

## Absorption, emission and absorption saturation of Cr<sup>4+</sup> ions in calcium aluminate glass

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### Abstract

Absorption, luminescence and absorption saturation of Cr ions in a calcium aluminate glass are studied. In the absorption spectrum, the absorption bands of Cr<sup>3+</sup>, Cr<sup>4+</sup> and Cr<sup>6+</sup> ions are revealed. The emission spectrum presents luminescence of Cr<sup>3+</sup> ions centered at 0.82 μm and that of Cr<sup>4+</sup> ions at 1.3 μm. The luminescence signal demonstrates short decay times of 120 ± 10 ns and 300 ± 20 ns for Cr<sup>3+</sup> and Cr<sup>4+</sup> ions, respectively. Absorption saturation measurements allowed an estimate of the ground-state absorption cross-sections for Cr<sup>4+</sup> ions at 1.06 μm of 0.7 × 10<sup>-18</sup> cm<sup>2</sup> and at 0.69 μm of 1.5 × 10<sup>-18</sup> cm<sup>2</sup>.

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### 1. Introduction

The need for progress in fibre-based systems and in fibre lasers has stimulated research in new materials for active and passive media for fibre lasers. As compared with crystals, glasses doped by transition-metal or rare-earth ions are more easily incorporated in fibre systems, thus a study of various glasses doped with such ions is an important task.

Tunable solid-state lasers have a wide field of application in communication, in medicine, in scientific research, etc. It is known that tetrahedrally coordinated chromium (IV) ions are among those few ions which act as active ions for efficient tunable laser oscillation. Being embedded in different crystal or glass matrices, they emit radiation in 1.2–1.6 μm spectral range [1–11]. On the other hand, materials with Cr<sup>4+</sup> ions are used as effective saturable absorbers for 1 μm neodymium [12–14], 1 μm ytterbium [15], 0.8–0.9 μm Cr:LiSAF, Cr:LiCAF [16,17] and 0.7 μm ruby

[18,19] lasers. Thus, Cr<sup>4+</sup> doped glasses are expected to promise numerous applications.

Previously it was shown that stable Cr<sup>4+</sup> oxidation state was achieved only in calcium-aluminate, aluminosilicate and gallate glasses with large modifier content [7,20–23]. Luminescence of Cr<sup>4+</sup> ions in aluminate, aluminosilicate, calcium aluminate, soda-lime silicate glasses [6–10], as well as their absorption saturation at 0.8 μm in aluminate and silicate glasses [20] was studied earlier. In this paper we study Cr<sub>2</sub>O<sub>3</sub>-doped calcium aluminate glass with low ratio value of calcium to aluminum oxides (CaO/Al<sub>2</sub>O<sub>3</sub> = 1.5) and with the presence of modifiers (up to 25 mol%). For this glass, absorption, emission spectra and luminescence decay measurements as well as absorption saturation data are presented.

### 2. Experimental procedure

#### 2.1. Glass preparation

The base composition of the glass under study is (mol%): CaO – 45, Al<sub>2</sub>O<sub>3</sub> – 30, BaO – 10, MgO – 10. It also

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Table 1  
Principal compositions of Cr<sup>4+</sup>-doped calcium aluminate glasses (mol%)

Ingredients	This paper	Choi et al. [9] <sup>a</sup>	Murata et al. [21]	Veinberg et al. [22]	Wu et al. [27]
CaO	45	55	60–68	45–61	35–45
Al <sub>2</sub> O <sub>3</sub>	30	35	40–32	26–41	47–57
MgO	10	10	–	7	0–10
BaO	10	–	–	2	7.5
Other	5	–	–	4	–

<sup>a</sup> Figure in brackets correspond to numbers listed in references.

contains small additions (about 5%) of other components. Batches were prepared from carbonates of alkaline-earth metals and from oxides of other components. Chromium in the form of Cr<sub>2</sub>O<sub>3</sub> was added in an amount of 0.1 wt%. The composition of our glass in comparison with other calcium aluminate glasses studied earlier is presented in Table 1.

Undoped glasses and glasses doped by chromium oxide were melted in a platinum crucible in a laboratory electric furnace with Globar heating elements in air at 1450–1500 °C. The melts were stirred by a platinum stirrer for 30 min and then were poured into a graphite mould. The glasses were annealed at 600 °C.

XRD patterns of powdered glasses were measured using CuK<sub>α</sub> radiation with a Ni filter.

Absorption spectra in the spectral range 190–2500 nm were measured using a double beam spectrophotometer. In order to reveal the absorption bands of Cr ions hidden under the absorption edge of the glass, the spectrum of the glass with Cr ions was measured versus the undoped glass placed into a reference channel of the spectrophotometer.

Excitation of the NIR luminescence has been made by the filtered Xe lamp irradiation (wavelengths interval 300–800 nm). Visible luminescence has been excited by the second harmonics of the 1.06 μm electro-optically Q-switched Nd:YAG laser delivering 15 ns pulses. The same laser has been used for luminescence decay measurements. Intensity-dependent transmission have been registered at 1.06 μm using the above mentioned Nd:YAG laser, and at 0.694 μm with the aid of 50 ns pulses from the passively Q-switched ruby laser. The pump intensity has been changed with a set of filters.

### 3. Results and discussion

According to X-ray diffraction analysis data, the undoped glass and that doped with Cr<sub>2</sub>O<sub>3</sub> are X-ray amorphous. The undoped glass is colourless and transparent. The glass doped with chromium oxide is blue–green coloured and transparent. Fig. 1(a) presents its absorption spectrum, which has a broad absorption band at around 600 nm which extends to 1400 nm. It has pronounced maximums at 620, 690, 790 nm, and around 1100 nm. At the slope of the glass absorption edge there is a band at about 490 nm. According to previous studies of aluminate glasses, Cr ions exist in these glasses in form of Cr<sup>3+</sup>,

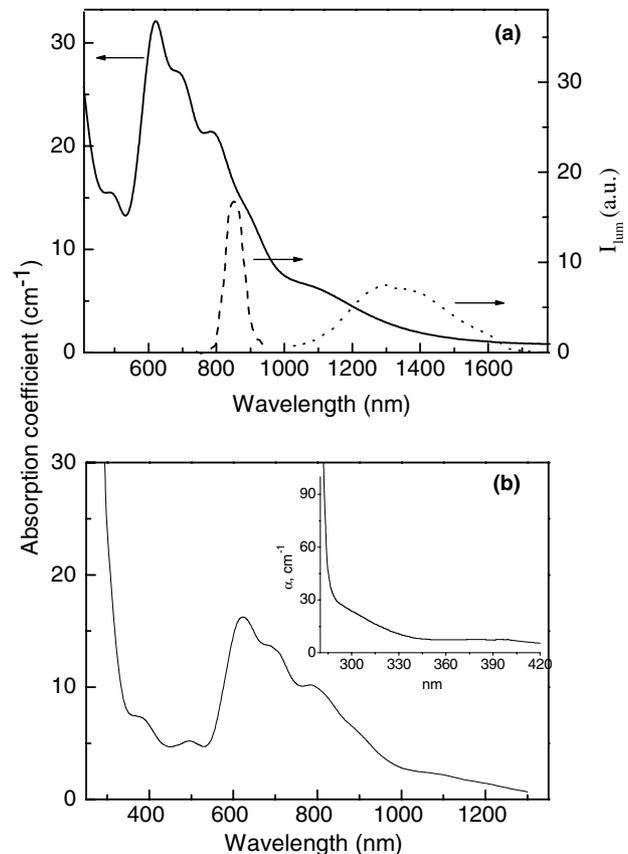


Fig. 1. (a) Absorption (solid line) and luminescence (dashed and dotted lines) spectra of 0.1Cr:calcium-aluminate glass. (b) Absorption spectrum of 0.1Cr:glass versus undoped glass. Inset is the same spectrum but wider scaled for absorption.

Cr<sup>4+</sup>, and Cr<sup>6+</sup>. The shape of the absorption band in the range of 600–1400 nm is similar to that of Cr<sup>4+</sup> ions in oxide crystals [2,3] and in other alkaline-earth aluminate, gallate and alumino-silicate glasses with modifier content  $\geq 60\%$  [21–23]. Because of this similarity, we attribute the main absorption features to the  ${}^3A_2 \rightarrow {}^3T_1({}^3F)$  (0.6–0.9 μm) and the  ${}^3A_2 \rightarrow {}^3T_2({}^3F)$  (around and longer than 1 μm) transitions in tetrahedrally coordinated Cr<sup>4+</sup> ions [21]. According to [24,25], the smaller absorption bands at around 1.2 μm are ascribed to the Fano antiresonance due to the interaction of  ${}^1E$  and vibrationally broadened  ${}^3T_2$ . However the band nearby 490 nm cannot be attributed to absorption of tetrahedrally coordinated Cr<sup>4+</sup> ions. It can be assigned either to the  ${}^4A_2 \rightarrow {}^4T_1$  transition of octahedrally coordinated Cr<sup>3+</sup> ions [26], or to octahedrally coordinated Cr<sup>4+</sup> [27], or to tetrahedrally coordinated Cr<sup>6+</sup> [28]. Though we cannot completely exclude the possibility of formation of traces of two latter species, we believe that the band at 490 nm is caused by the presence of Cr<sup>3+</sup> ions. It is proved by the results of emission spectrum data listed below. It is well-known that the Cr<sup>3+</sup> ion has two absorption bands due to d–d transitions, one located at about 450 nm and another centered at about 650 nm. We believe that the latter band of Cr<sup>3+</sup> ions located at 550–800 nm (due to spin-allowed, but parity forbidden  ${}^4A_2 \rightarrow {}^4T_2$  tran-

sition and spin and parity forbidden  ${}^4A_2 \rightarrow ({}^2T_1, {}^2E)$  ones) overlaps with the absorption band of  $Cr^{4+}$  ions. According to Murata et al. [21], in calcium aluminate glasses, the redox reaction of Cr ions results in formation of  $Cr^{3+}$  and  $Cr^{6+}$  ions. The  $Cr^{6+}$  ion usually demonstrate strong absorption bands centered at 270 and 370 nm due to charge transfer transition [21,29]. To reveal any absorption in this spectral range, we have measured absorption spectrum of glass doped by 0.1%  $Cr_2O_3$  versus the undoped glass (Fig. 1(b)). In this case absorption edge due to glass matrix is eliminated from the spectrum and absorption bands of  $Cr^{6+}$  ions at about 380 nm and 300 nm (inset in Fig. 1(b)) are revealed. One can see that absorption of  $Cr^{6+}$  ions at 380 nm is remarkably lower than intensity of absorption attributed to  $Cr^{4+}$  ions. This is not usually observed in calcium aluminate glasses melted in air [9,21]. Murata et al. [21] demonstrated that the relative content of  $Cr^{6+}$  increased with increasing basicity of glass. We believe that this small amount of  $Cr^{6+}$  ions is the consequence of the glass modification as compared with calcium aluminate glasses studied in other works.

The emission spectrum data of the glass are presented in Fig. 1(a). It should be noted that bands near 0.8 and 1.3  $\mu m$  have been registered under excitation by different wavelengths, so their relative intensities cannot be compared. The wide band with maximum at 1.3  $\mu m$  (excited by the filtered Xe lamp irradiation) is characteristic for the  $({}^3T_2 \text{ or } {}^1E) \rightarrow {}^3A_2$  transition of  $Cr^{4+}$  ions in aluminate glass [8–10,20,29] and oxide crystals [2,30,31]. Rather narrow emission band around 0.82  $\mu m$  (excited by the second harmonics of Nd:YAG laser at 0.53  $\mu m$ ) is attributed to  $Cr^{3+}$  ions. This band can be assigned to vibronically broadened  ${}^4T_2 \rightarrow {}^4A_2$  transition of octahedrally coordinated  $Cr^{3+}$  ions [26,29].

Fig. 2 demonstrates luminescence decay for  $Cr^{3+}$  and  $Cr^{4+}$  ions emission bands. Decay measurement for  $Cr^{3+}$  ions emission has been registered as the change of the luminescence signal in the spectral range of 0.75–0.9  $\mu m$ . Temporal change of the integral luminescence signal in the spectral range of 1.1–1.6  $\mu m$  shows the emission decay for  $Cr^{4+}$  ions. Both signals have clear exponential decay with characteristic times  $\tau$  of  $300 \pm 20$  ns (red luminescence) and  $120 \pm 10$  ns (NIR). The NIR emission band

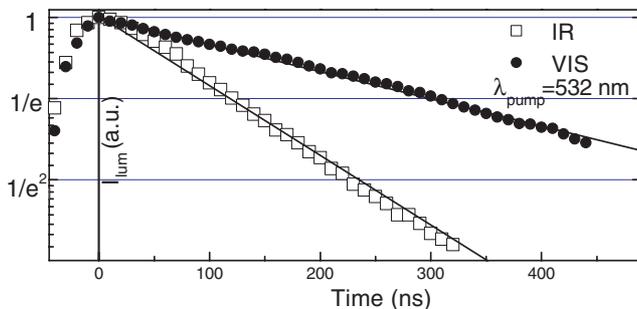


Fig. 2. Integral luminescence signal decay in the range of the band with the maximum at 0.82  $\mu m$  (●) and 1.3  $\mu m$  (□) after 10 ns pump at 0.53  $\mu m$ .

decay time is much shorter than 130  $\mu s$  registered for magnesium calcium barium aluminate glass [7], and 426  $\mu s$  obtained in [29] for aluminosilicate glass. Our data are in accordance with the fast relaxation time of 130 ns presented in [20] for aluminate glass. It should be noted that in contrast to [20] where the second “slow” component in the luminescence decay with characteristic time of 650 ns was registered, in our case the mono exponential relaxation down to the level of  $1/e^2$  is observed. The data for luminescence properties of the studied glass are presented in Table 2.

Single crystals doped with  $Cr^{4+}$  ions are known as saturable absorbers for a number of red-NIR lasers [12–19]. So  $Cr^{4+}$ -containing glasses could be perspective saturable absorbers for existing or next generation fibre lasers emitting in the range of 0.7–1.2  $\mu m$ .

Fig. 3 presents results on intensity-dependent transmission measurements for Cr-glass at 0.69 and 1.06  $\mu m$ . One can see that for both wavelengths the glass demonstrates clear bleaching effect. However the residual absorption is

Table 2  
Emission properties of Cr-doped calcium aluminate glass

$Cr^{3+}$ ions		$Cr^{4+}$ ions	
$\lambda_{max}$ ( $\mu m$ )	$\tau$ (ns)	$\lambda_{max}$ ( $\mu m$ )	$\tau$ (ns)
0.820	$120 \pm 10$	1.300	$300 \pm 20$

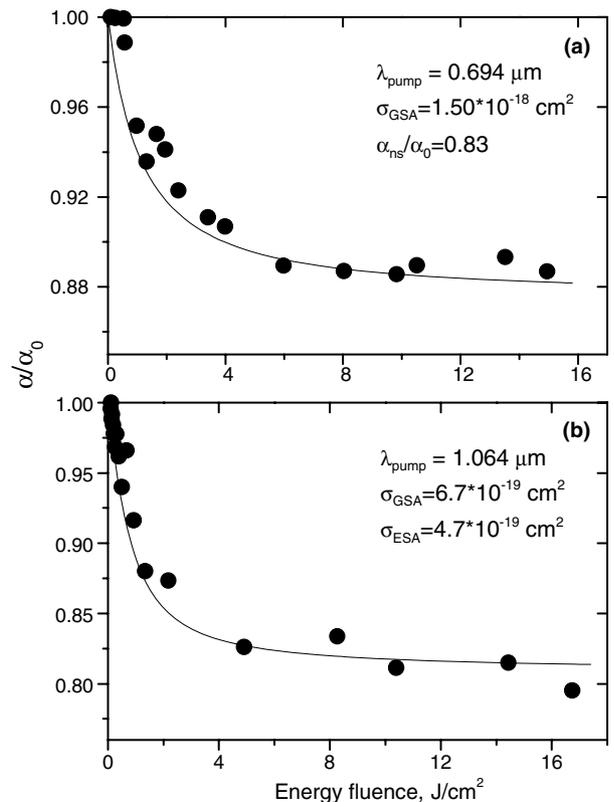


Fig. 3. Intensity-dependent relative absorption at 0.69  $\mu m$  (a) and 1.06  $\mu m$  (b). Solid lines are the best fits in the frameworks of Eqs. (2) and (1), respectively.

Table 3  
Absorption saturation data for Cr<sup>4+</sup>-doped crystals and glasses

Material	Wavelength (μm)			
	1.06		0.69	
	$\sigma_{\text{GSA}}, 10^{-18} \text{ cm}^2$	$\sigma_{\text{ESA}}/\sigma_{\text{GSA}}$	$\sigma_{\text{GSA}}, 10^{-18} \text{ cm}^2$	$\alpha_{\text{ns}}/\alpha_0$
Cr:YAG [13]	0.3–0.6	0.2		
Cr:Mg <sub>2</sub> SiO <sub>4</sub>	0.45–0.6 [12]	0.4 [12]	3.1 [19]	0.5 [19]
Cr:Y <sub>2</sub> SiO <sub>5</sub> [19]			2	0.33
Cr:CaGd <sub>4</sub> (SiO <sub>4</sub> ) <sub>3</sub> O [33]	0.3–1.1	0.05–0.45	2	0.35
Cr:aluminate glass [20]				0.7–0.85 <sup>a</sup>
Cr:calcium–aluminate glass (this work)	0.7	0.70	1.5 ± 0.2	0.83

Figure in brackets are in accordance with the references.

<sup>a</sup> Data are measured at 0.8 μm.

rather high, especially at 0.69 μm. As pump laser pulse durations used in these experiments have been short in comparison with luminescence decay times, one can analyze these data in the frameworks of the model for a slow relaxing saturable absorber [32]. As soon as absorption at 1.06 μm is mainly due to Cr<sup>4+</sup> ions, it is possible to evaluate the Cr<sup>4+</sup> ion excited-state and ground-state absorption cross-sections ( $\sigma_{\text{ESA}}$  and  $\sigma_{\text{GSA}}$ ) at this wavelength from intensity-dependent transmission measurements [32]:

$$\frac{dE}{dz} = -hv[\ln(1/T_0)/(L\sigma_{\text{GSA}})](1 - \sigma_{\text{ESA}}/\sigma_{\text{GSA}}) \times [1 - \exp(-\sigma_{\text{GSA}}E/hv)] - \ln(1/T_0)\sigma_{\text{ESA}}E/(L\sigma_{\text{GSA}}), \quad (1)$$

where  $E$  is the input energy fluence,  $T_0$  is the small signal transmission, and  $L$  is the length of the sample. The best fit to the experimental data has been obtained with the values of  $\sigma_{\text{GSA}} = (6.7 \pm 0.3) \times 10^{-19} \text{ cm}^2$  and  $\sigma_{\text{ESA}}/\sigma_{\text{GSA}} = 0.70$  at 1.06 μm (Fig. 3(b)).

In contrast, it is evident that at 0.69 μm there is a remarkable absorption of Cr<sup>3+</sup> ions, so it is hard to evaluate excited-state absorption for Cr<sup>4+</sup> ions at this wavelength from intensity-dependent transmission data. It is better to analyze these data taking into account non-saturable absorption  $\alpha_{\text{ns}}$  (which accumulates excited-state absorption of Cr<sup>4+</sup> ions and absorption of impurities, Cr<sup>3+</sup> ions first of all):

$$\frac{dE}{dz} = -hv[\ln(1/T_0)/(L\sigma_{\text{GSA}})][1 - \exp(-\sigma_{\text{GSA}}E/hv)] - \alpha_{\text{ns}}L. \quad (2)$$

The best fit to the experimental data has been obtained with  $\sigma_{\text{GSA}} = (1.5 \pm 0.2) \times 10^{-18} \text{ cm}^2$  and  $\alpha_{\text{ns}}/\alpha_0 = 0.83$  at 0.69 μm ( $\alpha_0$  – is small-signal absorption coefficient).

Absorption saturation data for the studied glass in comparison with some other Cr<sup>4+</sup>-doped materials are collected in Table 3. One can see that the ground-state absorption cross-sections at both wavelengths have values similar to those for other materials (at 1.06 μm it is even higher than for Cr:YAG and Cr:forsterite). However the excited-state absorption for Cr<sup>4+</sup> ions (or non-saturable absorption) in the studied glass is rather high. Nevertheless we believe that

future optimization of the glass composition and synthesis procedure will lead to acceptable results for laser saturable absorber applications of Cr-doped calcium aluminate glasses.

#### 4. Conclusion

The absorption and emission properties of Cr<sup>4+</sup> ions in calcium aluminate glasses have been studied. It is shown that the formation of Cr<sup>6+</sup> ions in developed glass melted in air is suppressed as compared with previously studied calcium aluminate glasses. Luminescence of Cr<sup>4+</sup> ions (centered at 1.3 μm) and of Cr<sup>3+</sup> ions (centered at 0.82 μm) has mono exponential decay with characteristics times of  $300 \pm 20 \text{ ns}$  and  $120 \pm 10 \text{ ns}$ , respectively. Ground-state absorption cross-sections for Cr<sup>4+</sup> ions have been estimated as  $1.5 \times 10^{-18} \text{ cm}^2$  and  $0.7 \times 10^{-18} \text{ cm}^2$  at 0.69 μm and 1.06 μm, respectively.

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