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The effect of pressure on luminescence properties of Cr^{3+} ions in $LiSc(WO_4)_2$ crystals—Part II: Pressure- and temperature-dependent luminescence kinetics

M. Grinberg[a,*], J. Barzowska[a], Y.R. Shen[b], K.L. Bray[c], J. Hanuza[d,e], P.J. Dereń[d]

[a] *Institute of Experimental Physics, University of Gdańsk, Wita Stwosza 57, 80-952 Gdańsk, Poland*
[b] *High Pressure Science and Engineering Center and Department of Physics, University of Nevada, Las Vegas, Nevada 89154-4002, USA*
[c] *Department of Physics and Astronomy, University of Georgia, Athens, Georgia 30602-2451, USA*
[d] *Institute of Low Temperature and Structural Research, Polish Academy of Science, Wrocław, Poland*
[e] *Department of Bioorganic Chemistry, Faculty of Engineering and Economics, Academy of Economics, Wrocław, Poland*

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Abstract

Luminescence kinetics of the $LiSc(WO_4)_2$ crystals doped with trivalent chromium has been investigated by high-pressure spectroscopy in the pressure range from ambient to 227 kbar, at temperatures from 20 K to room. For pressure range146–181 kbar we observed that pressure induced the structural transformation where the broad band emission related to $^4T_2 \rightarrow {}^4A_2$ transition was gradually replaced by sharp R-lines emission, related to $^2E \rightarrow {}^4A_2$ transition. We have found that both the broad band and R-line luminescence decays obtained at different pressures and temperatures are non-exponential. Distribution of the R-line luminescence decay constants has been analyzed quantitatively in the context of inhomogeneous Cr^{3+} sites distribution.

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Keywords: Luminescence decays; Chromium; High pressure photoluminescence; Inhomogeneous broadening

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1. Introduction

Cr^{3+} dopant ions in low-field octahedrally coordinated substitutional sites are characterized by a broad band emission originating from a spin allowed $^4T_2 \rightarrow {}^4A_2$ transition, whose energy is proportional to the crystal field strength $10Dq$ [1]. The emission is strongly broadened by electron–phonon interactions and in disordered crystals and glasses is additionally inhomogeneously broadened by site-to-site crystal field variations. Disordered crystal, glass and ceramic

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*Corresponding author. Tel.: +48 58 55 29544; fax: +48 58 3413175.
E-mail address: fizmgr@julia.univ.gda.pl (M. Grinberg).

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materials are promising for technological applications as tunable solid-state lasers and active media for short pulses generation because of large spectral bandwidth. Thus, the investigation of the inhomogeneous broadening of Cr^{3+} luminescence is important from both fundamental and application perspective.

Since the energy of the $^4T_2$ state is strongly dependent on the crystal field strength $10Dq$, one observes a pressure-induced blue shift of the $^4T_2 \rightarrow ^4A_2$ emission band in low field Cr^{3+} system. On the other hand, the energy of the ^2E state is almost independent of $10Dq$ (one observes a small red shift related to nephelauxetic effect). Therefore, applying pressure to low-field materials, one can observe a $^4T_2$-^2E electronic crossover. In the disordered materials, this crossover takes place slowly and sequentially over the many sites present by sinning at lower pressures with the sites for which the ^2E-$^4T_2$ energy difference is the smallest and continuing at higher pressure with the sites for which the ^2E-$^4T_2$ energy difference is the greatest. As a direct benefit, one can use the effect of pressure-induced $^4T_2$-^2E crossover for analysis of crystal field strength inhomogeneous distribution in the disordered material. Recently, we have used high-pressure spectroscopy to investigate the inhomogeneous broadening of the $^4T_2 \rightarrow ^4A_2$ and $^2E \rightarrow ^4A_2$ luminescence in Cr^{3+}-doped $LiTaO_3$ [2], lanthanum lutetium gadolinium garnet [3] and CaO–Ga_3O_3–GeO_2 glasses [4,5]. In the preceding paper [6] we have observed pressure-induced $^4T_2$-^2E crossover in the Cr^{3+}-doped $LiSc(WO_4)_2$ crystal. A detailed analysis of the dependence of the ratio of the intensity of the R-line emission to the total luminescence intensity on pressure and temperature has provided us the inhomogeneous distribution of the crystal field strength in $LiSc(WO_4)_2$.

In this paper, we focus on the analysis of effect of inhomogeneous disorder of the $LiSc(WO_4)_2$ on the Cr^{3+} luminescence decay. Disorder of host lattice causes inhomogeneous broadening of both, the Cr^{3+} luminescence lineshape and the Cr^{3+} luminescence lifetime. In low-field materials the broad band $^4T_2 \rightarrow ^4A_2$ lifetime distribution is related to the site-to-site distribution of the odd parity crystal field, an effect that allows electric dipole transition at the $^4T_2 \rightarrow ^4A_2$ band and distribution of the height of the energy barrier for non-radiative processes that reduces the quantum efficiency of the system and diminishes the emission lifetime. In high-field materials the $^2E \rightarrow ^4A_2$, R-line luminescence lifetime distribution is related to the distribution of energetic separation between the $^4T_2$ and ^2E states.

2. Experiment

High pressure was generated by a modified Merrill–Bassett type diamond anvil cell (DAC). Details concerning pressure application are described in our preceding paper [6]. Below ~100 kbar and at temperatures between RT and 20 K, Cr^{3+} in $LiSc(WO_4)_2$ exhibited a broad $^4T_2 \rightarrow ^4A_2$ band, fast decaying emission. Above 116 kbar, Cr^{3+} luminescence consists of a broad $^4T_2 \rightarrow ^4A_2$ emission band and a sharp $^2E \rightarrow ^4A_2$ (R-lines) long living emission. Over 181 kbar the emission consists mainly of the R-lines. The details of the continuous-wave (static) Cr^{3+} luminescence properties are described in our preceding paper [6].

For purpose of luminescence kinetics measurements we have excited the sample with a wavelength of $\lambda = 532$ nm (the second harmonic of a pulsed Nd^{3+}:YAG laser, continuum NY-61). Luminescence was dispersed with a 1 m spectrometer (SPEX 1704/02). The luminescence decays were detected by a Hamamatsu photomultiplier (R31602) and recorded with a digital storage oscilloscope (Lecroy-LS140). The broad band $^4T_2 \rightarrow ^4A_2$ luminescence decays have been measured at ambient pressure, at 146 and 157 kbar at seven different temperatures (20, 50, 100, 150, 200, 250 K and RT). The emission wavelength has been monitored at the maximum of the band. Since the emission maximum shifts to higher energy with increasing pressure, the monitored wavelength was different at different pressure. Selected luminescence decays are presented in Fig. 1a–c. The distribution of the decay constants has been recovered according to the methods described in Appendix A. The histograms describing the distribution of the decay constants for each temperature are collected in Fig. 2a–c. Actually,