorted in three series. Series I contains samples with different chromium concentrations, prepared in inert atmosphere (nitrogen). Series II contains samples with different chromium concentrations but the melting atmosphere was a mixture of argon with 2.5% of oxygen. In Series III, the dopant concentration is constant while the amount of oxygen in the melting atmosphere changed from zero to 2.5%. If we adopt the ratio T_b/T_0 as a first measure of the contrast between the bleached transmission T_b and the small signal transmission T_0 , when we compare the samples of Series I with those samples of Series II, we observe that the ones melted in inert atmosphere show larger contrasts between both transmission regimes. Further, comparing the samples listed in Series III it is observed that when the amount of oxygen in the melting atmosphere is increased from zero to 2.5%, the value of the contrast ratio T_b/T_0 reduces from 1.49 to 1.04. A better picture for this interesting phenomenon may be seen in Fig. 5. The upper trace in this figure corresponds to those samples melted in inert atmosphere and the lower one to those samples melted in oxygen containing atmosphere. The intermediate trace corresponds to those samples prepared with varying oxygen content and is observed to shift from the upper curve to the lower curve as the oxygen fraction increases.

A four-level scheme with excited state absorption (ESA) has been introduced [18] to explain the residual absorption observed in most of the practical saturable absorbers. Such residual absorption causes the transmission at high radiation intensity to reach a maximum value lower than one. This feature is observed in all materials studied in this work, as may be seen in

Table 2. Low signal transmission (T_0) and bleached transmission (T_b) for the chromium-doped saturable absorbers. Data were corrected for reflection losses at both uncoated surfaces. The excitation was at 800 nm with pulse duration of about 49 ns

Sample code	Length (mm)	Concentration (%)	Melting atmosphere	T_0	T_b	T_b/T_0
Glass series I						
AC-1	2.75	0.02	N ₂	0.206	0.325	1.58
AC-3	5.19	0.01	N ₂	0.240	0.367	1.53
AC-4	4.25	0.005	N ₂	0.563	0.677	1.20
Glass series II						
A2CO11	5.57	0.025	Ar + 2.5%O ₂	0.150	0.183	1.22
A2CO5	5.22	0.020	Ar + 2.5%O ₂	0.262	0.309	1.181
A2CO9	5.40	0.015	Ar + 2.5%O ₂	0.260	0.284	1.091
A2CO2	4.95	0.010	Ar + 2.5%O ₂	0.641	0.686	1.070
Glass series III						
A2CO15	5.40	0.010	Ar + 0.0%O ₂	0.228	0.340	1.493
A2CO3	4.35	0.010	Ar + 1.0%O ₂	0.499	0.580	1.162
A2CO13	5.61	0.010	Ar + 2.5%O ₂	0.733	0.765	1.043
Crystals						
Ca ₂ Al ₂ SiO ₇	2.93	2%	—	0.360	0.464	1.29
Y ₂ SiO ₅ (E a)	12.3	2%	—	0.094	0.22	2.34
Y ₂ SiO ₅ (E b)	12.3	2%	—	0.150	0.250	1.67

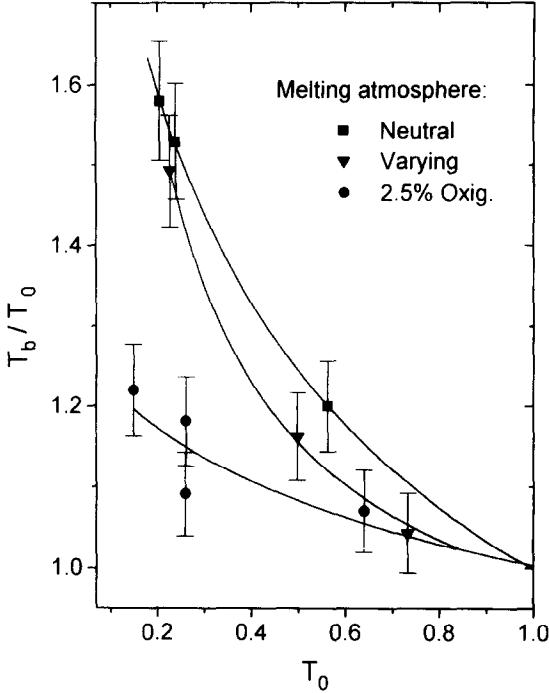


Fig. 5. Plot of the contrast ratio T_b/T_0 as a function of T_0 for the Cr-doped glasses. The points represented by triangles correspond, from the left to the right, to samples melted in atmosphere containing 0%, 1% and 2.5% of oxygen, respectively.

Table 2. A saturation curve showing the behavior for one of the glass samples is disclosed in Fig. 6. A similar curve for the Cr: YSO crystal was reported in our previous paper [4]. The solid curve shown in Fig. 6 was obtained by fitting the following formula for the intensity-dependent absorption coefficient α , to the experimental data,

$$\alpha = \frac{\alpha_0}{1 + I/I_s} + \alpha_1 \quad (1)$$

where α_0 is the low signal absorption coefficient, I is the incident radiation intensity, I_s is the saturation intensity and α_1 accounts for the residual losses in the bleached regime. This analysis allow us to assert that, within the experimental uncertainties shown by the error bars in Fig. 6, the transmission at high incident intensities has reached its saturated value.

The case in which ESA is the unique loss mechanisms that is present in the saturable absorber has been treated by Hercher [18]. He found that in this case the transmission in the bleached state equals to $T_0^{\sigma_{es}/\sigma_{gs}}$, where σ_{es} and σ_{gs} are the excited state and ground state absorption cross sections, respectively. We may generalize this relationship writing

$$T_b = T_0^\eta \quad (2)$$

where η may be interpreted as a performance-limiting factor which includes most of the loss mechanisms

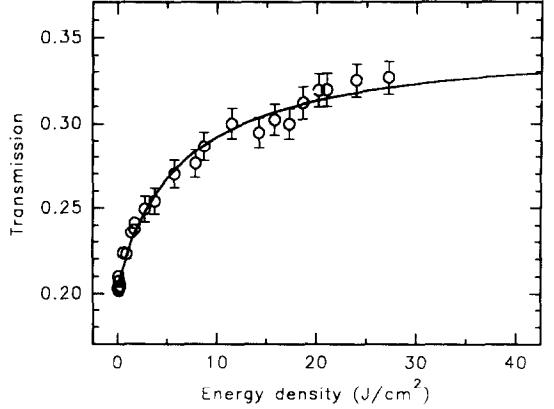


Fig. 6. Intensity dependent transmission for a Cr: aluminate glass doped at 0.02% (AC-1 sample), prepared in an inert atmosphere. The excitation was at 800 nm with a pulse duration of 49 ns. The solid line corresponds to the theoretical curve given by eqn (1), with the parameter I_s equal to 4.9 J/cm^2 .

that may reduce the efficiency of a saturable absorber, such as the losses due to ESA, the losses arising from relaxation to the ground state via radiative and non radiative decay, losses due to scattering centers in the bulk and possibly other minor contributions. Taking the negative of the logarithm in both sides of eq (2), we find a linear relationship between the absorber optical density in the bleached state OD_b and the low signal optical density OD_0 :

$$OD_b = \eta OD_0 \quad (3)$$

Although η may depend on the duration of the excitation pulse, in those cases in which we have a steady state excitation this constant is valuable as a parameter to compare the performance of different saturable absorbers. We then define a figure of merit (FOM) for a saturable absorber as:

$$FOM = 1/\eta. \quad (4)$$

A high value for such a FOM means a low loss absorber. In the present work, although the condition of steady state excitation is not satisfied, we may still use this FOM to make a comparison, because the response times of our absorbers do not differ significantly and the excitation conditions are nearly the same. A plot of OD_b vs OD_0 for the absorbers listed in Table 2 is shown in Fig. 7. The solid lines in that picture are the fitted curves obtained by using eq (3). The FOM values extracted from the slope of the curves are listed in Table 3. It may be observed that chromium glasses melted in inert atmosphere exhibit a higher FOM than those melted in atmosphere containing oxygen. Further, the FOM for the glasses prepared in inert atmosphere is very close to that for the pure Cr^{4+} systems (the YSO and CAS crystals), indicating that the Cr^{4+} ion should be responsible for

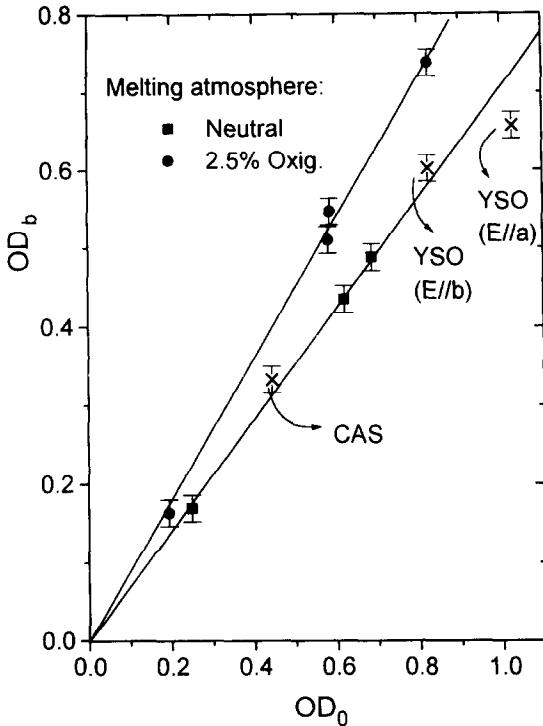


Fig. 7. Plot of the absorbers optical density in the bleached state ($-\log T_b$) against the low signal optical density ($-\log T_0$). The solid lines were obtained by fitting eqn (3) to the experimental data. The inverse of the slope of the curves may be interpreted as the figure of merit for the absorber.

the intensity-dependent absorption observed in our glass samples. This result reinforces the conclusion previously obtained from the spectroscopic data: in the aluminate glass composition, the incorporation of the tetravalent chromium is favored when the samples are prepared in inert atmosphere. This conclusion should be taken into account in the development of a glass host for the Cr^{4+} ion.

Among the materials we investigated, the $\text{Cr}^{4+}:\text{Y}_2\text{SiO}_5$ was the one with the highest FOM. Passive Q-switching of a Cr:LiSAF laser by using this crystal has been reported in Ref. [4]. It is opportune to mention that the glass used in this work were small melt volume samples which contained striations. These defects may have contributed to the increased loss in the glass samples studied. It may be expected that by improving the optical quality of the glasses, their FOM value could approach that of the Cr: YSO

Table 3. Figures of merit for the saturable absorbers investigated in this work

Material	FOM $1/\eta$
Glasses melted in Ar + O ₂ atmosphere	1.11
$\text{Cr}^{4+}:\text{Ca}_2\text{Al}_2\text{SiO}_7$	1.33
$\text{Cr}^{4+}:\text{Y}_2\text{SiO}_5(\text{E} \text{b})$	1.37
Glasses melted in inert atmosphere	1.42
$\text{Cr}^{4+}:\text{Y}_2\text{SiO}_5(\text{E} \text{a})$	1.56

Table 4. FOM ($1/\eta$) for the Cr: YSO crystal, determined at different wavelengths from the measured low signal (T_0) and bleached (T_b) transmissions

$\lambda(\text{nm})$	T_0	T_b	T_b/T_0	FOM
		E b, k c		
800	0.15	0.25	1.67	1.37
840	0.23	0.35	1.52	1.40
900	0.49	0.65	1.33	1.66
		E a, k c		
800	0.094	0.21	2.34	1.51
840	0.17	0.31	1.82	1.51
900	0.41	0.59	1.44	1.69

crystal in its best orientation (E||a). The dependence of the FOM with the wavelength for the Cr: Y_2SiO_5 sample is shown in Table 4. The increase in the value of the FOM as the excitation wavelength becomes longer indicating that Cr^{4+} -based saturable absorbers would have improved performance at the Nd: YAG laser wavelength.

CONCLUSIONS

In summary, we report on the processing and characterization of various glass hosts doped with the chromium ion. Depending on the base glass composition and on the processing conditions, we obtained glasses that exhibit absorption and luminescence properties similar to those seen in crystalline hosts doped with chromium in tetravalent (+4) coordination. In these glasses, broad spectral emission was observed, covering the communication window and the eye-safe region around $1.5 \mu\text{m}$. Saturable absorption in chromium doped glasses and crystals has been investigated. Processing conditions were found to strongly affect the capability of the glasses to become transparent when excited with high intensity radiation. The intensity dependent absorption in our glass samples arises from the presence of the Cr^{4+} ion which is incorporated in larger concentrations into four-fold coordination sites when the samples are melted under an inert atmosphere. We have found that preparing the glasses in oxygen free atmospheres of argon and nitrogen creates an absorber with better performance, compared to those glasses melted in an oxidizing condition. Among the materials we studied, $\text{Cr}^{4+}:\text{Y}_2\text{SiO}_5$ has the highest FOM. Our data indicate that some of the chromium glasses studied could be efficient solid state switches for lasers operating around $1.06 \mu\text{m}$.

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