Laser materials on basis of disordered crystals with $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ structure

A. Nosenko, R. Leshchuk, V. Kravchishin

► To cite this version:

A. Nosenko, R. Leshchuk, V. Kravchishin. Laser materials on basis of disordered crystals with $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ structure. Journal de Physique IV Proceedings, 1994, 04 (C4), pp.C4-455-C4-458. 10.1051/jp4:19944109 . jpa-00252558

HAL Id: jpa-00252558

<https://hal.science/jpa-00252558>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Laser materials on basis of disordered crystals with $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ structure

A.E. NOSENKO, R.Ye. LESHCHUK and V.V. KRAVCHISHIN

Lviv State University, Dragomanov Str. 50, Lviv 290005, Ukraine

The spectroscopic properties of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, $\text{La}_3\text{Ga}_5\text{GeO}_{14}$ crystals doped with Cr^{3+} , Cr^{4+} , Mn^{3+} and Ti^{4+} ions have been investigated. In the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Cr}$ crystals broad-band continuous tunable within $0.77\pm 0.96\ \mu\text{m}$ stimulated emission of Cr^{3+} ions (${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ channel) at room temperature has been obtained.

In modern physics and spectroscopy of laser crystals the grant attention to the search and investigations of disordered compounds with broad-band emission as potential tunable laser materials is paid. Among such crystals the compounds of $\text{A}_3\text{B}_x\text{C}_{6-x}\text{O}_{14}$ composition ($\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ -type structure, space group P321) doped with Cr^{3+} ions are distinguished, which are known as active elements of wavelength tunable lasers.^{1,2} These acentric compounds open the way for the design of tunable solid-state lasers with frequency self doubling as well.

The $\text{A}_3\text{B}_x\text{C}_{6-x}\text{O}_{14}$ single crystals have been growth by Czochralski method in platinum crucibles.²⁻⁴ The crystal structure of the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ type is formed by tetrahedral layers oriented perpendicular to the c-axis, separated by inter-layers consisted of distorted Thomson cubes (3e positions with symmetry 2), occupied by large ions (Ca^{2+} , Sr^{2+} , La^{3+}), and octahedra (1a site with symmetry 32).⁵ The tetrahedral layers include the tetrahedra of two types: the first ones are placed on third-order axis (2d positions with symmetry 3), and the others are grouped around the octahedra by the triple-axis rule (3f sites with symmetry 2). The X-ray data analysis and spectral characteristics of $\text{A}_3\text{B}_x\text{C}_{6-x}\text{O}_{14}$ crystals show that these crystals belong to disordered materials.^{2,5} In $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ and $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ the disorder is due to the statistical occupation of 1a and 3f positions by Ga^{3+} and Ge^{4+} ions, in $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ and $\text{La}_3\text{Ga}_5\text{GeO}_{14}$ the tetrahedral 2d position are randomly occupied by Ga^{3+} and Si^{4+} (Ge^{4+}) ions.

The absorption and luminescence spectra of the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ -type crystals were measured by conventionally methods within the temperature interval $80\pm 300\ \text{K}$. The results obtained are illustrated

in Fig.1 and summarized in Table. It was established, that in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ the chromium and manganese ions being form the Cr^{3+} and Mn^{3+} substitutional centers in octahedral positions 1a. The titanium impurity ions in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ are in the valent state Ti^{4+} and the bands in the absorption and luminescent spectra (Fig.1) correspond to transition in the $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ charge-transfer band.⁴

Fig.1. Absorption (2-4) and luminescence (5,6) spectra of Ti^{4+} (2,5), Cr^{3+} (3,6) and Mn^{3+} (4) ions in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystal (1 - reference absorption spectra of undoped crystal). Dashed area indicates the laser-tuning range

In the absorption spectra of $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Cr}$, $\text{La}_3\text{Ga}_5\text{SiO}_{14}:\text{Cr}$ and $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}$ crystals, besides the bands typical for Cr^{3+} ions in the octahedral symmetry field, the another bands due to transitions of Cr^{4+} ions in octahedral positions were observed (see Table).

Table. Absorption and luminescence characteristics of chromium ions in $\text{A}_3\text{B}_x\text{C}_{6-x}\text{O}_{14}$ crystals.

Crystal	Peaks of absorption bands (μm)						Peaks of luminescence bands	
	Cr ⁴⁺		Cr ³⁺					
	³ T ₁ ⇒ ⇒ ³ T ₁	³ T ₁ ⇒ ⇒ ³ T ₂	⁴ A ₂ ⇒ ⁴ T ₁ (Y)		⁴ A ₂ ⇒ ⁴ T ₂ (U)		Cr ³⁺ ions (μm)	
			E c	E⊥c	E c	E⊥c		
Ca ₃ Ga ₂ Ge ₄ O ₁₄			0.463	0.442	0.623	0.632	0.865	0.696
Sr ₃ Ga ₂ Ge ₄ O ₁₄	0.390	0.495	0.445	0.435	0.603	0.618	0.830	0.694
La ₃ Ga ₅ SiO ₁₄	0.365	0.500		0.423	0.630	0.633	0.910	
La ₃ Ga ₅ GeO ₁₄	0.360	0.495		0.430	0.635	0.639	0.930	

The absorption spectra are indicative of strong dichroism of crystals under investigation. So, for $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Cr}$ the relation

of Cr^{3+} ions absorption bands intensities is: $Y_{\parallel}:Y_{\perp}:U_{\perp}:U_{\parallel} = 1:1.25:0.47:1.78$. Fano antiresonances are visible in absorption spectra of $\text{A}_3\text{B}_x\text{C}_{6-x}\text{O}_{14}:\text{Cr}$ crystals, due to superposition of ${}^2\text{E}$ and ${}^2\text{T}_1$ energy levels with the quasi-continuum of the vibrationally broadened ${}^4\text{T}_2$ level. In $\text{A}_3\text{B}_x\text{C}_{6-x}\text{O}_{14}:\text{Cr}$ crystals a photochromic effect has been found that is connected with the recharging of the impurity chromium ions ($\text{Cr}^{3+} \rightleftharpoons \text{Cr}^{4+} + e$).

The emission of Cr^{3+} in $\text{A}_3\text{B}_x\text{C}_{6-x}\text{O}_{14}$ crystals is a mixture of the two types of transition: wide-band emission on ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition and R-line (${}^2\text{E} \rightarrow {}^4\text{A}_2$ channel) with its vibronic recurrences. Calculated of phonon energies are in good agreement with phonon frequencies in infrared and Raman spectra. The luminescence spectra in the R region are characterized by significant line width ($\Delta = 40 \pm 60 \text{ cm}^{-1}$). The near-neighbours of Cr^{3+} ions in crystals with $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ structure are represented by six cations in the tetrahedral $3f$ position and three cations in the Thomson cube sites $3e$, all nine are bonded with Cr^{3+} ions via oxygen ions. The second Cr^{3+} coordination sphere contains of the cation in $2d$ tetrahedra and the cations in octahedra located above and below (along the c-axis) the Cr octahedron. The random occupation of $3e$, $1a$ and $2d$ positions by cations with different valency (Ga^{3+} and Ge^{4+} or Si^{4+}) could make the crystal field a title varying from one Cr site to another resulting in inhomogeneous broadening of the R-lines.

The spectroscopic experiments with stimulated emission of Cr^{3+} ions (vibronic ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ channel) in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals were carried out at 300 K using dispersion or nonselective optical resonator and a ruby laser, which was used for pumping of active elements.² A strong dichroism of the sample absorption allowed to achieve an optimal (70-75%) absorption level of pumping emission in the crystal by simple turn of the element around the resonator axis.

By using of nonselective laser resonator the dependence of energy parameters versus excitation level has been investigated (Fig.2). The threshold of generation relative the energy absorbed in the crystal was $\approx 35 \text{ mJ}$ with differential output efficiency $\eta=12\%$. The generation pulse was shifted by 10 ns relative to the pumping pulse (Fig.2b). Duration of generation was $\approx 8 \text{ ns}$. The broadband tunable stimulated emission has been realized within $0.77 \pm 0.97 \mu\text{m}$ in dispersion resonator using the diffraction lattice as a selective element.

Fig.2. The energetic parameters of the laser on the basis of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Cr}$ crystals vs absorbed energy of excitation (a) and the time profile of the pump (1) and generation (2) pulses (b).

The spectral region of luminescence and stimulated emission being obtained is not in agreement with data.¹ These discrepancies, perhaps, are due to the statistical disorder in the cation sublattice of the matrix. Such crystallochemical peculiarity of the crystals under investigation leads to nonreproducibility of crystalline field in chromium ions locations. The dependence of ion energy levels on the crystalline field causes the changes of spectral characteristics of Cr^{3+} ions in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ matrices being grown in somewhat various conditions. Therefore, in case of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Cr}$ crystals changing the technology of active media preparation one can obtain the extremely broad-band tunable stimulated emission Cr^{3+} ions (from 0.77 to 1.21 μm).

References

- ¹A.A. Kaminskii, A.V. Butashin, A.A. Demidovich, V.G. Koptev, B.V. Mill and A.A. Shkadarevich, *Phys. Stat. Sol. (a)* 112, 197 (1989).
- ²A.P. Voltovich, A.E. Nosenko, A.G. Bazyiev, V.S. Kalinov, V.V. Kravchishin and R.Ye. Leshchuk, *Zhurnal Prikladnoy Spectroscopii* 51,705 (1989).
- ³A.E.Nosenko, R.Ye. Leshchuk and V.V. Kravchishin, *Ukrainskii fizicheskii zhurnal* 34,1306 (1989).
- ⁴A.E.Nosenko, R.Ye. Leshchuk and V.V.Kravchishin, *Zhurnal Prikladnoy Spectroscopii* 54, 321 (1991).
- ⁵A.A. Kaminskii, E.L. Beloconeva, B.V.Mill, Yu.V. Pisarevskii, S.E. Sarkisov, I.M. Silvestrova, A.B. Butashin and G.G. Khodzhabyan, *Phys. Stat. Sol. (a)* 86, 345 (1984).