

# Spectroscopy and high pressure spectroscopy of the Cr-doped glass materials

MAREK GRINBERG, JUSTYNA BORZOWSKA, BOHDAN PADLYAK\*, TADEUSZ NOWOSIELSKI, BENEDYKT KUKLIŃSKI

Institute of Experimental Physics, University of Gdańsk. ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

PETRO BUCHYNSKI

Lviv Scientific and Industrial Amalgamation "Karat", Stryjska St. 202, 79031 Lviv, Ukraine.

Optical spectroscopy nad high pressure optical spectroscopy of the Cr-doped glasses of CaO–Ga<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub> system have been used. Emission spectrum consists of the broad band at about 12700 cm<sup>-1</sup> and the sharper band with maximum peaked at 14495 cm<sup>-1</sup> (the R line emission). We have attributed the R line luminescence to the octahedral strong field Cr<sup>3+</sup> sites in the microcrystallites whereas the broad band luminescence has been related to the chromium in the glassy phase.

## 1. Introduction

Disordered crystals and glass matrices doped with transition and rare earth metal ions are still attractive as possible laser media [1], [2] and fibers [3].

In this paper, we present spectroscopic investigations of a glass of the Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> garnet (CGGG) composition doped with chromium. The CGGG:Nd<sup>3+</sup> is known as the laser material [4]. In the Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub> gallogermanate (CGGO) crystal doped with Cr, Cr<sup>3+</sup> ion occupies the octahedral site characterized by the weak field, which contributes mainly to the <sup>4</sup>T<sub>2</sub> → <sup>4</sup>A<sub>2</sub> broad band emission. Only a small number of sites from the strong field part of the crystal field distribution results in the weak R line emission related to the <sup>2</sup>E + <sup>4</sup>A<sub>2</sub> transitions [5]. On the other hand, in Ca<sub>3</sub>Sr<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> garnet (CSGG) doped with chromium, the Cr<sup>3+</sup> ion occupies only the weak field sites [6]. As far as the CGGG:Cr<sup>3+</sup> crystal is considered, the dominant is the R line luminescence [7] which corresponds to the existence of the strong field sites. In this paper, we present the luminescence emission and luminescence excitation spectra of Cr doped Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> glass (CGGG-glass). To consider the nature of the sharp lines and the broad band emissions we have measured the photoluminescence of the material under high hydrostatic pressure applied in diamond anvil cell (DAC).

---

\*On leave from Department of Physics, Ivan Franko National University of Lviv, Dragomanov Str. 50, 79-005, Lviv, Ukraine.

## 2. Sample preparation

The Cr-doped glasses of CaO–Ga<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub> system of high chemical purity and optical quality with different compositions were obtained in corundum crucibles by standard high-temperature synthesis [8]. The chromium impurity was added to the glass composition in the form of CrCl<sub>3</sub> liquid solution in amounts of 0.01–0.2 wt%. The colour of the CaO–Ga<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub> glasses of different composition varies from pale green to dark green depending on chromium concentration. Chemical composition of the glasses obtained was controlled by the X-ray microanalysis method using a Camebax apparatus. The glasses with stoichiometric composition of the calcium-gallium-germanium garnet (Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>) crystals with Cr of the concentration of 0.02–0.03 wt% were selected.

The structural investigations by X-ray diffraction technique show that the undoped compounds of CaO–Ga<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub> system with Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>, Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub> and Ca<sub>3</sub>Ga<sub>2</sub>O<sub>6</sub> stoichiometric compositions has a real glass structure with small traces of crystalline phases [9]. In the Cr-doped Ca–O–Ga<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub> materials the significant impurity of the calcium-gallium-germanium garnet and Ca-gallogermanate crystalline phases were included to the basic glass composition [10].

## 3. Experimental technique

The excitation spectra were measured using a system built at the Condensed Matter Spectroscopy Division of the Institute of Experimental Physics. A Hanovia 100 W xenon lamp was a light source, monochromator SPM2 (Carl Zeiss Jena) was used for selecting exciting wavelengths, the second one (the same type) was used for selecting an emission wavelength. Luminescence signal was measured with Hamamatsu R928 photomultiplier.

For high pressure spectroscopy measurements the sample was placed in diamond anvil cell Diacold 04 (modified Merrill-Basset design) made by Diacell Products. The R<sub>1</sub>-line of ruby was used for pressure calibration. Selective excitation of the sample and the ruby was performed, because R-lines from ruby overlap the R-line emission from the sample. Argon laser working in a single mode was used as an excitation source. The emission light was dispersed by monochromator adapted from spectrograph PGS2 (Carl Zeiss Jena), with a 651 grooves/mm grating, and detected with photon counting technique with Hamamatsu R943-02 photomultiplier tube.

## 4. Optical spectra

The photoluminescence spectrum of the CGGG glass consists of the broad band of about 1700 cm<sup>-1</sup> half-width, peaked at about 12700 cm<sup>-1</sup>, and the sharper band of 90 cm<sup>-1</sup> half-width with maximum at 14495 cm<sup>-1</sup>. We have not noticed any significant changes in the sharp line and broad band emission with varying

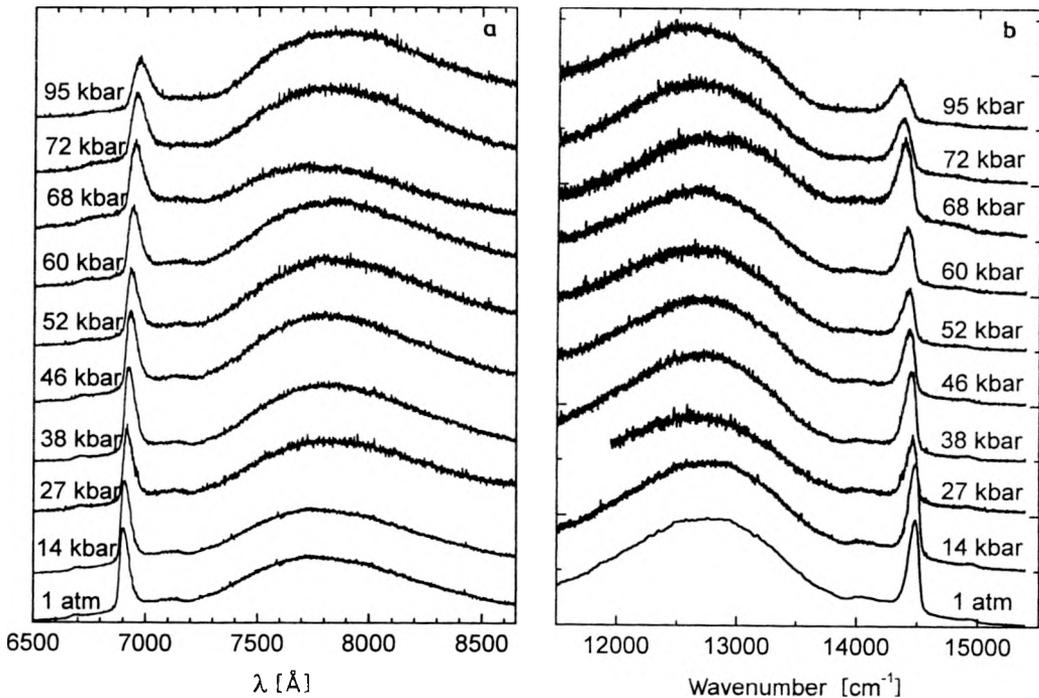


Fig. 1. Emission spectra of Cr-doped CGGG glass obtained for different pressures, photoluminescence spectra (a) and spectral line-shapes (b). All the spectra were obtained under excitation 457.9 nm.

excitation energy (457.9 nm, 488 nm and 514 nm). The emission spectra obtained under excitation 457.9 nm are presented in Fig. 1 a,b. In Figure 1a, spectra corrected with respect to the detector sensitivity are presented. In Fig. 1b, we present the line-shape of the spectra that is proportional to the intensity divided by the third power of photon energy.

One attributes the sharper band of energy  $14495\text{ cm}^{-1}$  to the  $R_1$  line emission related to the  ${}^2E \rightarrow {}^4A_2$  transition in strong field octahedrally coordinated  $\text{Cr}^{3+}$  sites. The large half-width of the  $R$  line as well as the fact that it is unsymmetrical is the result of the inhomogeneous broadening of the transition related to disorder of the glass host. As far as the broad band is considered it fits energetically to the  ${}^4T_2 \rightarrow {}^4A_2$  transition in weak field octahedrally coordinated  $\text{Cr}^{3+}$  sites. In CSGG crystal the band peaked at  $13000\text{ cm}^{-1}$  was related to the  ${}^4T_2 \rightarrow {}^4A_2$  transition in the  $\text{Cr}^{3+}$  substituted  $\text{Sr}^{3+}$  [6]. We have measured the excitation spectra of the luminescence monitored at  $14495\text{ cm}^{-1}$  and  $12700\text{ cm}^{-1}$ , respectively (all the excitation spectra are collected in Fig. 2). In the case of the  $14495\text{ cm}^{-1}$  emission, the excitation spectrum consists of two bands of the Gaussian shape peaked at  $17350\text{ cm}^{-1}$  (with half-width  $2567\text{ cm}^{-1}$ ) and  $23720\text{ cm}^{-1}$  (with half-width  $2708\text{ cm}^{-1}$ ), at a temperature of 85 K. One notices the strong temperature shift of both bands equal to  $-1.5\text{ cm}^{-1}/\text{K}$ . The excitation spectra of the  $R$  line emission confirm existence of the strong field  $\text{Cr}^{3+}$  ion in the octahedral coordination. The detected bands are related to the spin

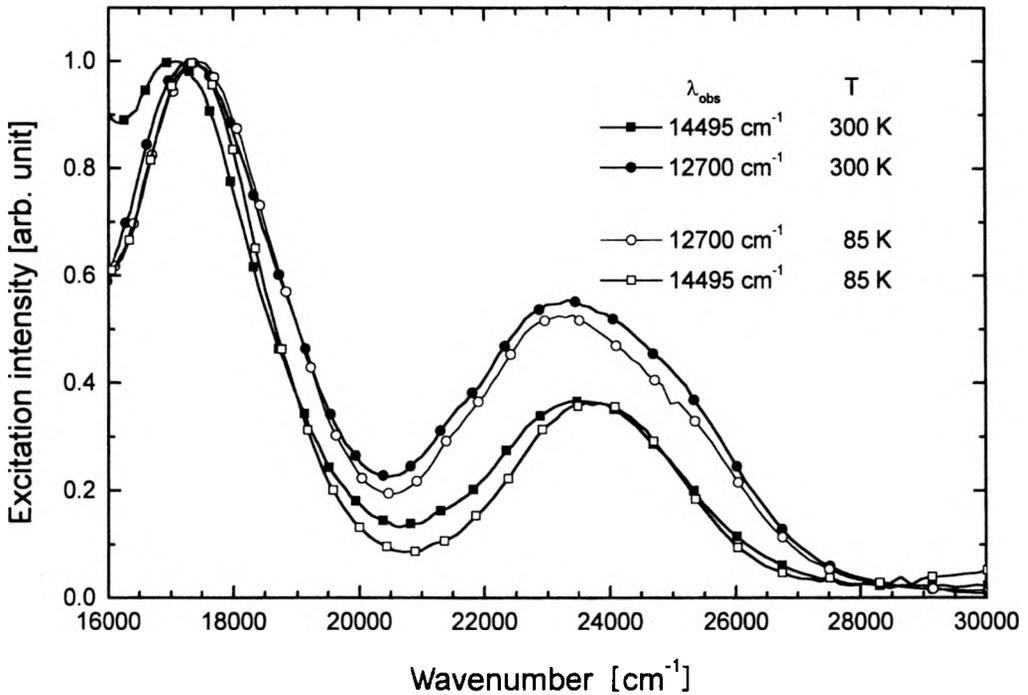


Fig. 2. Excitation spectra of the  $R_1$  line emission and broad band emission (detailed description in the figure).

allowed  ${}^4A_2 \rightarrow {}^4T_2$  and  ${}^4A_2 \rightarrow {}^4T_1$  transition. Using the crystal field model [11], one obtains the cubic crystal field strength  $10 Dq = 17350 \text{ cm}^{-1}$  and Racach parameters  $B = 627 \text{ cm}^{-1}$  and  $C = 3253 \text{ cm}^{-1}$ .

Excitation spectra of the broad band emission ( $12700 \text{ cm}^{-1}$ ) also consist of two bands. The lower energy band has a maximum at  $17450 \text{ cm}^{-1}$ . Instead of a single band corresponding to the  ${}^4A_2 \rightarrow {}^4T_1$  transition we have a double band that can be decomposed into two Gaussians, the first peaked at  $22270 \text{ cm}^{-1}$  and the second at  $24000 \text{ cm}^{-1}$ . Although one notices the above differences, the structure of the excitation spectra of the  $14495 \text{ cm}^{-1}$  and  $12700 \text{ cm}^{-1}$  emission is close enough to each other to relate them to the same center or very familiar centers. Specifically one notices the correspondence between the  $17350 \text{ cm}^{-1}$  and  $17450 \text{ cm}^{-1}$ ,  $23720 \text{ cm}^{-1}$  and  $2400 \text{ cm}^{-1}$  bands in the excitation spectra of  $R$  line and the broad band, respectively, as related to  ${}^4A_2 \rightarrow {}^4T_2$  and  ${}^4A_2 \rightarrow {}^4T_1$  transitions.

For additional analysis of the nature of the  $14495 \text{ cm}^{-1}$  and  $12700 \text{ cm}^{-1}$  luminescence we have measured the high-pressure photoluminescence spectra. Since the glass is very inhomogeneous, the ratio of integrated intensity of the sharp to the broad band depends on that which part of the sample has been excited. For high-pressure spectroscopy we have chosen the brightest pieces of the sample for which the respective ratio was between 0.05 and 0.1. In Figure 1, one can see that the  $R$  line abbreviates the significant shift, whereas the broad band with maximum at

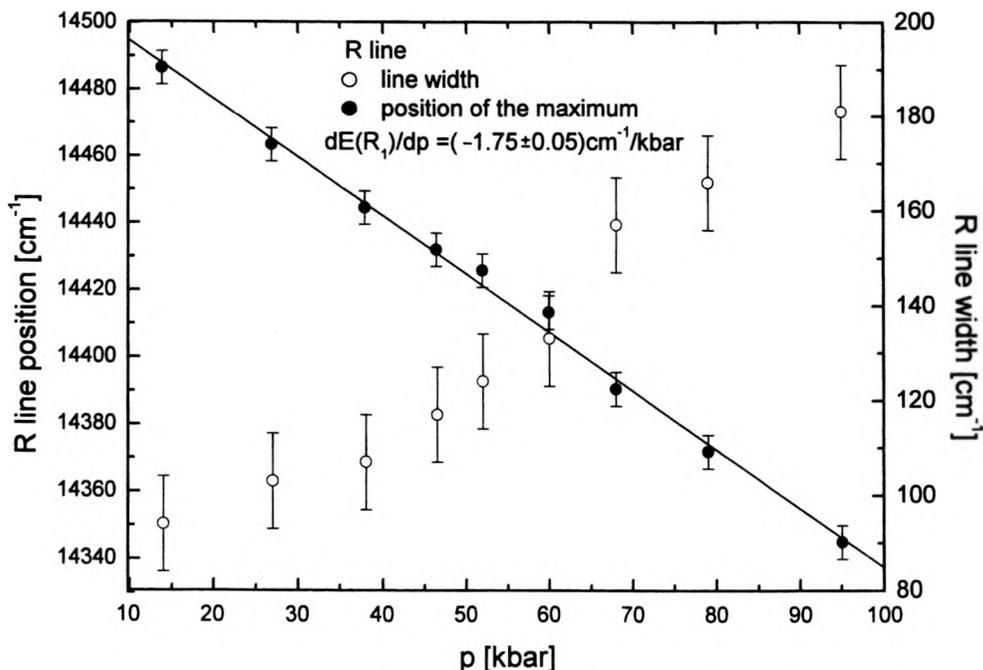


Fig. 3. Energy maximum and the half-width of the  $R_1$  emission vs. pressure (under excitation 457.9 nm).

$12700\text{ cm}^{-1}$  does not change the energy and the shape in any systematic way, when pressure is increased. The behaviour of  $R$  line with pressure is typical of the luminescence of the strong field  $\text{Cr}^{3+}$  sites [12]–[16]. The  $R_1$  line energy decreases linearly with increasing pressure (calculated pressure shift is  $-1.75 \pm 0.05\text{ cm}^{-1}/\text{kbar}$ ). In Figure 3, the energy and the half-width of the  $R$  line versus pressure is presented. It is not surprising that the  $R_1$  line half-width increases with pressure. We attribute this effect to the lattice disorder being induced by pressure. A similar effect has been observed for ruby [17].

To predict the position of the minimum of the  ${}^4T_2$  electronic manifold one has to calculate the electron–lattice coupling energy  $S\hbar\omega$ . If the absorption and emission involves the same state one can calculate the quantity of  $S\hbar\omega$  as the half of the Stokes shift between the excitation (absorption) and emission line-shape maxima. Since in our case this condition is not satisfied we estimate the electron–lattice coupling energy directly from analysis of the excitation band. The electron–lattice energy of the system in the excited  ${}^4T_2$  state can be related to the standard dispersion  $\sigma_{\text{hom}}$  of the homogeneously broadened absorption/excitation band as follows [11]:

$$S\hbar\omega = \frac{\sigma_{\text{hom}}^2}{\hbar\omega \cosh\left(\frac{\hbar\omega}{2kT}\right)}$$

Here we relate the measured dispersion of the band to the temperature 0 K,  $\hbar\omega$  is the energy of active phonon mode. We have performed calculations assuming  $\hbar\omega = 300 \text{ cm}^{-1}$  and  $S\hbar\omega = 2460 \text{ cm}^{-1}$ . Thus one obtained the minimum of the energy of the  ${}^4T_2$  electronic manifold equal to  $14890 \text{ cm}^{-1}$ , which is much above the energy of the  ${}^2E$  state.

## 5. Conclusions

Our high pressure optical spectroscopy of chromium doped CGGG glasses, performed for pressure range from ambient to 95 kbar has shown that the sharp line emission peaked under ambient pressure at  $14495 \text{ cm}^{-1}$  behaves with pressure as a typical  $R_1$  line related to the strong field octahedrally coordinated  $\text{Cr}^{3+}$  center. On the other hand, the broad band emission peaked at  $12700 \text{ cm}^{-1}$  does not depend on pressure. Despite the similarity of the excitation spectra, the lack of systematic pressure shift of the broad band emission allows us to formulate the conclusion that this emission is not related to the  ${}^4T_2 \rightarrow {}^4A_2$  transition in octahedrally coordinated  $\text{Cr}^{3+}$  center.

However, although the broad emission band and the R line emission are from different centers they seem both to be related to chromium dopants. The X-ray analysis of our glasses has shown that Cr doping yields the garnet and gallogermanate precipitates in the glass phase [10]. This is the reason why we attribute the R line luminescence to the octahedral strong field  $\text{Cr}^{3+}$  sites in the garnet microcrystallites whereas the broad band luminescence is related to chromium in the glassy phase. The charge state as well as the coordination symmetry of these sites remain open questions.

*Acknowledgments* – This paper was supported by the Polish State Committee for Scientific Research (KBN), under the Grant No. 2P03B00313, and Gdańsk University, Grant No. 5200-5-0299-0.

## References

- [1] DRUBE J., STRUVE B., HUBER G., *Opt. Commun.* **50** (1984), 45.
- [2] KENYON P., ANDREWS L., MC COLLUM B., LEMPICKI A., *IEEE J. Quantum Electron.* **18** (1982), 1189.
- [3] YEH D.C., SIBLEY W.A., SUSCAVAGE M., DREXHANGE M.G., *J. Appl. Phys.* **62** (1987), 266.
- [4] JAQUE D., CALDINO U., ROMERO J.J., GARCIA SOLE J., *J. Lumin.* **83–84** (1999), 477.
- [5] GRINBERG M., MACFARLANE P.L., HOLLIDAY K., HENDERSON B., *Phys. Rev. B* **52** (1995), 3917.
- [6] CAVALLI E., ZANNONI E., BELLETTI A., *Opt. Mater.* **6** (1996), 153.
- [7] NOSENKO A.E., BILY A.I., KOSTYK L.V., KRAVCHISHIN V.V., *Opt. Spektrosk.* **57** (1984), 837 (in Russian).
- [8] PADLYAK B.V., BUCHYNSKII P.P., Patent of Ukraine, No. UA 24235 A, 1998.
- [9] PADLYAK B., MUDRY S., HALCHAK V., *et al.*, *Opt. Appl.* **30** (2000), 691.
- [10] MUDRY S., HALCHAK V., private communication.
- [11] HENDERSON B., IMBUSH G.F., *Optical Spectroscopy of Inorganic Solids*, Clarendon Press, Oxford 1989.
- [12] DOLAN J.F., KAPPERS L.A., BARTRAM R.H., *Phys. Rev. B* **33** (1986), 7339.

- [13] GALANCIAK D., PERLIN P., GRINBERG M., SUCHOCKI A., *J. Lumin.* **60**, **61** (1994), 223.
- [14] HÖMMERICH U., BRAY K.L., *Phys. Rev. B* **51** (1995), 12133.
- [15] KAMIŃSKA A., SUCHOCKI A., GRINBERG M., *et al.*, *J. Lumin.* **87–89** (2000), 571.
- [16] WAMSLEY P.R., BRAY K.L., *J. Lumin.* **59** (1994), 11.
- [17] See, *e.g.*, EGGERT J.H., GOETTEL K.A., SILVERA I., *Phys. Rev. B* **40** (1989), 5724.

*Received September 18, 2000*