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Temperature dependence of the charge transfer and f–f luminescence of Yb³⁺ in garnets and YAP

I Kamenskikh^{1,2,4}, C Dujardin¹, N Garnier¹, N Guerassimova²,
G Ledoux¹, V Mikhailin², C Pedrini¹, A Petrosyan³ and A Vasil'ev²

¹ Laboratoire de Physico-Chimie des Matériaux Luminescents, UMR 5620 CNRS and Université Lyon 1, 69622 Villeurbanne Cedex, France

² Physics Department, M V Lomonosov Moscow State University, Moscow 119992, Russia

³ Laboratory of Crystal Growth of Luminescent Materials, Institute for Physical Research, 378410 Ashtarak-2, Armenia

E-mail: iak@opts.phys.msu.ru

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Abstract

For single crystals of YAG–15 mol% Yb, LuAG–15 mol% Yb and YAP–8 mol% Yb the temperature dependence of the charge-transfer (CT) and f–f luminescence of Yb³⁺ excited in the CT absorption band in the temperature range 7–300 K has been studied. Simulation of the experimental data taking into consideration three processes, photoionization of the CT state and radiative and non-radiative energy transfer to the 4f levels, has demonstrated that for adequate description of the relaxation of the CT state it is essential to get information on the temperature dependence of the direct excitation efficiency of the f–f luminescence as well as to study the role of intrinsic luminescence in the energy transfer to ytterbium ions. Excitation spectra of the CT and IR luminescence in the energy region 4–20 eV at RT and 10 K are presented and discussed.

1. Introduction

Charge transfer (CT) luminescence of ytterbium doped compounds, which was observed for the first time in 1978 by Nakazawa (1978), demonstrates properties attractive for scintillator applications (Van Pieterse *et al* 2000, Guerassimova *et al* 2001a, Bressi *et al* 2001, Yoshikawa *et al* 2002). These properties are fast luminescence with characteristic decay time of the order of a few to tens of nanoseconds with a small contribution of a slow component and in the case of oxide compounds emission wavelength in the UV–visible region (from 300 to 700 nm) convenient for detection. However, to make competitive scintillators of these compounds the

⁴ Address for correspondence: Physics Department, M V Lomonosov Moscow State University, Moscow 119992, Russia.

yield of the CT luminescence at RT (for typical values see, e.g., table 1 in Guerassimova *et al* (2002)) needs to be improved. The aim of the present paper was to investigate the limitations (if any) imposed on the yield of the CT luminescence in ytterbium doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) and YAlO_3 (YAP) crystals by the energy transfer to the IR luminescence originating from ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transitions between the Stark split levels of Yb^{3+} and through this study to acquire additional information on the mechanisms of energy transfer to the CT state and its relaxation channels.

2. Experimental details

The single crystals of YAG–Yb, LuAG–Yb and YAP–Yb were grown by the Bridgman technique using molybdenum crucibles in the Institute for Physical Research, Armenia. High-purity (4N) yttrium and rare-earth oxides and vacuum melted crystalline alumina were used. YAP–Yb single phase and colourless crystals were grown from melts of stoichiometric composition. The results presented here refer to YAG and LuAG with 15 mol% of Yb and YAP with 8% of Yb. Such a high dopant concentration was chosen for neutrino detection (Raghavan 1997).

Measurements of the luminescence spectra and quantum yield in the excitation region 4–25 eV and of fluorescence decay kinetics in the nanosecond range were performed using synchrotron radiation at the SUPERLUMI station of the Doris positron storage ring, HASYLAB, DESY, Hamburg (Zimmerer 1991). The samples were mounted on the cold finger of a LHeT flow type cryostat; the temperature range was 7–300 K. The luminescence spectra were detected using an SP-308 (ARC SpectraPro-300i) monochromator operating either as a monochromator or a spectrograph. In the former case a Hamamatsu Photonics R6358 PMT was used as a detector; in the latter case a liquid-nitrogen-cooled CCD was applied. Time-resolved luminescence and excitation spectra as well as luminescence kinetics were measured using the PMT; for the luminescence measurements in the IR region CCD detector was applied.

Direct excitation of the Yb^{3+} fluorescence in the IR was performed with a frequency doubled Nd:YAG laser (10 ns, 10 Hz) pumping a Quantel two-amplifier-stage dye laser containing a mixture of DCM and LD698 dyes and followed by a hydrogen Raman cell shifter to generate a beam in the 920–960 nm range. The crystal was mounted in the LHT cryostat. Infrared luminescence spectra were recorded using a Jobin Yvon HRS1 monochromator with a 600 grooves mm^{-1} grating blazed at 1 μm .

3. Results and discussion

Figure 1 shows the luminescence spectra of three compounds, and a schematic configurational coordinate diagram illustrating the CT process in ytterbium-doped compounds is presented. The CT process is often described as the transfer of an electron from the ligands to the ytterbium ion with the reorganization of the charge density distribution around the metal ion (see e.g. Van Pieterse *et al* 2000). The transition from the CT state to two 4f levels of the Yb^{3+} ion separated by ~ 1.2 eV forms two broad luminescence bands. In addition to two CT bands, several narrow lines in the IR region originating from ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transitions between Stark split levels of the Yb^{3+} ion are observed. Under excitation in the CT absorption band the 4f levels of Yb^{3+} can be populated either by non-radiative relaxation of the CT state via the cross-over point of the corresponding parabola or by radiative transition from the CT state. Thus analysis of the temperature dependence of two types of luminescence can provide information on the relaxation of the CT state. Such analysis for $\text{Y}_2\text{O}_2\text{S}$ doped with 1 mol% of Yb was

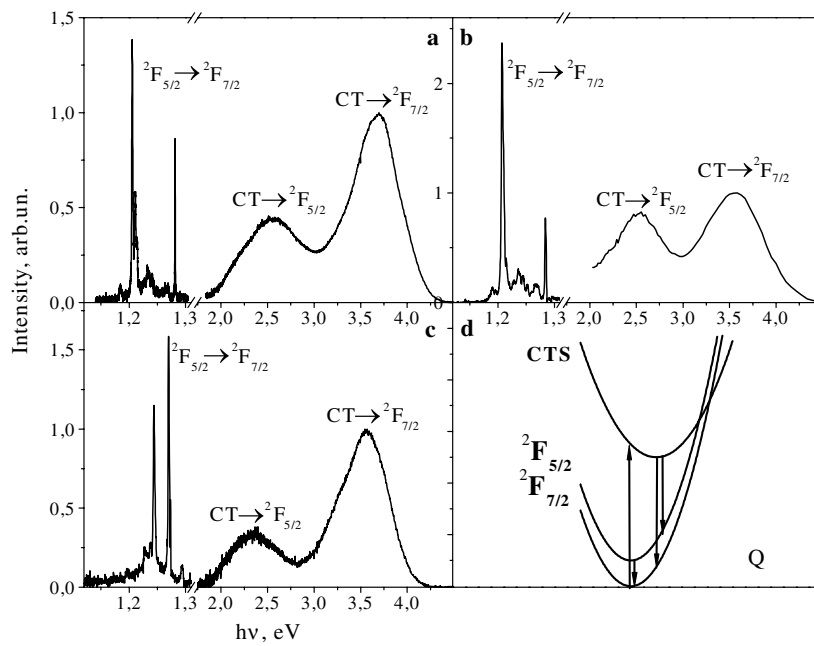


Figure 1. Luminescence spectra of YAG–Yb (15%) (a), LuAG–Yb (15%) (b) and YAP–Yb (8%) (c) excited in the charge transfer band; (d) configurational coordinate diagram for the CT process in Yb³⁺ in complex oxide matrices.

performed by Nakazawa (1979) in the 90–300 K range. We made similar measurements for higher ytterbium concentration in some other crystals in the temperature range 7–300 K. The temperature dependence of the CT and f–f luminescence in YAG–Yb is presented in figure 2 (the one for LuAG–Yb was very similar). Experimental points for CT luminescence temperature dependence were obtained both by the integration of the luminescence spectra and by the measurements of the decay time in the maximum of the first CT luminescence band (it was checked that the decay time and the excitation spectra were similar for the two bands; see, e.g. Guerassimova *et al* 2002 or Kamenskikh *et al* 2003). Both methods give the same result. For the IR emission the spectra have been integrated over the whole range of ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions (940–1060 nm). It can be seen that above 90 K the two curves are qualitatively similar to those obtained by Nakazawa (1979). Several authors observed pronounced quenching of ytterbium CT luminescence with temperature in different matrices (Nakazawa 1979, Van Pieterse *et al* 2000, Guerassimova *et al* 2001a, 2001b). In Van Pieterse *et al* (2000) two mechanisms that could account for such temperature dependence are discussed: thermally activated cross-over to the $4f^{13}$ ground state of Yb³⁺ and photoionization of the CTS with the escape of a hole to the valence band. To decide between the two possibilities we simulated the temperature dependence of the CTL and f–f luminescence of YAG–Yb and YAP–Yb. The following equation was describing the intensity of the CTL:

$$I_{CT} = \frac{I_{CT0} \times W_{rad}}{W_{rad} + C \times \exp\left(-\frac{E}{kT}\right) + C_1 \times \exp\left(-\frac{E_1}{kT}\right)}, \quad (1)$$

where $W_{rad} = W_1 + W_2$, W_1 is the probability of radiative transition from the CTS to the ${}^2F_{7/2}$ ground state; similarly, W_2 is the probability of radiative transition to the ${}^2F_{5/2}$ state; $C \times \exp\left(-\frac{E}{kT}\right)$ is the probability of thermally activated cross-over from the CT state to the

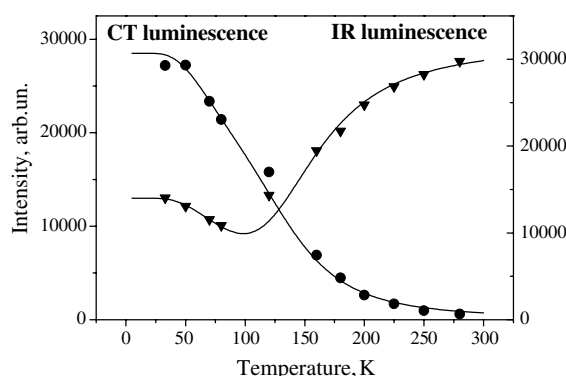


Figure 2. Temperature dependence of the CT and 4f luminescence of YAG–Yb (15 mol%) excited in the CT absorption band (6.0 eV): circles and triangles—experimental results; solid curves—simulation (y-axes for two luminescence types are independent).

$^2F_{5/2}$ level (non-radiative transition); and $C_1 \times \exp(-\frac{E_1}{kT})$ the probability of the ionization of the CT state (C is frequency factor, E the activation energy). For the IR luminescence the equation was as follows:

$$I_{IR} = \frac{I_{IR0} * (W_2 + C \times \exp(-\frac{E}{kT}))}{W_{rad} + C \times \exp(-\frac{E}{kT}) + C_1 \times \exp(-\frac{E_1}{kT})}. \quad (2)$$

The result of the simulation with the following parameters $W_1/W_2 = 1.3$, $E = 0.082$ eV, $E_1 = 0.019$ eV, $C \sim 10^{11}$ s $^{-1}$ and $C_1 \sim 10^9$ s $^{-1}$ is shown in figure 2 by solid curves. There is a reasonable correspondence between experimental points and the fit. However a very small value of the activation energy for the CT ionization as well as a small frequency factor for this process look suspicious. An obvious oversimplification of applied model is that it does not take into account the interaction of excitations in the ytterbium subsystem, which is known to be pronounced at such high concentrations. For Y_2O_2S with 1 mol% of Yb (Nakazawa 1979) the yield of the 4f luminescence under direct excitation in the temperature range 90–260 K changed only a little. However, the probability of interaction between Yb^{3+} ions increases with the concentration of ytterbium. The dominant mechanism at such high concentration is resonant energy transfer, resulting in the increased migration. As can be seen from the scheme of Stark split $^2F_{5/2}$ and $^2F_{7/2}$ levels of the Yb^{3+} ion in a garnet (plotted according to Basiev *et al* (1974) and adjusted to our spectra), resonant interaction between Yb^{3+} ions can occur via 1–5 transition. The interaction is temperature dependent through the temperature dependent width of participating transitions. In Basiev *et al* (1974) the effect of broadening of Yb^{3+} lines in $(Y_{0.46}Yb_{0.54})_3Al_5O_{12}$ crystal doped by 0.06 at.% of Eu (acting as a quencher) on the migration along ytterbium centres was studied. While in $Y_3Al_5O_{12}$ crystal with 0.07 at.% of Yb radiative lifetime of the excited $^2F_{5/2}$ state was 1.17 ms independent of the temperature in the range 4.2–300 K, in the heavily doped crystal the temperature dependence of the lifetime presented a minimum at 90 K, where quenching reduced the value of τ to 200 μs . Corresponding values at 4.2 and 250 K were about 450 and 850 μs . The observed dependence was explained by the temperature dependence of the ratio of inhomogeneous and homogeneous broadening. Though in our case quenchers were not introduced into the crystal intentionally and the concentration of Yb was ‘only’ 15%, still the temperature dependence of the 4f emission under direct excitation has to be taken into account. For the moment only preliminary measurements were performed, the results of which are presented in figure 3. The f–f emission spectra excited at 938 nm measured at RT and 20 K are presented. The

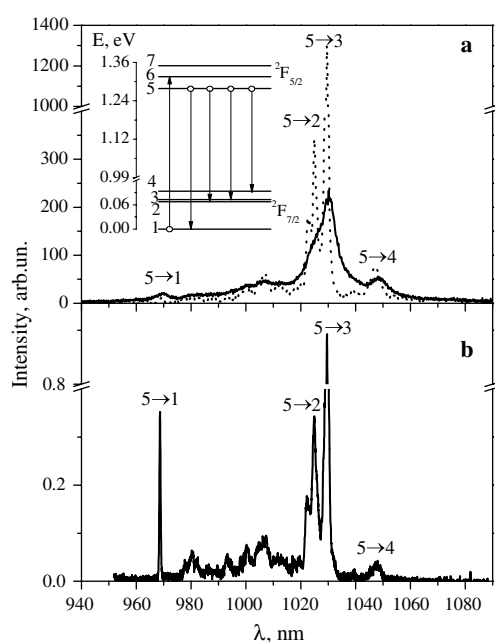


Figure 3. Spectra of the 4f luminescence of YAG–Yb (solid line—RT; dotted line—20 K) under direct excitation (a) and excitation in the CT band (b). In the inset—energy level diagram of Yb³⁺ ion.

ratio between integrated intensities was 1.4; however, the exact profile of the temperature dependence in the whole range was not yet obtained. Thus at high concentration of Yb the yield of 4f luminescence is no longer constant with temperature; the exact function deserves determination.

In the case of YAP–Yb the discrepancy between experimental results and a simple model is even more pronounced (figure 4). The temperature dependence of the f–f luminescence is presented by a curve with a deep minimum at ~ 70 K. Neither the change-over to the radiative population of the $^2F_{5/2}$ level nor the ionization of the CT state can account for such a dip since there is no correlation with the yield of the CT luminescence. It should be noted that unlike CT luminescence the rising part of the temperature dependence of the IR luminescence at low temperature was sample dependent, which could be due to different contributions from inadvertent impurities. However, analysis of the excitation spectra of the CT and IR luminescence demonstrates that temperature dependent yield of the IR luminescence cannot be the only complication that precludes using the simple model.

In figure 5 the excitation spectra of the CT and IR luminescence in the energy range 4–25 eV measured at RT and 7 K are presented (the spectra were normalized to coincide in the CT region). Similarly to temperature dependence measurements, experimental dots in the excitation spectra of the IR emission correspond to the 4f emission spectra integrated over the range 940–1060 nm. As was discussed in Kamenskikh *et al* (2003), strong reabsorption of some of the IR lines makes the resultant spectra dependent on the penetration depth of the exciting radiation; integration compensates for this effect. It should be noted that at RT the excitation spectra of both CT and IR luminescence are very similar, justifying the assumption that at this temperature emitting $^2F_{5/2}$ levels are populated via the CT state. For the CT luminescence the spectrum consists of a broad band in the region from 5 to 8 eV for YAG and LuAG and from 5 to 9 eV for YAP. In the case of YAG–Yb the first excitation peak at 6.0 eV is followed by a

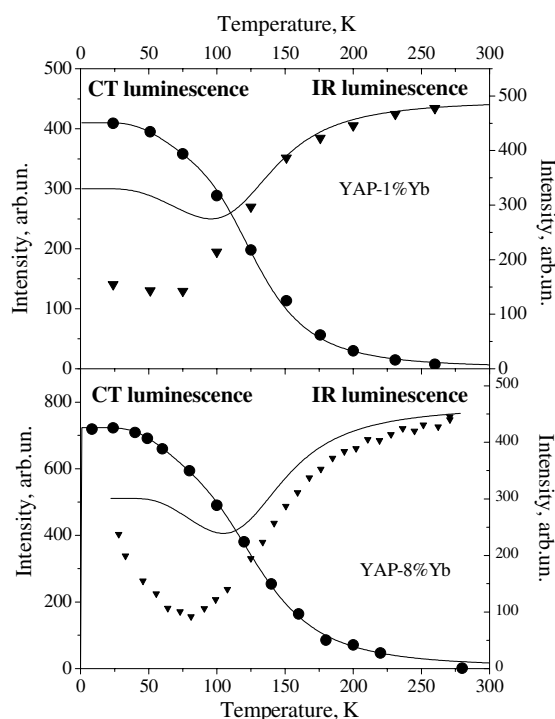


Figure 4. Temperature dependence of the CT and 4f luminescence of YAP–Yb (1 and 8 mol%) excited in the CT absorption band (6.0 eV): circles and triangles—experimental results; solid curves—simulation (y-axes for two luminescence types are independent).

dip at 6.6 eV and another peak at 6.8 eV. In the case of LuAG corresponding features are less pronounced at RT; they are manifested at low temperature at 7.0 and 7.2 eV, respectively. In the case of YAP–Yb the band is broader with the minimum at 7.7 eV and the maximum at 8.0 eV. We can compare these spectra with the excitation spectra of the same matrices pure or doped by other ions as indicated elsewhere (Kuznetsov *et al* 1985, 1989, Mürk *et al* 1995). Detailed study of the intrinsic luminescence of undoped crystals revealed that both in YAG and YAP the emission spectra are presented by two bands peaking at 4.2 and 4.9 eV in YAG and 4.2 and 5.9 eV in YAP. In YAG the low energy luminescence band has the excitation peak at 6.6 eV and the high energy one at 6.9 eV. For YAP respective values are 7.6 and 8.0 eV. In detailed discussion the authors attribute the lower energy band to the recombination of conduction-band electrons with self-trapped holes from the top part of the valence band formed by antibonding oxygen orbitals and the higher energy one to the self-trapped exciton. The position of the maxima of the excitation peaks of the intrinsic luminescence is indicated by arrows in figure 5. As one can see the first dip in the CT excitation spectra coincides quite well with the excitation maximum of the lower energy intrinsic luminescence band and from the second arrow (in fact at slightly lower energy) the yield of the CT luminescence starts to drop. Thus from this comparison we can conclude that intrinsic luminescence is a channel competing with the CT process. Competition between intrinsic luminescence and impurity luminescence is observed not only in ytterbium doped crystals. The excitation spectra of YAG doped by La in the energy range above 6.5 eV (Mürk *et al* 1995) and YAP doped by Eu and Nd above 7.5 eV (Kuznetsov *et al* 1982) are very similar to those of the CT luminescence, confirming that in this region the features of the excitation spectra are related to intrinsic electronic excitations of the matrices.

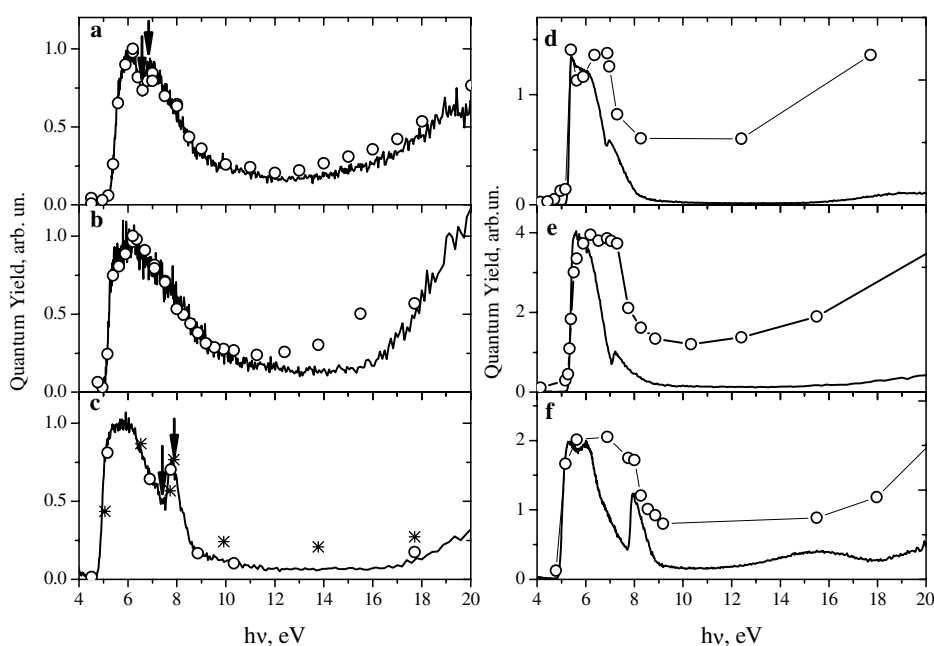


Figure 5. CT (solid lines) and 4f (open circles) luminescence excitation spectra at RT ((a)–(c)) and 7 K ((d)–(f)): YAG–Yb (a) and (d); LuAG–Yb (b) and (e); YAP–Yb (c) and (f).

At low temperature the excitation spectra of the IR luminescence no longer reproduce the features of the CT luminescence excitation spectrum (figures 5(d)–(f)): though the dip in the excitation spectra of the CT luminescence, which was attributed to the competition with the recombination-type intrinsic luminescence, becomes more pronounced (in agreement with temperature quenching observed for this type of luminescence), it disappears in the excitation spectra of the IR luminescence. A possible explanation of this fact is that self-trapped holes (probably specific holes from flat sub-bands responsible for the low-energy luminescence band of undoped crystals) can be trapped by Yb³⁺ centres with consecutive capture of electrons followed by the IR emission. This process, as well as temperature dependent mobility, can also result in the increase of the yield of IR luminescence at low temperature; it should be concentration dependent and inadvertent impurities competing with ytterbium centres can affect the yield of the 4f emission in the case of such a mechanism. Further measurements are envisaged to elucidate the mechanisms of the energy transfer at low temperature. Among them is the effect of the irradiation with 6.6 eV photons in the case of YAG and 7.6 eV photons in the case of YAP on the intensity of the 4f emission of ytterbium. In the fundamental absorption region where photons create separated electrons and holes at low temperature a fraction of the holes can be self-trapped. This fact can explain the increase of the IR emission yield (relative to the region of the CT) at these energies compared to RT. If we have an additional way of populating ytterbium 4f levels at low temperature, it creates another reason why in the low temperature range the model discussed above is no longer valid.

4. Conclusion

Doping of complex oxides by Yb³⁺ ions creates extremely interesting luminescent systems, in which the dopant participates in two types of luminescence processes, either consecutive

or alternative, namely charge transfer luminescence and f–f luminescence. The study of their temperature dependence provides information on the energy relaxation in these crystals. It has been shown that for the systems studied the dominant mechanism of the CT luminescence quenching at temperatures above 90 K is energy transfer to the 4f levels of ytterbium, not the ionization. It was observed that the yield of the f–f luminescence excited in the CT state increases with the decrease of temperature at $T < 70$ K. Further measurements are required to verify suggested mechanisms.

Acknowledgments

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