Spectral properties of Cr^{3+} in $SrLaGaO_4$ under high hydrostatic pressure

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Abstract—In this contribution the absorption, excitation and luminescence spectra of $SrLaGaO_4:Cr^{3+}$ at different temperatures and pressures are presented. It was found that luminescence related to $^2E\rightarrow{}^4A_2$ transition in Cr^{3+} shifts with pressure to the red region. The pressure shifts of the luminescence related to $^2E\rightarrow{}^4A_2$ transition and phonon sidebands are estimated.

Strontium lanthanum gallate, $SrLaGaO_4$ (SLG) and their solid solutions have been extensively investigated since they were considered as promising substrate for high temperature superconducting film. The review of their elastic and elastooptic properties has been presented in Ref. [1]. SLG doped with transition metal or rare earth ions was also considered as laser active media [2]. The SLG crystal belongs to the family of compounds with general formula $ABCO_4$, where A=Sr, Ca; B=La, Y and C= Al, Ga or other transition elements that crystallize in a perovskite like tetragonal type structure of I4/mmm space group [3]. In SLG trivalent impurity ions occupy sixfold coordinated (octahedral symmetry) Ga^{3+} sites. Specifically interesting dopand is Cr^{3+} ion which spectral properties are strongly dependent on crystal lattice [4]. Energetic structure of Cr^{3+} ion ($3d^3$ system) is described by a crystal field model where energies of localized states are determined by quantities of Racah parameters; B and C and crystal field strength $10Dq$ [5]. In octahedral symmetry the ground state of the Cr^{3+} is always $^4A_2$. The first excited state can be $^4T_2$ or ^2E state. In the low field case ($Dq<2.4B$) the first excited state $^4T_2$ that results in broad band emission related to $^4T_2\rightarrow{}^4A_2$ transition, whereas in high field case ($Dq>2.4B$) the first excited state is ^2E and broadband emission is replaced by a sharp line related to spin forbidden $^2E\rightarrow{}^4A_2$ transition. This emission is called often the R-line luminescence. Since crystal field strength Dq is proportional to ligand charge and to the R^{-5}, where R is the Cr^{3+}-O^{2-} distance all methods that can control the quantity of R can be an effective tool for investigation of the Cr^{3+} system. The most effective is high pressure spectroscopy, where hydrostatic pressure is applied in a diamond anvil cell (DAC). Compressing crystal pressure changes the crystal field strength Dq, which causes increase energy of the $^4T_2$ and $^4T_1$ states. As a result, one expects transformation of the system from low to high field, where $^4T_2\rightarrow{}^4A_2$ transition is replaced by $^2E\rightarrow{}^4A_2$ transition. On the other hand, in a high field system the pressure causes a small red shift of the $^2E\rightarrow{}^4A_2$ luminescence. Effect of red shift of the R–lines emission of ruby ($Al_2O_3:Cr^{3+}$) crystal has been applied in high pressure spectroscopy for pressure determination. One can find the review on high pressure spectroscopy of Cr^{3+} materials in the paper [6]. The possibility of obtaining a new pressure sensor is one of the reasons why Cr^{3+} in high field material is still investigated using high pressure spectroscopy. One of the purposes of this paper is possible application of $SLG:Cr^{3+}$ crystal as a high pressure sensor.

Basic ambient pressure optical spectroscopy of $SLG:Cr^{3+}$ has been investigated in previous papers [7]−[8]. In this contribution the absorption, excitation and luminescence spectra of $SLG:Cr^{3+}$ at different temperatures and pressures are presented. The pressure shift of the luminescence related to $^2E\rightarrow{}^4A_2$ transition is estimated.

The SLG: Cr^{3+} crystal with chromium concentration of 0.1at% was grown by the Czochralski method. The details of the growing process have been described in [8].

For high pressure experiment the Merrill-Bassett type diamond anvil cell was used. A piece of sample $SrLaAlO_4:Cr^{3+}$ was contained in a hole of diameter 250μm drilled in a metal gasket, placed between two diamond anvils. Polydimethylosiloxane oil was used as a pressure transmitting medium, and ruby as a pressure sensor.

Luminescence was excited with Ar ion laser (Lexel 95L), dispersed by 1m monochromator (Spex 1702/04) with 600 gr./mm and detected by a photomultiplier tube (Hamamatsu R-913) using standard photon counting technique.

For temperature dependent experiments closed-cycle helium cryostat (APD HC4) was used. All luminescence spectra were corrected for the instrumental response.

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Absorption was measured on a Varian Cary 5E spectrometer.

The ambient pressure luminescence spectra of SLG:Cr^{3+} obtained at different temperatures are presented in Fig. 1(a).

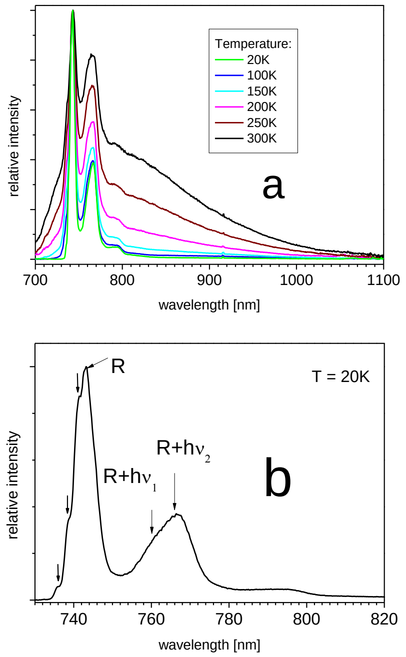

Fig. 1. (a) Ambient pressure luminescence spectra of SLG:Cr^{3+} obtained at different temperatures. (b) Sharp lines structure of the SLG:Cr^{3+} luminescence obtained at 20K.

One can notice that at 20K the emission spectrum consists of three sharp bands peaked at 743nm, 767nm and 792nm. At higher temperature an additional broad band appears, shifted to the red at a wavelength longer than 800nm.

The sharp line structure peaked at 743nm is related to $^2E \rightarrow {}^4A_2$ transition in the Cr^{3+}, whereas the other two bands are phonon repetitions of these structure. In Fig. 1(b) the details of the structure of the $^2E \rightarrow {}^4A_2$ transition at low temperature is presented. One notices that the emission band is in fact a superposition of four bands with maxima indicated by arrows. The weaker additional bands peak at wavelengths 736nm, 739nm and 741nm. This result shows that in fact the Cr^{3+} ions occupy four not equivalent sites in SLG. Actually, one expects inhomogeneous broadening of the $^2E \rightarrow {}^4A_2$ transition due to the random distribution of Sr^{2+} and La^{3+} ions in the lattice. The band peaked at 767nm has also the structure with a bump at 761nm. This structure can be attributed to two different phonon bands. We have labelled bands 761nm and 767nm by phonons by hν_1 and hν_2, respectively. An additional broad band in the red region extending to 1000nm is related to $^4T_2 \rightarrow {}^4A_2$ transition. This band is thermally activated since at ambient conditions $^4T_2$ state is already above the ^2E state.

In Fig. 2 the absorption and luminescence excitation spectra of SLG:Cr^{3+} crystal obtained at room temperature at ambient pressure are presented.

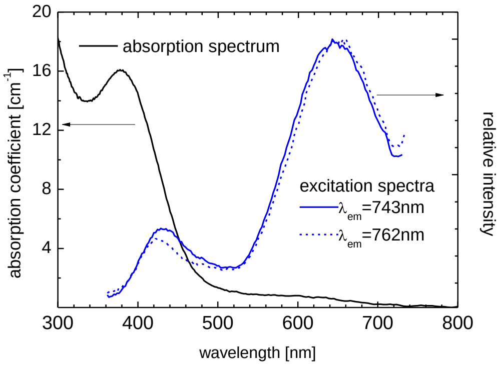

Fig. 2. Absorption (black curve) and luminescence excitation spectra of SLG:Cr^{3+} obtained at ambient pressure and ambient temperature. Emission spectra was monitored at 743nm (solid curve) and 762nm (dashed curve).

For obtaining the luminescence excitation spectra the luminescence was monitored at 743nm and 762nm. One notice that luminescence excitation spectra consist of two broad bands peaked at 649nm and 435nm, related to $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ in the Cr^{3+}, respectively. The structure of the absorption does not follow the luminescence excitation spectra. Only a weak bump for a wavelength shorter than 700nm, which overlaps the $^4A_2 \rightarrow {}^4T_2$ excitation band, is seen. The maximum of the absorption band peaked below 400nm can be related to charge transfer transition or SLG fundamental absorption.

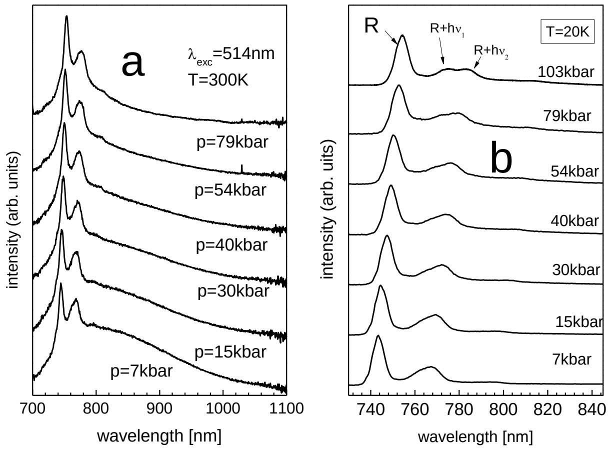

Fig. 3. (a) Luminescence spectra of SLG:Cr^{3+} obtained at different pressures at room temperature. (b) Luminescence spectra of SLG:Cr^{3+} obtained at different pressure at 20 K.

The luminescence spectra of the SLG:Cr^{3+} obtained at different pressures at room temperature and at 20K are presented in Figs. 3(a) and 3(b), respectively.

One notices that at room temperature the relative contribution of the $^4T_2 \rightarrow {}^4A_2$ transition decreases with increasing pressure. This effect is attributed to an increase of energy of the $^4T_2$ sate with respect to energy of the ^2E state with increasing pressure.

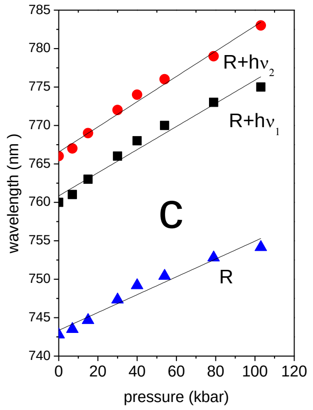

Fig. 3. (c) Energies of the zero-phonon line and phonon repetitions versus pressure (the lines represent the linear fits).

In Fig. 4 luminescence spectra obtained at 79kbar at different temperatures are presented.

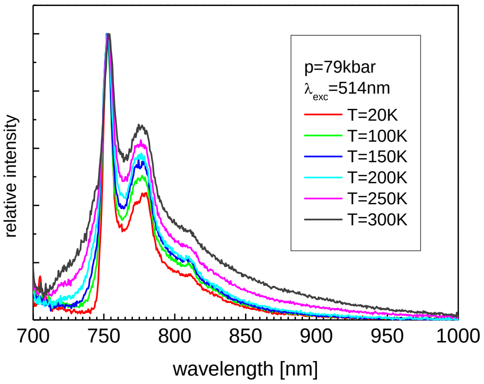

Fig. 4. Luminescence spectra of SLG:Cr^{3+} obtained at different temperatures under pressure 79kbar.

One can see that the spectrum weakly depends on temperature, which is related to the fact that at 79kbar the energy of the $^4T_2$ sate is much higher than the energy of the ^2E state and cannot be thermally occupied.

At 20K for all pressures only sharp line luminescence related to $^2E \rightarrow {}^4A_2$ transition is observed (see Fig. 3(b)). The resolution of the spectra does not allow us to recognize the structure of the $^2E \rightarrow {}^4A_2$ transition, but the structure of the phonon sideband is well resolved. The position of the maximum of the R-line, as well as phonon sidebands versus pressure are presented in Fig. 3(c). The dependence is almost linear in all cases.

Pressure shifts of the bands R-line at 743nm and phonon sidebands peaked at 761nm and 767nm were calculated resulting in 0.12±0.01nm/kbar, 0.15±0.01nm/kbar and 0.16±0.0 nm/kbar, respectively.

The pressure rate for lines representing phonon–replicas greater than the pressure rate for the zero–phonon line results from an increase in phonons energy with an increasing pressure.

In conclusions, the luminescence spectra of SLG:Cr^{3+} obtained at different pressures and temperatures were measured. It was shown that at ambient pressure and room temperature the spectrum consists of sharp lines emission peaked at 741nm, 761nm and 767nm related to $^2E \rightarrow {}^4A_2$ (R-lines) transition in the Cr^{3+} accompanied by a phonon sideband and broad band luminescence related to $^4T_2 \rightarrow {}^4A_2$ transition in the Cr^{3+}. Pressure causes an increase in the energy of the $^4T_2$ state and quenches the broad band $^4T_2 \rightarrow {}^4A_2$ luminescence. We have shown that Cr^{3+} occupies more than four different sites in LSG lattice,which is related to random distribution of Sr^{2+} and La^{3+} ions. We have estimated the pressure rate of the R-line emission and their phonon replicas R+hν_1 and R+hν_2. It has been shown that energies of phonons increase with pressure. All sharp R-lines and phonon repetitions seem to be too broad to be used to measure pressure with high accuracy.

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