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Luminescent properties of ytterbium-doped ternary lanthanum chloride

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ABSTRACT

Studies of the absorption and temperature dependence of photoluminescence spectra and luminescence decay times of the intra-shell *f*–*f* transitions ($^2F_{5/2} \leftrightarrow {}^2F_{7/2}$) of Yb^{3+} ions in $K_2LaCl_5:Yb^{3+}$ powders with 5, 10, 15 and 25% of ytterbium are presented. The spectroscopic properties of the powders with different ytterbium content are compared. Experiments were performed at the temperatures from 25 to 300 K. The strong emission around 982 nm has been observed under direct excitation of the luminescence center with 960 nm line of continuous wave Ti:sapphire laser pumped by Ar-ion laser. The temperature quenching effect of the luminescence was rather week, especially in the samples with higher concentration of ytterbium (15 and 25%). Additionally the probability of the *f*–*f* radiative transitions of the Yb^{3+} ions in these powders was almost temperature independent for more heavily doped samples (with 15 and 25% of Yb) and only weakly temperature dependent for less doped samples (with 5 and 10% of Yb). These results reveal high thermal stability of the optical properties of the examined powders.

1. Introduction

In the framework of investigations of the optical properties of rare earth halides K_2MX_5 (M = rare earth; X = Cl, Br, I) doped with various rare earth ions, the ternary lanthanum chloride doped with ytterbium ion has been synthesized and analyzed. Yb^{3+} ion spectroscopy is nowadays of considerable interest because of its potential laser emission around 1000 nm [1]. Due to the development of InGaAs laser diodes emitting near 980 nm, where the Yb^{3+} has a strong absorption peak, this ion is now the most promising for use as a non-Nd lasing center in the same range of emission wavelength [2–4].

The advantageous optical properties of chloride materials (high transparency, low phonon energy, high ionicity) and possibility of high doping with rare earth ions make them very promising materials for potential applications from phosphors to lasers [5]. However these compounds are usually hygroscopic and require precautions in handling, which limits attention paid to this material. Authors mostly focus on the studies of scintillation and luminescence properties of cerium-doped ternary lanthanum chloride [6–8]. Besides the detailed studies of excited state dynamics in the praseodymium and praseodymium co-doped by ytterbium ion ternary halides of $K_2(La)X_5$ ($X = Cl^-, Br^-, I^-$) type were reported by Cybińska et al. [9] and Legendziewicz et al. [10]. The comparison of spectroscopic properties of ytterbium-doped ternary halides of $K_2(La,Ln)X_5$ ($X = Cl^-, Br^-$) type and ytterbium-doped double phosphates of formula $A_3Lu(PO_4)_2$ (A = an alkali metal) were presented in the paper of Legendziewicz et al. [5].

The goal of the present work is focused mainly on the investigation of the luminescence efficiency and thermal stability of the $K_2LaCl_5:Yb^{3+}$ powders depending on the ytterbium concentration. The comparative studies of the absorption, luminescence and luminescence decay times of the intra-shell *f*–*f* transitions of Yb^{3+} ions in $K_2LaCl_5:Yb^{3+}$ powders with 5, 10, 15 and 25% of ytterbium at temperatures from 25 to 300 K are presented.

2. Samples and experimental techniques

The K_2LnCl_5 compounds preparation route requires using of pure and completely water free $LnCl_3$, thus the first step of synthesis was preparation anhydrous lanthanide chloride following the ammonium halide route [11]. The starting materials for the synthesis were commercial available M_2O_3, which was dissolved in HCl concentrated acid with the excess of ammonium chloride, to prevent the oxychlorides impurities. The acid was evaporated and the $(NH_4)_2[MCl_5]$ was formed. That salt was next decomposed and pure $LnCl_3$ was obtained. The mixed $K_2(La,Yb)Cl_5$ samples were synthesized in a quartz ampoule from a melt by using the Bridgman technique according to the procedure described earlier [12,13]. The melt was obtained by heating the appropriate amounts of the starting materials (KCl, $LaCl_3$ and $YbCl_3$) which were purified prior to the reaction by sublimation in a tantalum ampoule. Cooling of the melt from the starting temperature (900 °C) was carried out in two steps: first to 700 °C with a rate of 1°/h and then to the room temperature

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with a rate of 5°/h. All the samples used in these studies are moisture-sensitive, so they must be handled under anhydrous conditions.

The ternary lanthanum chloride, isotypic with K_2PrCl_5, crystallizes in orthorombic crystal structure with hexagonal arrangement of chains of edge-connected polyhedra ($LaCl_7$). The polyhedra may be viewed as distorted mono-capped trigonal prisms with the La^{3+} ion in the center [6,13]. The ytterbium dopant replaces the trivalent lanthanum cation in its crystal site, so the Yb^{3+} ions are coordinated by 7 Cl^- ions. The local symmetry of Yb^{3+} is C_S. The ionic radius of Yb^{3+} is equal to 0.925 Å for coordination number (CN) 7 and ionic radius of the La^{3+} replaced by ytterbium is equal to 1.1 Å [14].

For absorption spectra measurements the samples were squeezed into the form of parallel flat tablets. The optical absorption spectra were obtained from the scattered transmittance, measured with the use of the integrating sphere on a Cary 5000 UV–vis–NIR spectrophotometer. Continuous wave emission spectra were obtained using an Ar-ion laser pumped Ti:sapphire laser as the excitation source. The excitation wavelength was equal to 960 nm. For temperature measurements the samples were placed inside a closed circle helium refrigerator. The photoluminescence spectra were measured using a Horiba Jobin-Yvon FHR 1000 monochromator and a cooled linear InGaAs array detector.

The decay kinetics of the luminescence was measured with use of an SR430 Multichannel Scaler. A large number of decays were collected in order to obtain good signal-to-noise ratio. The exciting laser beam was chopped by a mechanical chopper with a transient time below 30 μs. The decay times of luminescence were obtained by fitting the decay kinetics with single-exponential dependencies.

3. Experimental results and their interpretation

3.1. Absorption spectra of Yb^{3+} ions in K_2LaCl_5:Yb^{3+} powders with 5 and 25% of ytterbium

The ternary lanthanum chloride is the isolating material and its energy gap is wide enough to contain the fundamental and excited energy levels of RE luminescent centers [5,6,9]. The typical transition energies between $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state levels of Yb^{3+} ions occur around 1.24 eV (1000 nm). In a crystal field of low C_S symmetry, as a consequence of the Stark effect, the $^2F_{7/2}$ level splits into four, and $^2F_{5/2}$ level into three Kramers doublets [15].

In principle, the electric-dipole transitions between the $^2F_{7/2}$ and $^2F_{5/2}$ states of Yb^{3+} ion are parity-forbidden and magnetic-dipole transitions should play an important role in the de-excitation of the excited $^2F_{5/2}$ state. However because of some admixture of an opposite parity electronic configuration to the pure 4*f* state as a result of the interaction of the dopant ion with a non-centrosymmetric crystal field the electric-dipole transitions happen to be dominating.

The room-temperature absorption spectra of K_2LaCl_5:Yb^{3+} powders with 5 and 25% of ytterbium in the IR–vis–UV spectral range are presented in Fig. 1. The available spectral range on the UV side reached 6.2 eV (about 50,000 cm^{-1}), which is still far from the absorption edge of the host. The absorption edges observed at about 300–320 nm originate from charge transfer (CT) absorption of ytterbium dopant, which is in accordance with the CT emission reported in the Ref. [5].

The normalized spectra in the region of the Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition are shown in the inset of Fig. 1. The main band in the absorption spectra of both samples consists of three electronic Stark components of the $^2F_{5/2}$ excited level situated at 9982, 10,250 and 10,454 cm^{-1} for the sample with 5% of ytterbium and at 9946, 10,210 and 10,480 cm^{-1} for the sample with 25% of ytterbium, with the total crystal field (CF) splitting of 472 cm^{-1} and 534 cm^{-1}, respectively. The increase of the CF splitting with increasing ytterbium content is not surprising taking into account the fact, that the ionic radius of Yb^{3+} is smaller than the ionic radius of La^{3+}, so the larger content of ytterbium can cause the decrease of the lattice constant and consequently – increase of the crystal field strength.

The absorption lines are relatively broad, which can be caused by the applied measurement technique with the use of the integrating sphere. This technique allows for obtaining absorption spectra of the powdered samples. The other reasons of the line broadening can be the existence of strong vibronic coupling often observed in Yb^{3+}-doped crystals and some disordering of the crystal structure of the powder [5,16].

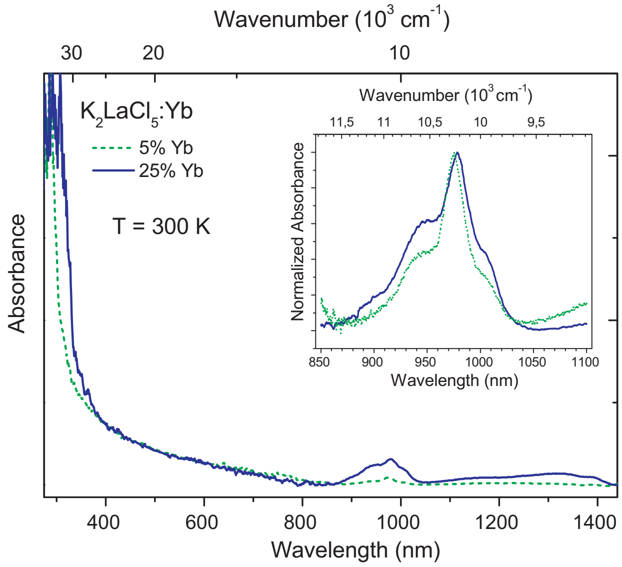

Fig. 1. Room-temperature absorption spectra of K_2LaCl_5:Yb^{3+} powders with 5 and 25% of ytterbium. In the inset: normalized spectra expanded in the region of the Yb^{3+} absorption.

3.2. Photoluminescence spectra of Yb^{3+} ions in K_2LaCl_5:Yb^{3+} powders

Fig. 2 shows a comparison of room-temperature absorption and luminescence spectra of Yb^{3+} in K_2LaCl_5:Yb^{3+} powders with

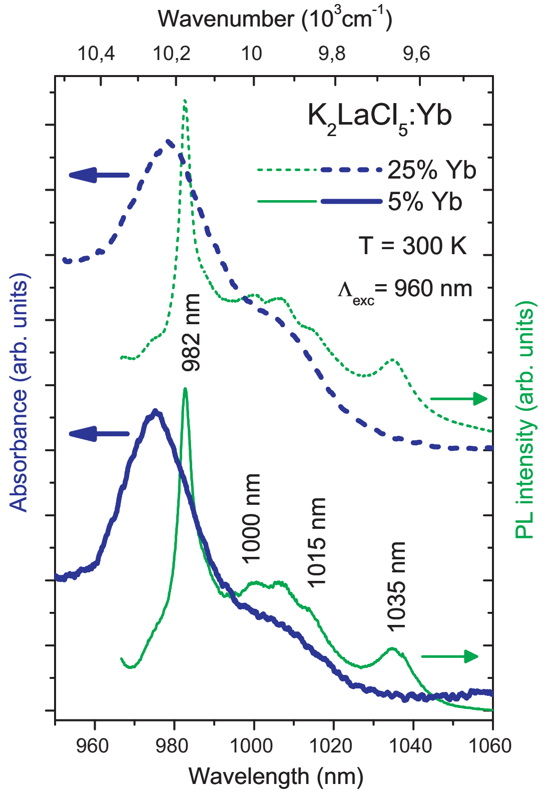

Fig. 2. Normalized absorption (thick line) and photoluminescence spectra (thin line) of the 5% (solid line) and 25% (dashed line) Yb^{3+}:K_2LaCl_5 powder at room temperature.

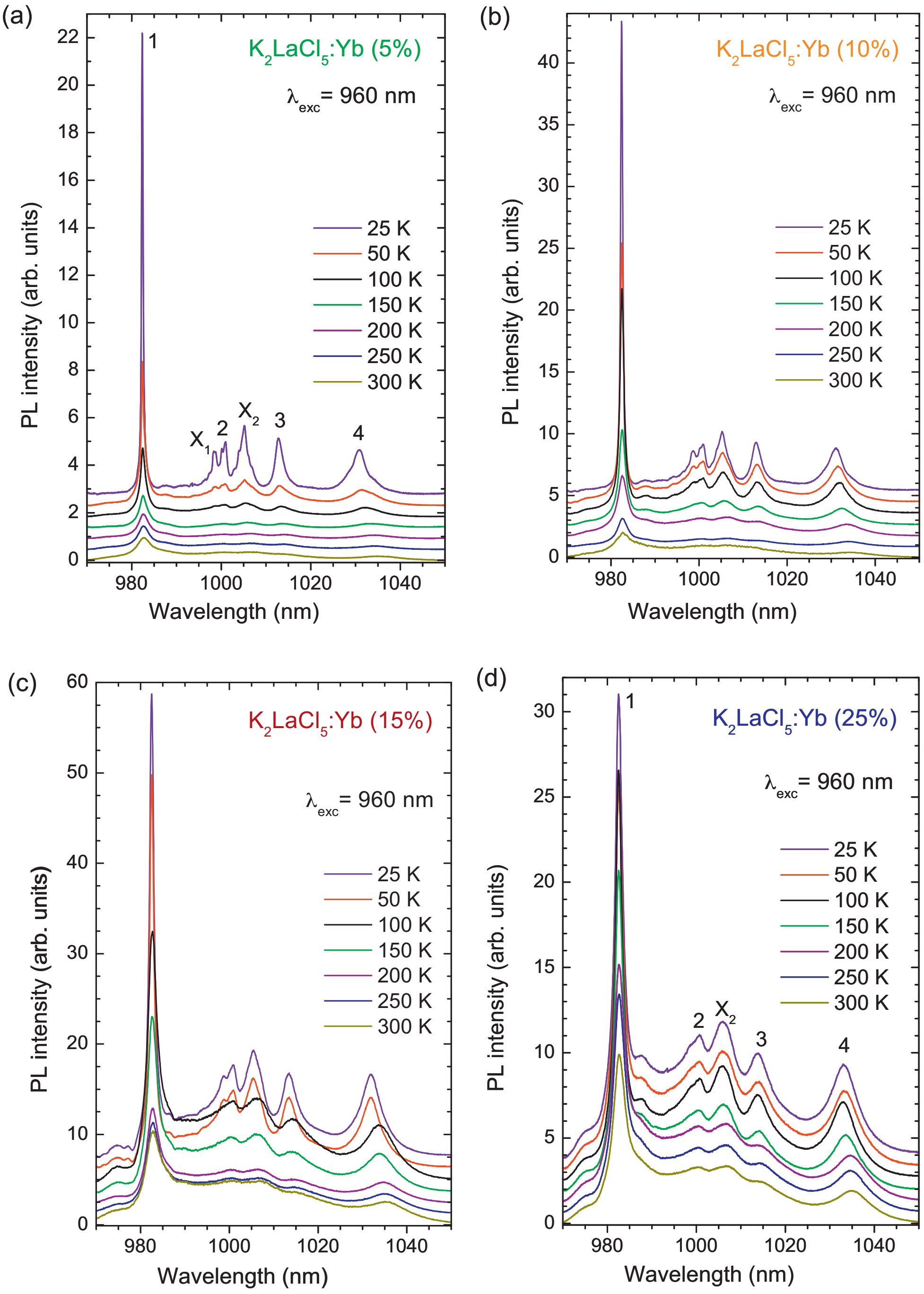

Fig. 3. Photoluminescence spectra of K_2LaCl_5:Yb^{3+} powders with (a) 5, (b) 10, (c) 15 and (d) 25% of ytterbium at temperatures from 25 to 300 K, excited with the 960 nm line of Ti:sapphire laser. The spectra are shifted along the vertical axis for clarity.

5 and 25% of ytterbium. The presence of satellites of several lines is the most probably associated with phonon-assisted emission. The electronic transition wavelength marked in the graph, have been assigned on the basis of the Ref. [5], where the detailed analysis of the emission, absorption and Raman spectra of 5% Yb^{3+}:K_2LaCl_5 single crystal has been performed. Both absorption and luminescence spectra are consistent with those reported in the Ref. [5], except the larger lines broadening.

The temperature dependence of the photoluminescence (PL) spectra of Yb^{3+} in K_2LaCl_5:Yb^{3+} powders with 5, 10, 15 and 25% of ytterbium are presented in Fig. 3. The power of the 960 nm line of Ti:sapphire laser was maintained at approximately the same level during the whole measurements. The temperature dependence of the integrated PL intensity is presented in Fig. 4. It is clearly visible, that the best emission efficiency is achieved for the sample containing 15% of ytterbium. The thermal stability, although sufficiently good for all the examined samples, is much better for samples with higher ytterbium concentration.

The spectral positions of the major luminescence lines and the total CF splitting of the $^2F_{7/2}$ ground level of all examined samples at temperature 25 K are collected in Table 1. As in the case of absorption, the increase of the CF splitting with increasing ytterbium content is observed, confirming the conclusion, that the larger ytterbium content causes the increase of the crystal field strength.

Table 1
Spectral positions and assignment of the major luminescence lines of Yb^{3+} in K_2LaCl_5 powders at temperature 25 K.

Line label (see Fig. 3)	Assignment	Yb^{3+} concentration (%)			
		5	10	15	25
		Line spectral position (cm^{-1})			
1	$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition	10,180	10,179	10,178	10,178
X_1	vibrational sideband	10,015	10,014	10,012	10,012
2	$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition	9992	9992	9992	9992
X_2	vibrational sideband	9949	9948	9946	9943
3	$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition	9874	9872	9868	9864
4	$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition	9701	9698	9690	9680
CF splitting of $^2F_{7/2}$ level (cm^{-1})		479	481	488	516

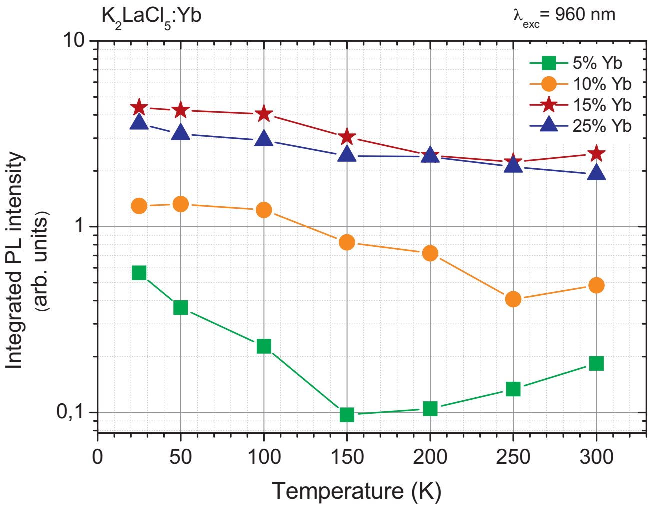

Fig. 4. Temperature dependence of the integrated PL intensity of the intra-shell *f–f* transitions of Yb^{3+} ions in K_2LaCl_5:Yb powders with 5, 10, 15 and 25% of ytterbium.

3.3. *Temperature dependence of the decay kinetics of luminescence of Yb^{3+} ions in K_2LaCl_5:Yb^{3+} powders*

Decay kinetics measurements as a function of temperature were performed for two the best resolved luminescence lines, peaked at about 982 nm (10,180 cm^{-1}) and 1031 nm (9700 cm^{-1}). The examples of decay kinetics of 982 nm luminescence lines of the K_2LaCl_5 powders at temperatures 25 K and 300 K are presented in Fig. 5. The kinetics for samples containing 5% and 10% of Yb are single exponential at low temperatures and became strongly non-exponential at elevated temperatures. Temperature dependencies of the decay times are presented in Fig. 6. In case of non-exponential kinetics the decay times were determined from the end part of the kinetics. The measured values of the decay times are consistent with typically observed decay times of $^2F_{5/2} \rightarrow {}^2F_{7/2}$ intra-4*f*-shell emission of Yb^{3+} in ionic materials, which are in the 500–2500 μs range [17–22]. The luminescence lifetimes decrease almost two times between 25 K and 300 K, i.e. from 850–900 μs to 440–470 μs. The temperature dependence of the decay times is presented in Fig. 6.

The temperature decrease of the luminescence decay time is much weaker for the sample containing 15% of Yb, whereas for the sample with 25% of Yb the decay time is almost temperature independent and decreases from about 705 μs at 25 K to 640 μs at room temperature. The observed temperature stability of the decay kinetics in the samples with higher ytterbium concentration is in good correspondence with the temperature stability of integrated luminescence intensity (see Figs. 4 and 6). In addition, the decay kinetics for these samples, presented in Fig. 5b are single exponential at each examined temperature.

The non-exponential decay kinetics observed at higher temperatures for less doped crystals accompanied by a decrease of the decay times with temperature (calculated from the end part of the decay kinetics) testify that the excitation energy transfer processes to some kind of the energy traps, which non-radiatively quench the luminescence are present in those crystals at these temperatures. The non-exponentiality of the decay kinetics is a fingerprint of such processes, which are the most probably of Forster–Dexter type [23,24]. Almost temperature independent decay time values observed for 25%Yb^{3+}:K_2LaCl_5, its purely exponential character in the whole examined temperature range, and faster decay time than recorded for less doped samples at low temperatures can be connected with so called fast diffusion [25] or diffusion-limited energy migration regimes, described for example, in Ref. [26] and [27]. A very weak temperature dependence of the decay times for this

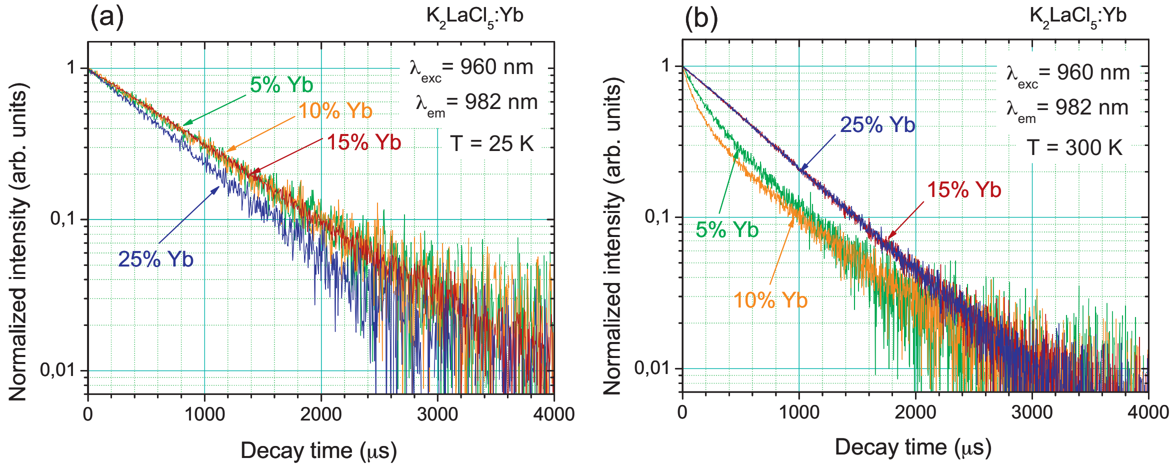

Fig. 5. The decay curves of 982 nm luminescence line measured in K_2LaCl_5:Yb powders with 5, 10, 15 and 25% of ytterbium, at temperatures (a) 25 K and (b) 300 K.

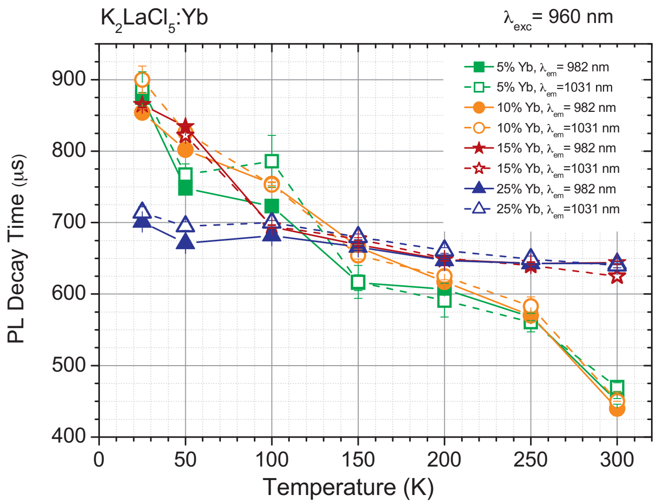

Fig. 6. Temperature dependencies of the decay kinetics of luminescence of Yb^{3+} ions in K_2LaCl_5:Yb powders with 5, 10, 15 and 25% of ytterbium.

sample may also testify about the some kind of bottleneck in the energy transfer to the quenching centers due to the very large content of the Yb^{3+} ions, which serve here as the system for the excitation energy migration. Generally, it is a process of the concentration quenching [1], very often observed in highly concentrated materials. The quantitative analysis of such processes is beyond the scope of this paper.

4. Summary and conclusions

A study of the influence of temperature on the radiative intra-shell *f*–*f* transitions ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) of Yb^{3+} ions in ternary lanthanum chloride powders hosts has been presented. The strong emission around 982 nm has been observed under direct excitation of the luminescence center with continuous wave 960 nm line of Ti:sapphire laser pumped by Ar-ion laser. The temperature quenching effect of the luminescence was rather week, especially in the samples with higher concentration of ytterbium (15 and 25%). Additionally the probability of the *f*–*f* radiative transitions of Yb^{3+} ions in these samples was almost temperature independent for more heavily doped samples (with 15 and 25% of Yb) and only weakly temperature dependent for less doped samples (with 5 and 10% of Yb).

These results confirm very good optical properties of ytterbium-doped ternary lanthanum chloride from the point of view of its potential applications.

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