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Luminescence in $La_3TaO_4Cl_6$

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The luminescence properties of $La_3TaO_4Cl_6$ are reported and discussed. The rare earth ions Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, and Tm^{3+} show characteristic absorption and emission lines. For Sm^{3+} and Eu^{3+}, broad absorption bands are also observed and are attributed to charge-transfer transitions. The line emissions of Tb^{3+} are only from $^5D_4$, even at low (1 at.%) concentration. Broad excitation and emission bands were observed with In^{3+}. These bands are attributed to In^{3+}–Ta^{5+} → In^{4+}–Ta^{4+} charge-transfer transitions. An additional broad absorption at 250 and 280 nm leading to broad emission at 410 nm is ascribed to OH^- impurities.

Introduction

Recently, Brixner *et al.* reported on the crystal structure of $Pr_3NbO_4Cl_6$ (*1*). The present paper deals with an isostructural compound, $La_3TaO_4Cl_6$. The crystal structure of these compounds contains infinite linear chains of corner-sharing $TaO_5(NbO_5)$ trigonal bipyramids with the equatorial oxygens corner-sharing the oxygens of the $LnCl_7O_2$ polyhedra. There is one crystallographic site for the La^{3+} ion. This ion is asymmetrically coordinated by seven chlorine ions at four different distances and two oxygen ions close to each other at one side of the lanthanide ion. The site symmetry is low, viz., C_s.

Blasse *et al.* reported on the luminescence properties of $La_3TaO_4Cl_6$ (*2*). The optical band edge at 300 K is at about 230 nm. Excitation with this wavelength yields a UV emission band with a maximum at 335 nm at 4.2 K. Because of the high-energy position of the band edge, $La_3TaO_4Cl_6$ is a suitable host lattice for the investigation of the luminescence properties of many activator ions. In this paper we report on the luminescence properties of Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Tm^{3+}, and In^{3+}.

Experimental

$La_3TaO_4Cl_6$ powder samples were prepared as follows. Stoichiometric quantities of LaOCl, $LaCl_3$, and Ta_2O_5 were ground in a mortar in a helium dry box. Dopants were introduced via the LaOCl component which was prepared as previously described (*3*). The powders were sealed under vacuum in fused quartz tubes, and heated for 18 to 24 hr at temperatures between 800 and 900°C. Small amounts of starting mate-

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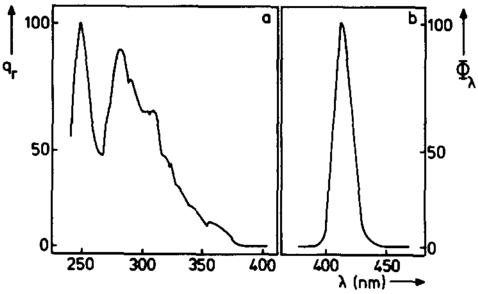

FIG. 1. Excitation (a) and emission (b) spectra of the additional luminescence which $La_{3-x}RE_xTaO_4Cl_6$ samples with RE = Eu, Tb, Dy, and Tm have in common at LHeT (λ_{exc} = 310 nm, λ_{em} = 410 nm). q_r denotes the relative quantum output in arbitrary units. Φ_λ gives the spectral radiant power per constant wavelength interval in arbitrary units.

rials were observed in the X-ray powder diffraction patterns even when the samples were reground and refired. Dopant concentrations were $\frac{2}{3}$ at.% for Sm^{3+} and Eu^{3+}; 1 at.% for Tb^{3+}, Dy^{3+}, and Tm^{3+}; $1\frac{2}{3}$ at.% for In^{3+}. The samples activated with Tb^{3+} and Tm^{3+} were gray, and those activated with all other ions were white.

Luminescence spectra were measured down to liquid helium temperature (LHeT) and at room temperature (RT) on a Perkin–Elmer spectrofluorometer MPF 3L as described in Ref. (*4*). Diffuse reflection spectra were measured on a Perkin–Elmer Lambda 7 UV/VIS spectrophotometer. Quantum efficiencies were estimated by comparison with standard phosphors.

Results

All $La_3TaO_4Cl_6$ samples show luminescence characteristics which can be ascribed to the particular activator ion. However, some samples, viz., $La_3TaO_4Cl_6$ activated with Eu^{3+}, Tb^{3+}, Dy^{3+}, and Tm^{3+}, respectively, show an additional and rather strong narrow band emission with the maximum at 410 nm. This emission corresponds to excitation bands peaking at about 250 and 280 nm. At LHeT these excitation bands have a complex structured shape (Fig. 1). The intensity of this emission increased after firing the samples at 400°C in a moist nitrogen atmosphere.

$La_{2.98}Eu_{0.02}TaO_4Cl_6$ shows a red luminescence with a quantum efficiency of less than 20% upon excitation into the charge-transfer state, but a much higher quantum efficiency on excitation into the $4f$ levels. Figure 2a shows the excitation spectrum of the red luminescence. We observe a broad band with a maximum at 315 nm, which we ascribe to the europium–oxygen (chlorine) charge-transfer transition and, at longer wavelengths, sharp excitation lines corresponding to transitions within the $4f^6$ shell of the Eu^{3+} ion. The emission consists mainly of the Eu^{3+} $^5D_0$ emission lines, but also some weak lines due to emission from the higher-lying $^5D_1$ and $^5D_2$ levels are observed in the emission spectrum for excitation into the $^5D_2$ or higher-lying levels. The ratio of the emission intensities originating from the $^5D_0$ and the ^5D_J ($J \geq 1$) levels depends on the excitation wavelength and is the highest for excitation into the charge-transfer band. Figure 2b shows the emis-

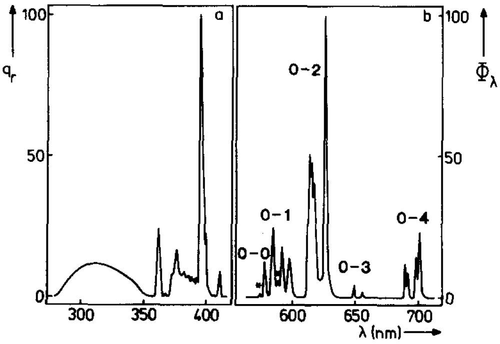

FIG. 2. (a) Excitation spectrum of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ emission (λ_{em} = 625 nm) of $La_{2.98}Eu_{0.02}TaO_4Cl_6$ at LHeT. (b) Emission spectrum for excitation into the europium–oxygen (chlorine) charge-transfer band at LHeT. The notation 0–J denotes the transitions $^5D_0 \rightarrow {}^7F_J$; * denotes the transitions $^5D_1 \rightarrow {}^7F_J$.

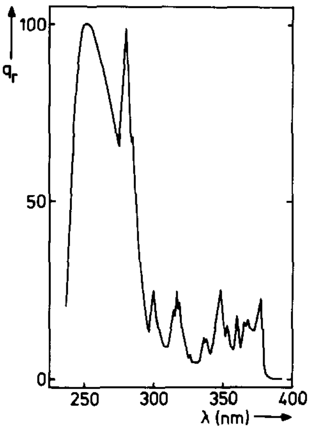

FIG. 3. Excitation spectrum of the Tb^{3+} $^5D_4 \rightarrow {}^7F_5$ emission (λ_{em} = 542 nm) of $La_{2.97}Tb_{0.03}TaO_4Cl_6$ at LHeT.

sion spectrum in the region of the $^5D_0$–^7F_J emission lines at LHeT for excitation into the charge-transfer band. A strong $^5D_0$–$^7F_0$ emission line is observed at relatively high energy, viz., 17,300 cm^{-1} (578 nm). The presence of one $^5D_0$–$^7F_0$ emission line in the emission spectrum indicates that there is one crystallographic site available for the Eu^{3+} ion, as expected from the crystal structure.

$La_{2.97}Tb_{0.03}TaO_4Cl_6$ shows a green luminescence with a quantum efficiency of about 60%. The emission spectrum of this sample shows only Tb^{3+} $^5D_4$ emission, independent of temperature and excitation wavelength. The excitation spectrum is dominated by a strong broad band at 265 nm with a shoulder at 285 nm (Fig. 3). At longer wavelengths we observe some weak sharp lines due to the characteristic transitions within the Tb^{3+} $4f^8$ shell.

$La_{2.97}Tm_{0.03}TaO_4Cl_6$ shows the characteristic luminescence properties for Tm^{3+}. The emission spectrum consists of sharp lines at about 460 nm, the excitation spectrum of sharp lines at about 360 nm. These are due to the $^1D_2$–$^3F_4$ and $^3H_6$–$^1D_2$ transitions, respectively. The luminescence output is weak, because of the weak absorption strength of the $^3H_6$–$^1D_2$ transition.

In the emission spectrum of $La_{2.98}Sm_{0.02}TaO_4Cl_6$, sharp lines at about 565, 600, 645, and 705 nm are observed due to emission from the $^4G_{5/2}$ level. The excitation spectrum of these emissions shows the transitions from the $^6H_{5/2}$ ground state to $^4G_{5/2}$ and higher-lying levels and in addition an excitation band at about 260 nm.

In the emission spectrum of $La_{2.97}Dy_{0.03}TaO_4Cl_6$ we observe sharp Dy^{3+} emission lines at about 480 and 580 nm due to emission from $^4F_{9/2}$ to $^6H_{15/2}$ and $^6H_{13/2}$, respectively. The corresponding excitation spectrum consists of sharp lines due to transitions from the $^6H_{15/2}$ ground state to $^4F_{9/2}$ and higher-lying levels. In addition, we observe in the emission spectrum the emission band at 410 nm at LHeT already described above, and a broad emission band with a maximum at 440 nm. The corresponding excitation band peaks at 255 nm. The nature of this band will be discussed below.

$La_{2.95}In_{0.05}TaO_4Cl_6$ shows a blue emission with a quantum efficiency of about 60%. Figure 4 shows the emission and excitation spectrum of this compound at LHeT. The emission spectrum consists of a broad emission band with the maximum at 500 nm; the corresponding excitation band

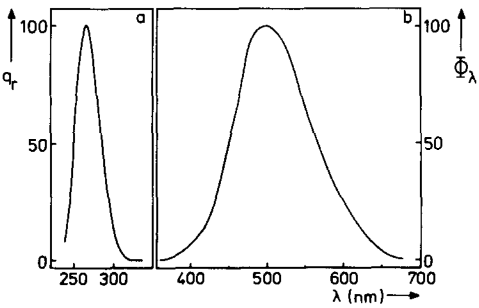

FIG. 4. Excitation (a) and emission (b) spectra of the luminescence of $La_{2.95}In_{0.05}TaO_4Cl_6$ at LHeT (λ_{em} = 480 nm, λ_{exc} = 280 nm).

peaks at 270 nm. The emission intensity does not change from LHeT to RT.

Discussion

The emission band at 410 nm and the corresponding structured excitation band observed for some of our samples cannot be ascribed to the host lattice or to the activator ions. Recently, the same kind of luminescence characteristics was reported for K_2TaF_7 and K_2NbF_7 (*5*). In these compounds there are strong indications that this luminescence is due to OH^- ions. Therefore, we ascribe the emission band at 410 nm also to OH^- ions. After preparation surface hydrolysis may take place. This view is confirmed by the fact that the emission intensity of this band increased after firing the samples at 400°C in a moist atmosphere. As in Ref. (*5*) we were not able to unravel the vibrational structure in the excitation band.

Another emission which is unlikely to originate from the activator ion is the broad emission band peaking at 440 nm observed for $La_{2.97}Dy_{0.03}TaO_4Cl_6$. The maximum of the excitation band is at 260 nm. These wavelengths correspond to those reported for the luminescence from defect tantalate groups in, e.g., $GdTaO_4$ and $YTaO_4$ (*6, 7*). However, this emission is not observed for our other samples and not even in unactivated $La_3TaO_4Cl_6$ (*2*). Therefore, it cannot be excluded that this emission is due to some kind of impurity, e.g., $LaTaO_4$ (*8*).

$La_3TaO_4Cl_6$: *Eu*

Figure 2b shows the emission spectrum of $La_{2.98}Eu_{0.02}TaO_4Cl_6$ between 570 and 700 nm. Most of the lines can be assigned to transitions from the $^5D_0$ to the ^7F_J levels. The point symmetry of the Ln^{3+} site in $La_3TaO_4Cl_6$ is C_s. For this low symmetry the ^7F level degeneracy is totally lifted, usually resulting in $2J + 1$ lines for each $^5D_0$–^7F_J transition. However, in our case the observed number of lines is less than the expected number. This can be explained by the fact that the Ln^{3+} site symmetry is close to C_{2v}.

The $^5D_0$–$^7F_0$ transition is allowed for compounds in which the Ln^{3+} site symmetry is C_{nv} or lower. In our compound the $^5D_0$–$^7F_0$ transition has a relatively high intensity. This is ascribed to the presence of a linear crystal field (*9, 10*). This can be understood from the crystal structure which consists of LaO_2Cl_7 polyhedra with the two oxygens situated on one side of these polyhedra and closer to the La^{3+} ion than the Cl^- ions. In addition it is known that the intensity of electric-dipole transitions increases if the energy of the charge-transfer state decreases (*11*). In $La_{2.98}Eu_{0.02}TaO_4Cl_6$ the charge-transfer state is at low energy, viz., at about 31,750 cm^{-1}.

The position of the $^5D_0$ level is at relatively high energy (17,300 cm^{-1}), and the splitting of the $^7F_1$ level is large, viz., about 385 cm^{-1}. These two phenomena are often observed together (*12, 13*). The energy of the $^5D_0$ level increases with increasing ionic radius of the host cation, which is usually attributed to the nephelauxetic effect (*14*). However, it is known that crystal-field effects can produce similar shifts in the position of the $^5D_0$ level (*15, 16*). The large splitting of the $^7F_1$ level suggests a strong ionic crystal-field effect on the ^7F multiplet, since the $^7F_1$ splitting arises mainly from the electrostatic contribution to the crystal field (*17*). The present case seems comparable to that of LaOBr: Eu (*13*). In that compound a coordination of the Eu^{3+} ion by oxygen and bromine ions in a host lattice with La^{3+} cations gives a $^7F_1$ crystal-field splitting of 346 cm^{-1}, while the $^5D_0$ energy level is situated at 17,300 cm^{-1}.

The broad band in the excitation spectrum of $La_{2.98}Eu_{0.02}TaO_4Cl_6$ corresponds to the Eu^{3+}–O^{2-} (Cl^-) charge-transfer transition. The maximum of the band is at 31,750 cm^{-1} (315 nm) which is at relatively low energy. This value is about equal to the value reported for $La_{2.97}Eu_{0.03}WO_6Cl_3$ in which the La^{3+} ions are in 10-coordination, with six O^{2-} ions on one side and four Cl^- ions on the other side (*18*). Hoefdraad has noted that the charge-transfer band moves to lower energy if the coordination of the Eu^{3+} ion is higher and if the Eu–O distance increases (*19*). In $La_{2.98}Eu_{0.02}TaO_4Cl_6$ the coordination number is relatively high, viz., nine, and the Eu^{3+} ion replaces the larger La^{3+} ion. The decrease in charge-transfer energy is due to the fact that the larger the radius of the host cation, the less stable is the O^{2-} ion, and thus less energy is required to remove an electron from the oxygen ion. In addition, the partial coordination by chlorine may also lower the energy of the charge-transfer state.

The presence of the charge-transfer state at low energies has an influence on the quantum efficiency of the luminescence. Upon excitation into the charge-transfer band, the quantum efficiency is low, viz., about 20%. The low position of this band promotes nonradiative transitions in the Eu^{3+} ion (*20*). Upon excitation into the $^5D_2$ or higher-lying $4f^6$ levels, the quantum efficiency is much higher. In that case more $^5D_1$ and $^5D_2$ emission, relative to the $^5D_0$ emission, is observed. This is due to the fact that for excitation into the charge-transfer band the excited state can relax directly to the $^5D_0$ level (*21*).

$La_3TaO_4Cl_6$: *Tb*

The absence of $^5D_3$ emission in the emission spectrum of $La_{2.97}Tb_{0.03}TaO_4Cl_6$ is remarkable. Even for excitation into the sharp $4f^8$ levels, no $^5D_3$ emission is observed. It is very unlikely that multiphonon relaxation is responsible for the absence of $^5D_3$ emission. At least seven phonons would be required to bridge the energy gap of 5500 cm^{-1} between the $^5D_3$ and $^5D_4$ levels, making the probability for multiphonon relaxation low (*6*). The absence of $^5D_3$ emission can also hardly be ascribed to cross-relaxation, since the Tb^{3+} concentration is only 1 at.%. It is more probable that the broad band observed in the excitation spectrum is responsible for the absence of $^5D_3$ emission. For excitation into this band the excited state can relax directly to the $^5D_4$ level. For excitation into the Tb^{3+} $4f^8$ levels it is possible that this band acts as an intermediate state by which the excited ion can relax from the $^5D_3$ to the $^5D_4$ level. Such a mechanism was described by Struck and Fonger (*22*) and was also applied to Pr^{3+} (*23*).

A similar behavior was described for the case of Tb^{3+} in $LaWO_4Cl$ (*24*). Here the Tb^{3+} $4f$–$5d$ transition is at even lower energy. It is interesting to note that $LaWO_4Cl$ and $La_3TaO_4Cl_6$ show a structural analogy, because in both structures the La^{3+} ions are on linear rows consisting of face-sharing polyhedra. Reference (*24*) describes how this situation can be responsible for a low-lying $4f^75d$ component.

$La_3TaO_4Cl_6$: *Sm*

Upon UV excitation the well-known red Sm^{3+} $^4G_{5/2}$ emission lines are observed. The excitation spectrum shows, in addition to the narrow Sm^{3+} $4f^5$ excitation lines, a broad excitation band at 260 nm (38,400 cm^{-1}). We ascribe this excitation band to the Sm^{3+}–$O^{2-}(Cl^-)$ charge-transfer transition. For the reasons described above for Eu^{3+}-activated $La_3TaO_4Cl_6$ this transition is at relatively low energies. The energy difference between the charge-transfer transitions in Sm^{3+}- and Eu^{3+}-activated $La_3TaO_4Cl_6$ is about 7000 cm^{-1}. This is in reasonable agreement with the energy differences reported for other host lattices activated with Sm^{3+} and Eu^{3+} (*25*).

$La_3TaO_4Cl_6$: *In*

The luminescence properties of In^{3+}- and Bi^{3+}-activated $La_3TaO_4Cl_6$ are different from those of rare-earth-activated La_3

TaO_4Cl_6. For In^{3+}-activated $La_3TaO_4Cl_6$ we observe one excitation and one emission band with a Stokes shift of about 17,000 cm^{-1}. As in In^{3+}-activated YVO_4 we ascribe the absorption and emission process in this phosphor to a charge-transfer transition from the filled 4*d* orbital of In^{3+} to the empty 5*d* orbital of Ta^{5+} (*26*). For $YNbO_4$–In and Y_2WO_6–In, similar emission and excitation bands have been observed (*27*).

In conclusion, the luminescence properties of several activators in the host lattice $La_3TaO_4Cl_6$ are rather peculiar.

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