ELSEVIER

Journal of Alloys and Compounds 300–301 (2000) 426–429

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Charge transfer luminescence of Yb^{3+} in orthophosphates

L. van Pieterson*, A. Meijerink

Debye Institute, Utrecht University, P.O. Box 80 000, 3508 TA Utrecht, The Netherlands

Abstract

Charge transfer luminescence of Yb^{3+} in the orthophosphates $REPO_4$ (RE=Sc, Lu, Y, La) has been investigated. Yb^{3+} shows charge transfer luminescence in the orthophosphates of cations with a relative small radius (Sc, Lu, Y). In $LaPO_4$, no proof for Yb^{3+} charge transfer luminescence has been found. The decay time of the charge transfer luminescence is about 150 ns in the three orthophosphates. The quenching temperature is around 250 K and is compared with the quenching temperature of Eu^{3+} luminescence in the orthophosphates after excitation in the charge transfer state.

Keywords: Charge transfer; Luminescence; Yb^{3+}

1. Introduction

In this century the luminescence of rare earth ions has been well studied [1]. Especially since the application of luminescence from rare earth ions in colour television, fluorescent tubes and X-ray phosphors, numerous papers have appeared on $4f^n$–$4f^n$ and $4f^{n-1}5d$–$4f^n$ emission. Yet, there is a third type of luminescence possible: charge transfer luminescence. This transition is the reverse of the well-known charge transfer absorption. Up until now, only three papers have reported charge transfer luminescence of a rare earth ion [2–4], although the charge transfer state is important for applications. For example, in the red phosphor used in fluorescent tubes (Y_2O_3:Eu^{3+}), UV radiation is efficiently absorbed in the charge transfer state (CTS) of the Eu^{3+} ion. After non-radiative decay to the lower 4f levels, luminescence occurs from the ^5D_J states of Eu^{3+}. In Eu^{3+}, luminescence from the charge transfer state cannot be observed, since there will always be fast relaxation to the $4f^6$ levels.

Yb^{3+} is an ion for which charge transfer luminescence can be expected [2,3]. In this ion the only excited 4f state, $^2F_{5/2}$, is located 10 000 cm^{-1} above the ground state $^2F_{7/2}$. Because of the large energy difference between the charge transfer state and the highest excited 4f state charge transfer luminescence can be expected.

Here we present a systematic study of charge transfer luminescence of Yb^{3+}. The influence of the host lattice and temperature on the charge transfer luminescence of Yb^{3+} ions in $REPO_4$ (RE=Sc, Lu, Y, La) is investigated. In these compounds, the size of the site available to the Yb(III) ion is varied. This is expected to have an influence on the charge transfer emission and quenching temperature of Yb^{3+}.

2. Experimental

Powder samples of $REPO_4$ (RE=Sc, Lu, Y, La) were prepared by firing RE_2O_3 (4 N) and $(NH_4)_2HPO_4$ in air at 1350°C for 3 h. The $REPO_4$ host lattices as well as the orthophosphates doped with 0.2, 1 and 3% Yb^{3+} and the orthophosphates doped with 1% Eu^{3+} were prepared. The powder samples were analyzed with X-ray diffraction using a Philips PW1710 Diffractometer Control using CuKα radiation (1.542 Å). $ScPO_4$, $LuPO_4$ and YPO_4 all have a tetragonal crystal structure (zircon-type), $LaPO_4$ has a monoclinic structure (monazite-type) [5].

Measurements on the $REPO_4$ host lattices and the Yb^{3+}-doped samples were performed at the HIGITI experimental station [6] of the Synchrotronstrahlungslabor HASYLAB at DESY (Hamburg, Germany). In excitation and reflection spectra the ultimate spectral resolution was better than 0.5 nm [7]. Reflection spectra were corrected for the spectral intensity distribution of the synchrotron radiation and the sensitivity of excitation and emission monochromators and detectors using MgF_2 reflection spectra as reference (100% reflection). Excitation spectra were corrected for the spectral intensity distribution of the synchrotron radiation using a reference spectrum provided by DESY. For emission

---

*Corresponding author.

0925-8388/00/$ – see front matter
PII: S0925-8388(99)00756-2

measurements in the region 250–1150 nm a Tektronics ccd-array was used. VUV–UV emission was detected using a Hamamatsu 1645U-09 Channelplate detector attached to an 0.4-m Seya-Namioka monochromator blazed at 150 nm [7]. The emission spectra shown here were not corrected for the spectral response of the monochromators and detectors. Therefore, spectra measured with both monochromators are shown, so comparison is possible. The SEYA monochromator and detector have a low sensitivity for wavelengths longer than 300 nm. The SPEX monochromator and ccd/PM detector have a low sensitivity for wavelengths shorter than 300 nm. The Eu^{3+} doped orthophosphates were measured on a SPEX 1680 spectrofluorometer, equipped with 0.22 m double monochromators. This apparatus was adapted for VUV excitation measurements [7]. With this set-up measurements up to 850 K were possible, using a home-built heater.

3. Results

To distinguish between Yb^{3+} charge transfer luminescence and luminescence of the host lattice, it is necessary to have a good knowledge of host lattice luminescence. Then, extra bands in reflection or luminescence spectra of Yb^{3+} doped phosphates, not observed in host lattice spectra, can be assigned to Yb^{3+}.

Fig. 1 shows the reflection spectra of $ScPO_4$ and $ScPO_4$ doped with 3% Yb^{3+}. The host lattice absorption edge is observed at 168 nm. At 195 nm a broad extra absorption is observed in the Yb^{3+}-doped sample. This absorption can be assigned to the charge transfer absorption of Yb^{3+}.

Fig. 2 shows the emission and excitation spectra of $ScPO_4$ and $ScPO_4$ doped with 1% Yb^{3+}. The emission spectrum of the $ScPO_4$ host lattice shows several broad bands with maxima at 211, 350 and 470 nm. The center emitting at 211 nm can only be excited with radiation of energies higher than the bandgap ($\lambda<168$ nm). The other emission bands can also be excited at wavelengths greater than 168 nm and are attributed to defect centers in the $ScPO_4$ lattice.

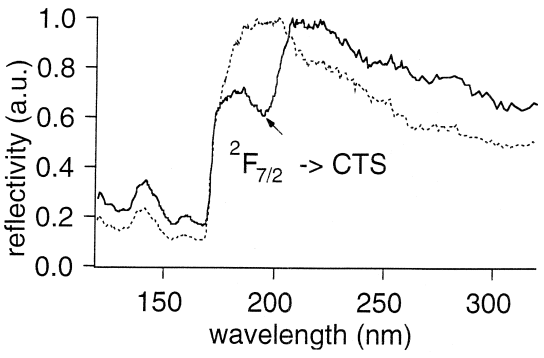

Fig. 1. Reflection spectrum of the $ScPO_4$ host lattice (broken line) and $ScPO_4$ doped with 3% Yb^{3+} (solid line), measured at 10 K.

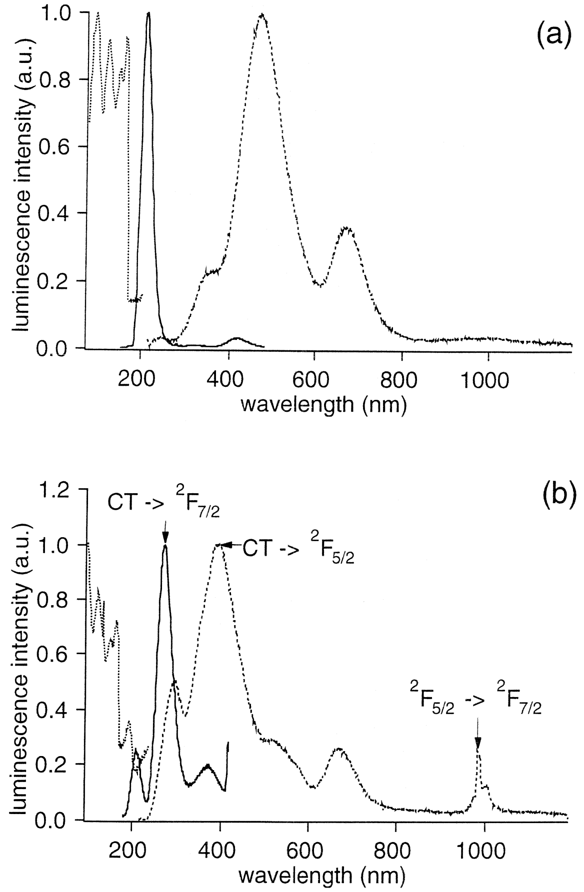

Fig. 2. Emission and excitation spectra of the $ScPO_4$ host lattice (a) and of $ScPO_4$ doped with 1% Yb^{3+} (b). The visible emission recorded with the ccd-array is represented by a broken line, the UV emission recorded with the SEYA monochromator is represented by a solid line.

If we compare the emission spectrum of $ScPO_4$ doped with Yb^{3+} with the spectrum of the host lattice, two strong extra bands are observed with maxima at 270 and 370 nm. These bands correspond to transitions from the charge transfer state to the $^2F_{7/2}$ resp. $^2F_{5/2}$ state of Yb^{3+}. The energy separation between these emission bands is 10 000 cm^{-1}, in agreement with the separation between the $^2F_{5/2}$ and $^2F_{7/2}$ state of Yb^{3+}. The full width at half maximum (FWHM) of the bands is 6000 cm^{-1} and the Stokes shift is 14 200 cm^{-1}. The transition between the two 4f states can be observed as sharp peaks in the infrared at 979 nm.

In the excitation spectrum of the emission at 270 nm, the host lattice absorption edge is observed at 168 nm. At longer wavelengths, an extra band is observed which can be assigned to the transition between the $^2F_{7/2}$ ground state to the charge transfer state of Yb^{3+}. The position of this excitation band is in good agreement with the charge transfer absorption band in the reflection spectrum.

A decay time of 163±25 ns has been measured for the Yb^{3+} CT luminescence in $ScPO_4$, in agreement with the decay time measured for Yb^{3+} charge transfer luminescence in $LuPO_4$ and YPO_4 by Nakazawa [2,3]. In Fig. 3

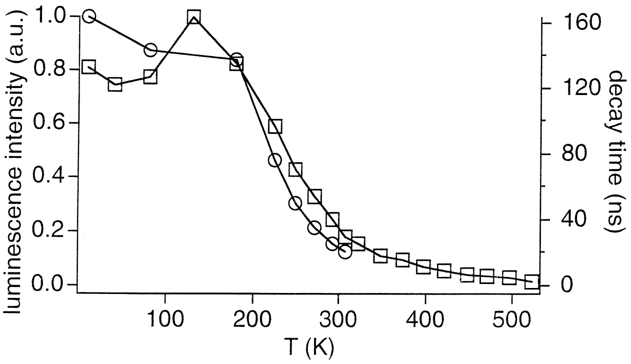

Fig. 3. Luminescence intensity (□), on the left axis, and decay time (○), on the right axis, of the charge transfer luminescence at 270 nm as a function of temperature.

the CT luminescence intensity and the decay time are given as a function of temperature. The CT luminescence measured at 270 nm is monitored, since at this wavelength the overlap with host lattice luminescence is small. If we define the quenching temperature as the temperature at which the luminescence intensity and decay time have decreased to half of its initial value, the quenching temperature of the Yb^{3+} charge transfer luminescence can be estimated at 225 K.

Table 1 summarizes the results of the orthophosphates doped with Yb^{3+}. In $LaPO_4$ no convincing evidence for Yb^{3+} charge transfer luminescence could be obtained. For comparison, the luminescence of Eu^{3+} doped orthophosphates under charge transfer excitation was measured as a function of temperature. In Table 1 the quenching temperature of the Eu^{3+} luminescence under CT excitation is also given.

4. Discussion

In all lattices, the Yb^{3+} and Eu^{3+} charge transfer absorption band shifts to longer wavelengths when the rare earth ion is incorporated on a larger cationic site. For example in $ScPO_4$ (cation radius is 0.87 Å for VIII-coordination), the Yb^{3+} CT band is located at 195 nm, whereas in $LaPO_4$ (cation radius is 1.18 Å for VIII-coordination), the Yb^{3+} CT band is observed at 228 nm. In 1975 Hoefdraad showed that for VIII and XII coordination the position of the Eu^{3+} CT band in oxides shifts to longer wavelength when the Eu^{3+}–O^{2-} distance increases [8].

From the luminescence spectra and decay time measurements of the Yb^{3+}-doped orthophosphates and the undoped host lattices, it is clear that the Yb^{3+} ion shows charge transfer luminescence in the orthophosphates of cations with a relatively small radius (Sc, Lu, Y). The FWHM is ≈6000 cm^{-1} and the Stokes shift is ≈14 000 cm^{-1}. The charge transfer transition is an allowed transition, with a large change in equilibrium constant. Therefore, broad bands are expected and the relaxation in the excited state can be large. The charge transfer emission shifts towards longer wavelengths going from $ScPO_4$ to YPO_4, just as the charge transfer absorption bands.

It is interesting to discuss the quenching of the charge transfer luminescence. Based on a simple configuration-coordinate model [1], one would expect the lowest quenching temperature for Yb^{3+} on the largest site. Indeed, for Yb^{3+} in $LaPO_4$ the charge transfer luminescence is quenched at the lowest temperatures. However, the behaviour for the quenching of the charge transfer luminescence in $ScPO_4$, $LuPO_4$ and YPO_4 is not in agreement with what is expected: the Yb^{3+} charge transfer luminescence in $ScPO_4$ (smallest site) is quenched at lower temperatures (225 K) than in the YPO_4 and $LuPO_4$ host lattices. The reason for this is not clear. It may be due to a strong distortion of the local environment of Yb^{3+} on the much smaller Sc^{3+} site. Another explanation may be that the quenching mechanism is not thermally activated cross-over from the excited state to the $4f^{13}$ ground state, but photoionization. If this is the case, the position of the charge transfer state in the bandgap determines the quenching temperature and it is hard to predict how the energy difference between the charge transfer state and the conduction band varies in the different host lattices.

Finally it is interesting to compare the results on the Yb^{3+} charge transfer luminescence with the results obtained for Eu^{3+}. The Eu^{3+} emission ($^5D_0 \rightarrow {}^7F_J$) under charge transfer excitation quenches at much higher temperatures: $T_q \approx 760$ K in $ScPO_4$, 850 K in $LuPO_4$, 970 K in YPO_4 and $T_q \approx 400$ K for Eu^{3+} in $LaPO_4$. We see that the

Table 1
Charge transfer luminescence properties of Yb^{3+} and Eu^{3+} in orthophosphate host lattices; for decay time (τ) measurements (at 10 K) and determination of the Yb^{3+} quenching temperature (T_q), the CT→$^2F_{7/2}$ emission is monitored; for determination of the Eu^{3+} quenching temperature, the $^5D_0 \rightarrow {}^7F_J$ emission under CT excitation is monitored

	Absorption (nm)	Emission (nm)	Stokes shift (cm^{-1})	τ (ns)	T_q (K) Yb^{3+}	Absorption (nm) Eu^{3+}	T_q (K) Eu^{3+}
$ScPO_4$	195	270, 370	14 200	163	225	205	760
$LuPO_4$	210	290, 440	13 100	175	250	215	850
YPO_4	210	304, 445	14 700	120	290	218	970[a]
$LaPO_4$	228	–	–	–	–	251	400

[a] Estimation.

quenching order is the same for Yb^{3+} and Eu^{3+}. The lower quenching temperature for the Eu^{3+} emission in $LaPO_4$ is in agreement with the low quenching temperature for charge transfer luminescence from Yb^{3+} in this host lattice. In the host lattices with very high quenching temperatures for the Eu^{3+} emission under charge transfer excitation, Yb^{3+} luminescence is observed, but it is quenched below room temperature.

The much lower quenching temperature for Yb^{3+} can be explained in two ways. Thinking in terms of the configuration-coordinate model, we see that for Eu^{3+}, fast non radiative decay to the ^5D_J states ($\tau \approx$ps) must compete with non-radiative decay to the ^7F_J states. Once the ^5D states are populated, luminescence occurs. For Yb^{3+}, on the other hand, the much slower ($\tau \approx 150$ ns) radiative decay to the ^2F_J states must compete with fast non-radiative decay to these states. Another reason for the much lower quenching temperature for Yb^{3+} may be the lower stability of Yb^{2+} compared to Eu^{2+}. This will shift the CTS closer to the conduction band causing quenching due to photoionization to occur at lower temperatures.

5. Conclusion

Charge transfer luminescence of Yb^{3+} in the orthophosphates $REPO_4$ (RE = Sc, Lu, Y, La) has been investigated. Yb^{3+} shows charge transfer luminescence in the orthophosphates of cations with a relative small radius (Sc, Lu, Y). The position of the charge transfer absorption and emission band shifts towards longer wavelengths from Sc to La. In $LaPO_4$, no convincing evidence for charge transfer luminescence has been obtained. In this lattice, a large relaxation in the charge transfer of Yb^{3+} is possible because of the large site Yb^{3+} occupies. The decay time of the charge transfer luminescence is typically 150 ns and the quenching temperature of the charge transfer luminescence is around 250 K for Yb^{3+} in (Sc, Lu, Y)PO_4.

References

[1] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer–Verlag, Berlin, Heidelberg, 1994.

[2] E. Nakazawa, Chem. Phys. Lett. 56 (1978) 161.

[3] E. Nakazawa, J. Luminescence 18/19 (1979) 272.

[4] E. Danielson, M. Devenney, D.M. Giaquinta, J.H. Golden, R.C. Haushalter, E.W. McFarland, D.M. Poojary, C.M. Reaves, W.H. Weinberg, X. Di Wu, Science 279 (1998) 837.

[5] A.T. Aldred, Acta Cryst. B40 (1984) 569–574.

[6] U. Hahn, N. Schwentner, G. Zimmerer, Nucl. Instrum. Methods 152 (1978) 261.

[7] R.T. Wegh, H. Donker, A. Meijerink, Phys. Rev. B 56 (1997) 13841.

[8] H.E. Hoefdraad, J. Sol. State Chem. 15 (1975) 175–177.