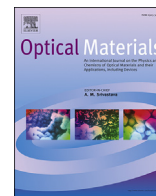




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Influence of charge transfer state on Eu^{3+} luminescence in LaAlO_3 , by high pressure spectroscopy

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ABSTRACT

The contribution presents spectroscopic characterization of LaAlO_3 doped with 0.5 mol % Eu^{3+} . We measured steady state luminescence, luminescence excitation spectra, as well as the time resolved spectra and luminescence kinetics. The experiments were performed at high hydrostatic pressure applied in diamond anvil cell (DAC) which was changed from ambient to 250 kbar. We found that for all pressures the emission from the $^5\text{D}_0$ and $^5\text{D}_1$ excited emitting state of Eu^{3+} was delayed in time after excitation pulse whilst emission from the $^5\text{D}_2$ appear immediately after excitation. At pressure above 12 kbar the strong magnification of the luminescence lines related to the transitions from the $^5\text{D}_3$ state which were very weak at ambient condition is observed. The emission decay of the $^5\text{D}_3$ luminescence become slower when pressure is increased. All these effects are attributed to pressure-induced increase of the energy of the ground electronic configuration $4f^6$ of the Eu^{2+} with respect to the valence band edge which results in the charge transfer state, and $^5\text{D}_3$ level crossing.

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1. Introduction

Control of the electron transfer from the dopant cations to the conduction band and from the valence band to the dopant cations in inorganic compounds is crucial for luminescence materials performance, since such transitions can be responsible for the luminescence quenching. Specifically it is well known that ionization processes which take place in the excited 5d states of Ce^{3+} ions can quench the Ce^{3+} luminescence in many materials, [1–3]. The effect of the Eu^{3+} luminescence quenching caused by relaxation to a charge transfer state has been also investigated since the seventies of the twentieth century [4–6] up to the present time [7,8]. Awareness is growing that the energy of the localized states related to luminescence centers, specifically the Ln^{3+} and Ln^{2+} , with respect delocalized states of conduction band and valence band can strongly affect the efficiency luminescence of excited lanthanide ions, [9,10].

The unique technique that allows to determine the exact position if the localized states of Ln^{3+} ions in the bandgap is high

pressure spectroscopy. High hydrostatic pressure compress the crystal and diminishes the Ln ion-the ligands bound lengths. As the result the energies of all localized states belonging to the $4f^n$ electronic configuration increases with pressure with respect to the conduction and valence band edges, by almost the same amount [11]. On the other hand pressure almost does not influence the energies of the internal f-f transitions. As the result pressure induced crossing of the excited emitting states with the conduction band can be observed and can result in the luminescence quenching. From such experiment one obtains the exact energetic distance between the ground state of Ln ion and conduction band for given pressure and when pressure shift is known the location of the ground state at ambient conditions can be calculated. This method has been used to estimate the location of the ground states of Tb^{3+} and Pr^{3+} with respect to conduction band in many materials [12–21].

LaAlO_3 doped with Eu^{3+} has been investigated first by Blasse et al. [4] where three types of radiationless transitions, which control the decay of the Eu^{3+} luminescence has been discussed. However the first whole $\text{LaAlO}_3:\text{Eu}^{3+}$ spectra were published by Dereń and Krupa in 2003 [22]. The work was focused on LaAlO_3 monocrystal and first report on spectroscopic properties of this perovskite doped with europium in the nanoscale was published by

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Hreniak et al. [23].

In this article, the pressure-dependent structure and optical behavior of $\text{LaAlO}_3:\text{Eu}^{3+}$ are investigated in details using Eu^{3+} luminescence, luminescence excitation and Raman scattering methods. Specifically the analysis of the pressure dependence of the luminescence and luminescence excitation spectra allowed to determine the energy of the Eu^{2+} ground state with respect to the conduction and valence band of the host. It is shown that pressure recover the luminescence originated from the highest excited emitting state of Eu^{3+} the $^5\text{D}_3$ state, which is almost invisible at ambient conditions. Actually the emission from the $^5\text{D}_3$ state has been reported in the papers [22,23] as a weak luminescence lines in the spectral region below 450 nm decaying in the time shorter than single μs , which is very short in comparison to the decay time of $^5\text{D}_2$, luminescence (tenths μs), $^5\text{D}_1$ luminescence (hundred μs) and decay of the $^5\text{D}_0$, luminescence (equal to single ms). In this paper it is shown that the intensity of the luminescence originated from the $^5\text{D}_3$ state increases significantly, which is accompanied with elongation of the $^5\text{D}_3$ luminescence decay, with increasing pressure.

2. Experimental

The samples were prepared according to the method described in our previous work [23]. For present measurements the LaAlO_3 samples doped with 0.5 at % of Eu^{3+} (where Eu^{3+} replace with La^{3+} at D_3 site symmetry) and annealed at 1100 °C was selected. The average nanocrystalites size was 50 nm.

Luminescence excitation and emission spectra at ambient pressure were measured using a steady-state Horiba Jobin Yvon spectrofluorometer model FluoroMax-4P TCSPC equipped with a 150 W xenon lamp as the excitation source and a R928 Hamamatsu photomultiplier as the detector.

Luminescence excitation spectra at high pressure were acquired using a system consisting of a 450 W Xe lamp two monochromators SPM2 (one in the excitation and one in the detection line) and two photomultipliers (the first for the luminescence and the second for reference signal detection).

The experimental setup for luminescence kinetics and time-resolved spectroscopy was described in detail in Ref. [24]. The excitation part consists of a PL 2143 A/SS laser and a PG 401/SH parametric optical generator that provides 30 ps laser pulses with a frequency of 10 Hz. The luminescence was dispersed with a Bruker Optics 2501S spectrograph and recorded by a C4334-01 Hamamatsu Streak Camera. Time-resolved luminescence spectra in different pressures were collected by integration of the streak camera images over the time intervals, whereas luminescence decays were collected by integration of the streak camera images over the wavelength intervals.

The Raman spectra in different pressures were obtained by integrated confocal micro-Raman system containing LabRam Aramis (Horiba Jobin Yvon) 460 mm spectrometer coupled to a Peltier-cooled CCD detector, an Olympus optical microscope and He-Ne laser with wavelength 633 nm as the excitation source.

High hydrostatic pressure was applied in a Merrill Bassett type [25] diamond anvil cell (DAC). Poly(dimethylsiloxane) oil was used as the pressure-transmitting medium and the pressure was measured by the shift of the R_1 luminescence line of ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$).

3. Results

3.1. Pressure dependence of the luminescence and luminescence excitation spectra

Luminescence excitation and emission spectra of $\text{LaAlO}_3:\text{Eu}^{3+}$

are presented in Fig. 1a and b, respectively. The luminescence excitation spectrum monitored at 593 nm (Fig 1a) is dominated by the broad band with maximum approximately at 314 nm ($31\,850\text{ cm}^{-1}$), attributed to charge transfer transition (CTT) from the O^{2-} to Eu^{3+} ions. In this paper we consider the CTT as a transition from the valence band to the localized Eu^{2+} state, more precisely, as it will be explained later, the creation of the europium trapped exciton (EuTE). The EuTE is considered as a system of Eu^{2+} , with a hole attracted by Coulomb potential of negatively charged Eu^{2+} (the charge is negative since Eu^{2+} replaces the La^{3+}) bounded at the state energy over the valence band, [11]. Additionally the weak sharp lines in the spectral region 350–550 nm associated with transitions from the ground state $^7\text{F}_0$ to the $^5\text{L}_6$ and $^5\text{D}_j$ excited states of Eu^{3+} ions are observed. For better consideration we shown this spectral region with magnification 5 times In Fig. 1a this spectrum is represented by red curve labeled 5x. The room-temperature luminescence spectrum of $\text{LaAlO}_3:\text{Eu}^{3+}$ excited with 315 nm is presented in Fig. 1b. The spectrum consists of two strong lines with maxima at 593 nm and at 618 nm corresponding to transitions from the $^5\text{D}_0$ to $^7\text{F}_1$ and $^7\text{F}_2$ states, respectively. The several weak peaks in the spectral region from 460 to 560 nm are attributed to transitions from the $^5\text{D}_1$ and $^5\text{D}_2$ to the $^7\text{F}_j$ states and the peaks in the spectral range 640–720 nm are related to the $^5\text{D}_0 \rightarrow ^7\text{F}_3, ^7\text{F}_4$ transitions. For better consideration we repeat this part of spectrum and presented them by red curve labeled $\times 5$ in Fig. 1b. Detailed assignment of the lines is presented in Fig. 1a and b. One notices that in this experiment no luminescence related to the transitions from the highest excited state $^5\text{D}_3$ are observed due to limited sensitivity of our apparatus.

The spectroscopic data allow to reconstruct of the energetic structure of the system that and consider the excitation, non-radiative relaxation in the excited states and the luminescence processes in details. Deduced energetic diagram is presented in Fig. 2a. The location of the ground state of Eu^{2+} ion with respect to the top of the valence can be estimated directly since it is related to the energy of CTT. The differences between the ground state and excited states of $4f^6$ electronic configuration can also be unambiguously obtained from the Eu^{3+} luminescence spectrum. On the other hand the location of the ground state of the Eu^{3+} with respect to the valence band cannot be measured directly in our experiment. We located the $^7\text{F}_6$ ground state of Eu^{3+} at about 3 eV below the top of the valence band. This location is not exact but we are sure that

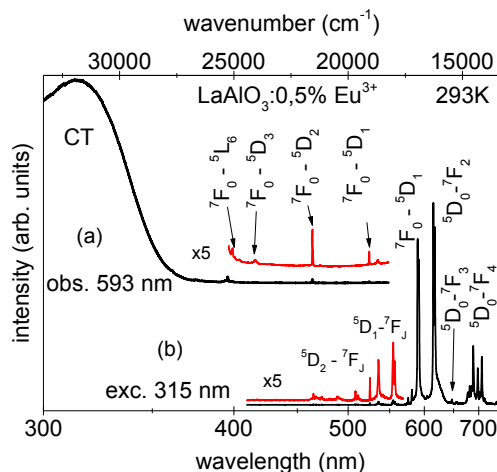


Fig. 1. (a) Excitation spectra of the $\text{LaAlO}_3:\text{Eu}^{3+}$ emission monitored at 593 nm related the $\text{Eu}^{3+} ^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. (b) Emission spectra of the $\text{LaAlO}_3:\text{Eu}^{3+}$ excited at 315 nm. All spectra were obtained at room temperature.

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