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Quenching of Lanthanide Emission by Intervalence Charge Transfer in Crystals Containing Closed Shell Transition Metal Ions

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Abstract: The quenching of the luminescence originating from the excited states 3P_0 and 1D_2 of Pr^{3+} and 5D_3 and 5D_4 of Tb^{3+} has been studied in oxide crystals containing closed shell transition metal ions, such as titanates, vanadates, niobates, and tantalates. It has been shown that the emission from these excited states can be quenched by an intervalence charge transfer mechanism. The temperature dependence of the emission intensities has allowed estimating indicative activation energies for the crossover to the intervalence charge transfer state. In the case of Tb^{3+} , the quenching gives rise to relatively short decay times for the 5D_4 state.

Keywords: Crystals, intervalence charge transfer, lanthanides, luminescence

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INTRODUCTION

Electron transfer between different metal ions in solids, usually referred to as metal-to-metal charge transfer, or intervalence charge transfer (IVCT), can have a deep impact on the optical spectroscopy of the involved centers.^[1] In particular, it has been shown that electron transfer from a trivalent lanthanide ion (Ln^{3+}) to a closed shell transition metal ion (M^{n+}) implies the formation of a low-lying charge transfer state formally of the type $\text{Ln}^{4+} + \text{M}^{(n-1)+}$. The transition $\text{Ln}^{3+} + \text{M}^{n+} \rightarrow \text{Ln}^{4+} + \text{M}^{(n-1)+}$ appears as a strong broad absorption or excitation band in the optical spectra (see Fig. 1 and Fig. 5 of Ref. 2), and the IVCT can cause the quenching of the luminescence from certain excited levels of the lanthanide center. In fact, the IVCT potential energy curve can cross the ones relative to the emitting levels of the Ln^{3+} ion, providing efficient quenching channels (Fig. 1).^[3] This behavior has been widely studied in the case of Pr^{3+} , where the depopulation of the $^3\text{P}_0$ state by IVCT leads to the population of the red emitting $^1\text{D}_2$ state through a “virtual recharge” mechanism.^[4] This has been shown to occur in several crystalline materials containing closed shell transition metal ions, such as titanates, vanadates, and so forth, making the development of efficient red phosphors based on Pr^{3+} possible. Systematic investigations carried out in order to determine the position of IVCT in these materials allowed formulation of a preliminary criterion to predict in which crystals this mechanism will be operative at room temperature.^[2,5-8]

Although it is well-known that also the Tb^{3+} ion, in general very efficiently luminescent, can be quenched by IVCT processes, not many studies have been devoted to this problem. For instance, it is well-known that the $\text{Tb}^{3+} \ ^5\text{D}_4$ level is not luminescent in YVO_4 ,^[9,10] but detailed knowledge about its behavior in other hosts containing closed shell transition metal ions is scarce.^[11]

For the reasons stated above, we found it interesting to extend the investigations previously carried out on the influence of IVCT on the excited

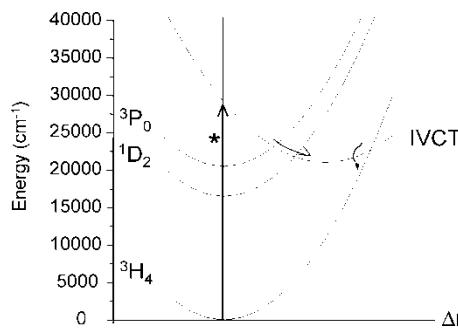


Figure 1. Schematic configurational coordinate diagram showing the quenching of $^3\text{P}_0$ and $^1\text{D}_2$ excited states of Pr^{3+} by IVCT in a typical host. The star indicates the electronic transition to the IVCT state. The situation is similar for the $^5\text{D}_3$ and $^5\text{D}_4$ levels of Tb^{3+} .

state dynamics for Pr^{3+} to the case of the much less studied Tb^{3+} ion. We have considered host materials that can be regarded as model matrices for the development of efficient lanthanide-doped phosphors, such as titanates, vanadates, niobates, and tantalates. In this paper, we will investigate the effect of IVCT on the quenching of Tb^{3+} $^5\text{D}_4$ luminescence in these hosts and show that the quenching efficiency is related to the nature of the host crystal. Moreover, we will extend our previous results relative to the excited state dynamics of Pr^{3+} in the same hosts, by reporting results on the thermal quenching of the visible emission of this ion. Both in the case of Pr^{3+} and Tb^{3+} , the spectroscopic results relative to the crystals containing closed shell transition metal ions will be compared with the ones obtained for hosts in which no IVCT is possible, such as phosphates. The results will be discussed in the perspective of the possible applications of these materials in the field of phosphors.

MATERIALS AND METHODS

Good-quality single crystals of YPO_4 , YVO_4 , and LaVO_4 , suitably doped with low amounts of Pr^{3+} or Tb^{3+} (0.1–1.0 mol%), were grown by spontaneous nucleation using the flux growth technique, as previously described.^[5,11,12] The other materials under investigation (CaTiO_3 , YNbO_4 , YTaO_4 , LaTaO_4) were prepared as crystalline powders by solid-state reactions using conventional techniques. All samples were checked to be single phase by X-ray powder diffraction. Photoluminescence data were measured using a Triax 550 monochromator (Jobin-Yvon-Horiba Symphony system, Longjumeau, France) equipped with both a CCD camera and a photomultiplier. The incoming light was selected from a xenon lamp using a Triax 180 monochromator. Data were acquired in the temperature range 300–600 K with the help of a homemade copper holder heated by a thermocoax wire connected to a Thermolyne regulator (Calgary, AB, Canada). The heating rate was fixed at 3 K/min. The spectra were recorded using a CCD camera, and the intensity of the signals was evaluated as the integrated area of the emission bands. The 485-nm radiation was the first anti-Stokes line generated in a H_2 Raman cell positioned at the output of a dye laser operated with a mixture of rhodamines 610 + 640 and pumped with a pulsed frequency doubled Nd:YAG laser. The decay profiles were collected with a 400 MHz LeCroy Oscilloscope (Chestnut Ridge, NY, USA).

RESULTS AND DISCUSSION

Pr^{3+} -Doped Crystals

The behavior of the emission intensity from the $^3\text{P}_0$ and $^1\text{D}_2$ excited states of the Pr^{3+} ion (see Fig. 2 for the energy level diagram) was investigated in the temperature range 300–600 K. Figure 3 shows the thermal quenching of the

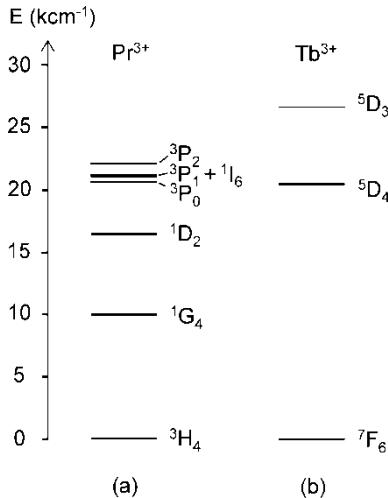


Figure 2. Simplified energy level diagrams of (a) Pr^{3+} and (b) Tb^{3+} .

red $^1\text{D}_2$ emission in YPO_4 , YVO_4 , and CaTiO_3 after citation in the $^3\text{P}_2$ level at 445 nm. The thermal quenching of the $^3\text{P}_0$ emission could not be studied for YVO_4 and CaTiO_3 , as in these crystals this level is nonluminescent. Inspection of the figure shows that the thermal quenching for YPO_4 is rather weak; this quenching has to be attributed to multiphonon relaxation across the gap to the $^1\text{G}_4$ state and possibly also to weakly temperature-dependent cross-relaxation processes.^[13] On the other hand, the thermal quenching of the $^1\text{D}_2$ emission is much stronger for YVO_4 and CaTiO_3 , leading to a strong decrease of the emitted intensity already slightly above room temperature. We point out

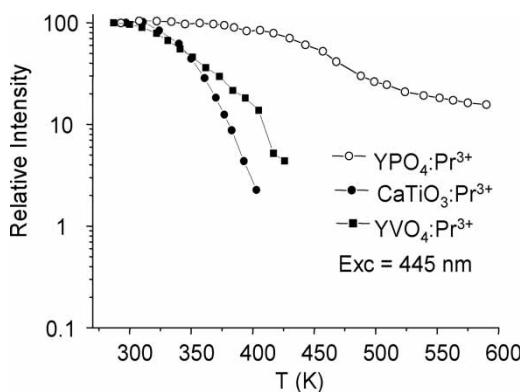


Figure 3. Temperature dependence of $^1\text{D}_2$ emission intensity in $\text{YPO}_4:1\%\text{Pr}^{3+}$, $\text{YVO}_4:1\%\text{Pr}^{3+}$, and $\text{CaTiO}_3:0.1\%\text{Pr}^{3+}$. Excitation was at 445 nm. The lines are a guide for the eye.

that this different thermal behavior cannot originate from multiphonon relaxation, as the highest vibrational wavenumbers are distinctly higher for YPO_4 (1058 cm^{-1}) than for YVO_4 and CaTiO_3 (950 and 639 cm^{-1} , respectively). On the other hand, it has already been suggested by some of us^[7] that in vanadate and titanate crystals having a short Pr^{3+} – V^{5+} (Ti^{4+}) distance, such as YVO_4 and CaTiO_3 , the low position of the IVCT state can induce quenching of the ${}^1\text{D}_2$ emission. For these reasons, we attribute the strong thermal quenching of ${}^1\text{D}_2$ to the crossover to a Franck–Condon shifted state, in this case the IVCT state. The thermal quenching of Ln^{3+} excited states by crossover to charge transfer and $4f^{n-1}5d$ states has been widely observed and discussed in the past,^[14,15] but the effect of the temperature on IVCT quenching has been described only in a limited number of cases.^[16] In Figures 4a and 4b, the thermal quenching of ${}^1\text{D}_2$ is shown for YVO_4 and CaTiO_3 , after excitation at various wavelengths. It is possible to note that excitation at 320 nm (inside the strong absorption band typical of the vanadate or titanate groups) and at 370 or 380 nm (inside the IVCT band) gives rise to thermal quenching behaviors that are similar to the ones obtained by excitation in a $4f^2$ state (${}^3\text{P}_2$) just above the emitting level. This observation is at variance with the results obtained for $\text{La}_2\text{O}_2\text{S}$,^[15] the

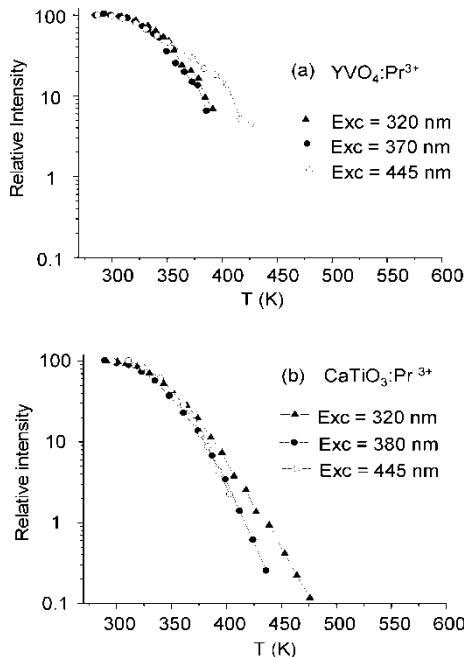


Figure 4. Temperature dependence of ${}^1\text{D}_2$ emission intensity in (a) $\text{YVO}_4:1\%\text{Pr}^{3+}$ and (b) $\text{CaTiO}_3:0.1\%\text{Pr}^{3+}$ with various excitation wavelengths. The lines are a guide for the eye.

different behavior could be due to the fact that in the materials under investigation, high-energy excitation does not give rise to states where free electrons and holes are trapped before the $4f^2$ configuration is reached, therefore providing additional quenching channels.^[15] For this reason, the thermal quenching results obtained in this study upon UV excitation are considered to be representative of the quenching of $4f^n$ levels.

Figure 5 shows the thermal quenching of the luminescence for $\text{LaVO}_4:\text{Pr}^{3+}$. In this case, the $^3\text{P}_0$ level is luminescent at room temperature^[5] although it is partly quenched by the IVCT state; it was then possible to measure its thermal quenching. It is evident that the quenching is relatively weak for $^1\text{D}_2$, whereas the one for $^3\text{P}_0$ is much more dramatic. These data suggest that both excited states are quenched by the IVCT mechanism and are in qualitative agreement with the observations of a higher energy position of the IVCT excitation band in LaVO_4 than in CaTiO_3 and YVO_4 ,^[7] causing a stronger quenching in the latter crystals.

Following the model proposed by Struck and Fonger,^[15] in the case of crossover to Franck–Condon shifted states, the temperature dependence of the emission intensity I is described by:

$$\frac{I(T)}{I_0} = \left[1 + A \exp\left(\frac{-E}{KT}\right) \right]^{-1} \quad (1)$$

In this equation, A is close to 10^7 and E is the activation energy from the $4f^n$ state to its crossover with the quenching state. The experimental data for the thermal quenching of the Pr^{3+} emission in the various crystals could be reasonably fitted by Eq. (1).

The data can be reproduced with activation energies around 4000 cm^{-1} for $^1\text{D}_2$ in CaTiO_3 , 3500 cm^{-1} for $^1\text{D}_2$ in YVO_4 , 5500 cm^{-1} for $^1\text{D}_2$ in LaVO_4 , and 4500 cm^{-1} for $^3\text{P}_0$ in LaVO_4 . We point out that, especially in the latter case, the curves could be affected by the presence of multiphonon relaxation, which would introduce an additional relaxation channel and complicate the situation.^[15] Moreover, the thermalization of the $^3\text{P}_1$ level, located just above $^3\text{P}_0$, could also introduce further complications. Given all these problems, the current activation energies have to be considered only as indicative of the magnitude of the energy barrier; however they can be compared with the value of 590 cm^{-1} obtained from the low-temperature data relative to the emission from $^3\text{P}_0$ in CaTiO_3 , for which the quenching is much stronger.^[16] This comparison shows that the activation energy seems to be rather strongly dependent on the host crystal. In fact, it is reasonable to expect that the details of the IVCT potential energy curve will depend on the optical electronegativity of M ,^[7] on the $\text{Ln}–M$ distance in the crystal,^[7] and on the stiffness of the crystal lattice,^[17] and this will strongly influence the activation energy to the crossover point.

Tb³⁺-Doped Crystals

As mentioned above, it is well-known that YVO₄:Tb³⁺ is nonluminescent as the Tb³⁺ emission is quenched by IVCT.^[10] Similarly, we point out that in the current study, no luminescence has been observed for CaTiO₃:Tb³⁺ at room temperature. In contrast, LaVO₄:Tb³⁺ appears to be luminescent, but the weak intensity at room temperature did not allow us to measure satisfactory continuous wave luminescence spectra in the experimental conditions available. However, we present in Figure 6 a 300 K emission spectrum of this crystal under laser excitation at 485 nm; it is composed of features assigned to the $^5D_4 \rightarrow ^7F_J$ ($J = 5, 4, 3$) transitions. This result indicates that quenching of 5D_4 by IVCT is weaker in LaVO₄ than in YVO₄.

The investigation on Tb³⁺-doped hosts was extended to the fergusonite type crystals YNbO₄ and YTaO₄. Figure 7a shows the 300 K emission spectra of these crystals doped with Tb³⁺, measured upon excitation in the UV. For comparison, the spectrum of YPO₄:Tb³⁺ is also shown. It is worth noting that the three materials contain the same concentration of the dopant (i.e., 0.5%). Whereas the YPO₄ spectrum clearly shows emission bands assigned to transitions originating from both 5D_4 and 5D_3 , the other two crystals only show strong transitions originating from 5D_4 , indicating that 5D_3 is quenched. This different behavior cannot be due to multiphonon relaxation, as the highest vibrational wavenumber is higher in YPO₄ (1058 cm^{-1}) than in YNbO₄ (830 cm^{-1}) and YTaO₄ (825 cm^{-1}), nor to cross-relaxation, as this should have approximately the same probability in the three crystals having the same low dopant concentration. For this reason, we attribute the processes quenching the 5D_3 emission in YNbO₄ and YTaO₄ to an IVCT mechanism. In the excitation spectra (Fig. 7b), the features located around 380 and 490 nm are assigned to *f-f* transitions of Tb³⁺ ($^7F_6 \rightarrow ^5D_3$ and $^7F_6 \rightarrow ^5D_4$, respectively); however, the broad bands peaking at

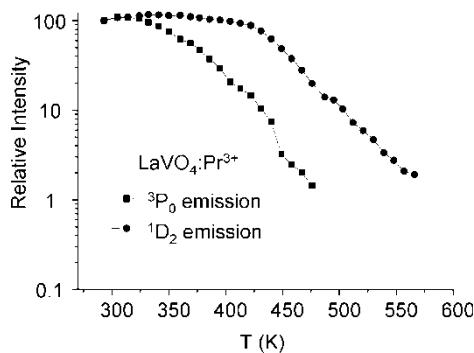


Figure 5. Temperature dependence of 3P_0 and 1D_2 emission intensity in LaVO₄:1% Pr³⁺. Excitation was at 320 nm. The lines are a guide for the eye.

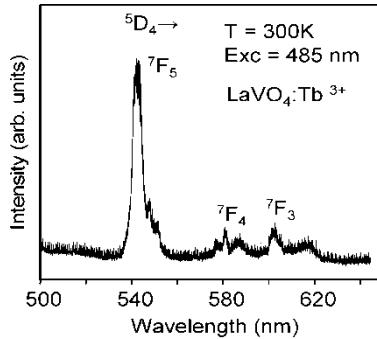


Figure 6. Laser-excited luminescence spectra of $\text{LaVO}_4:0.5\%\text{Tb}^{3+}$ and $\text{YPO}_4:0.5\%\text{Tb}^{3+}$ at 300 K. Excitation was at 485 nm, the delay time was 200 μs . The emission bands are assigned to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 5, 4, 3$) transitions.

~ 310 nm for YNbO_4 and ~ 275 nm for YTaO_4 cannot be assigned to $f\text{-}f$ transitions. We note that in the two cases, the spectral features are not exactly symmetrical, so that the observed line shape could be due to the superposition of several components. It is important to note that the intrinsic excitation bands of the two undoped host crystals are located at about 265 nm for YNbO_4 and 230 nm for YTaO_4 ^[18] and thus cannot explain the origin of the features lying at longer wavelength. Similar to

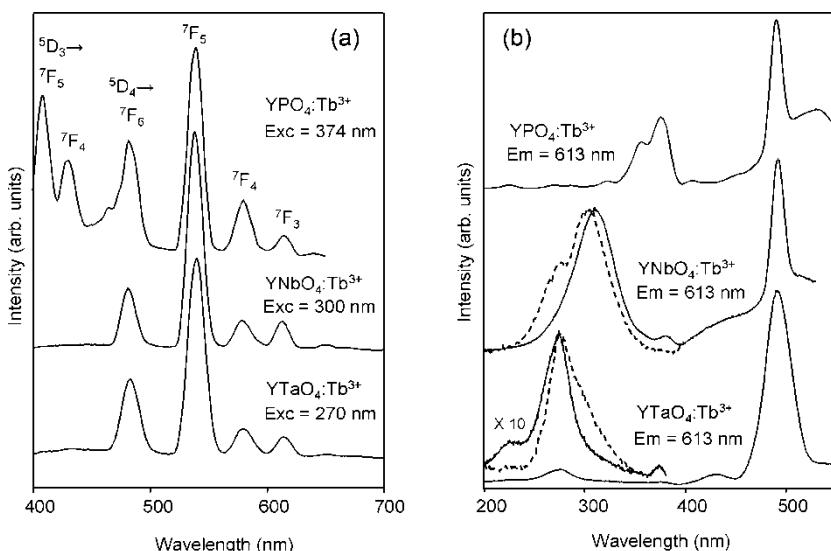


Figure 7. (a) Emission and (b) excitation spectra of $\text{YPO}_4:0.5\%\text{Tb}^{3+}$, $\text{YNbO}_4:0.5\%\text{Tb}^{3+}$, and $\text{YTaO}_4:0.5\%\text{Tb}^{3+}$ at 300 K. In (b), the 300 K excitation spectra of $\text{YNbO}_4:0.5\%\text{Pr}^{3+}$ and $\text{YTaO}_4:0.5\%\text{Pr}^{3+}$ are also shown (dashed lines).

the case of Pr^{3+} -doped YNbO_4 and YTaO_4 , the weak contribution of the host bands to the excitation spectra indicates relatively inefficient host sensitization.^[6,19] It is possible to assign the broad bands peaking at ~ 310 nm for YNbO_4 and ~ 275 nm for YTaO_4 to IVCT transitions, but we point out that also interconfigurational f - d transitions are expected to lie in this region.^[20] The situation is analogous to the case of Pr^{3+} -doped YNbO_4 and YTaO_4 (Fig. 7), but we note that in the case of YNbO_4 , the broad band is at lower energies in the case of Tb^{3+} than for Pr^{3+} . On the basis of the model proposed by Dorenbos,^[20] the first spin-allowed f - d transition of Tb^{3+} should lie about 1000 cm^{-1} above the first f - d transition of Pr^{3+} . On the other hand, a red shift of the IVCT band moving from Pr^{3+} to Tb^{3+} is in qualitative agreement with a lower value of the optical electronegativity of Tb^{+4} ions (2.55) compared with Pr^{+4} ions (2.6).^[21]

In the case of YPO_4 , the f - d transitions are predicted to lie outside the spectral range under investigation. For the sake of comparison, the excitation spectra of $\text{YNbO}_4:\text{Pr}^{3+}$, and $\text{YTaO}_4:\text{Pr}^{3+}$, where a similar situation occurs, are also shown in Figure 7b. We also note that the current excitation spectrum for $\text{YTaO}_4:\text{Tb}^{3+}$ is similar to the one reported by Blasse and Bril for $\text{GdTaO}_4:\text{Tb}^{3+}$ with a band peaking around 260–270 nm.^[22]

The room temperature decay curves of the $^5\text{D}_4$ emission of Tb^{3+} in the materials under investigation are shown in Figure 8. In the case of $\text{YPO}_4:\text{Tb}^{3+}$, included for comparison, and $\text{YTaO}_4:\text{Tb}^{3+}$, the curves are perfectly exponential, with decay times of 2.0 and 0.90 ms, respectively. The value obtained for YTaO_4 is comparable with the one reported by Blasse and Bril for Tb^{3+} -doped tantalates with the fergusonite structure.^[22] The other crystals are characterized by decay curves slightly deviating from an exponential behavior; for this reason, average decay times were evaluated using the equation:

$$\tau_{\text{avg}} = \frac{\int tI(t)dt}{\int I(t)dt} \quad (2)$$

The average decay times are 0.59 ms for $\text{YNbO}_4:\text{Tb}^{3+}$ and 0.37 ms for $\text{LaVO}_4:\text{Tb}^{3+}$. These values appear to be shorter than the decay times usually observed for Tb^{3+} (1 ms or more in anhydrous inorganic crystals) and are possibly indicative of IVCT quenching of the $^5\text{D}_4$ level, as already suggested by Blasse for YNbO_4 , on the basis of the reduced efficiency of the $^5\text{D}_4$ emission.^[1]

Figure 9 shows the temperature dependence of the $^5\text{D}_4$ emission intensity for $\text{YPO}_4:\text{Tb}^{3+}$, $\text{YNbO}_4:\text{Tb}^{3+}$, and $\text{YTaO}_4:\text{Tb}^{3+}$. It was not possible to collect meaningful data for $\text{LaVO}_4:\text{Tb}^{3+}$, due to its weak emission intensity. Inspection of the figure shows that the quenching of the Tb^{3+} emission in YPO_4 is weak, presumably due to multiphonon relaxation across the large energy gap typical of Tb^{3+} . In the case of YTaO_4 , the thermal quenching is even weaker than for YPO_4 , indicating that the eventual IVCT quenching of $^5\text{D}_4$ is not efficient in this material, and that multiphonon relaxation is less

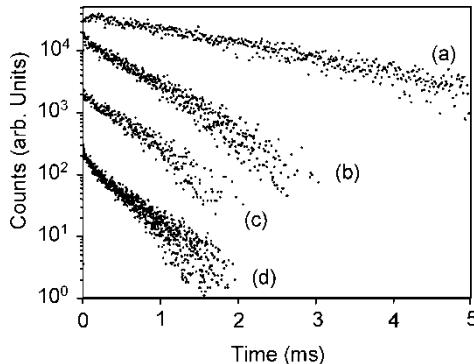


Figure 8. The 300 K decay curves of the 5D_4 emission in (a) $YPO_4:0.5\%Tb^{3+}$, (b) $YTaO_4:0.5\%Tb^{3+}$, (c) $YNbO_4:0.5\%Tb^{3+}$, and (d) $LaVO_4:1\%Tb^{3+}$. Excitation was at 485 nm.

probable than for the phosphate, as expected on the basis of the lower vibrational wavenumbers (see above). On the other hand, thermal quenching appears to be efficient for $YNbO_4:Tb^{3+}$; this quenching is attributed to crossover to the IVCT state, in agreement with the short room temperature decay time observed for 5D_4 .

The temperature dependence of the 5D_4 emission intensity of $YNbO_4:Tb^{3+}$ could be reproduced using Eq. (1) and an activation energy of about 4500 cm^{-1} . In this case, the model is expected to be more strictly applicable than for Pr^{3+} , due to the weak multiphonon relaxation typical of 5D_4 and the absence of thermalization of upper lying states. The activation energies are again expected to be dependent on the nature of the host crystal of the Tb^{3+} ion and will significantly influence the efficiency of the quenching of the 5D_4 level, in crystals in which the IVCT mechanism is operative.

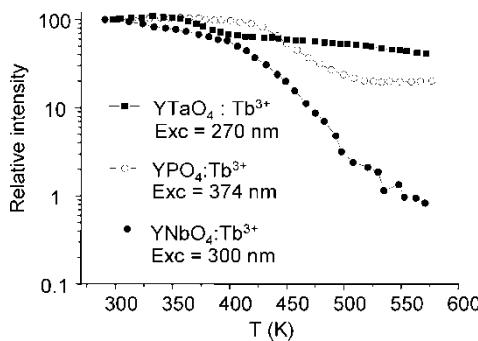


Figure 9. Temperature dependence of 1D_2 emission intensity in $YPO_4:0.5\%Tb^{3+}$, $YTaO_4:0.5\%Tb^{3+}$, and $YNbO_4:0.5\%Tb^{3+}$. Excitation was at 445 nm. The lines are a guide for the eye.

CONCLUSIONS

In this study, we have investigated the IVCT quenching of the Pr^{3+} and Tb^{3+} luminescence in various crystals containing closed shell transition metal ions, such as titanates, vanadates, niobates, and tantalates. In the case of Pr^{3+} , thermal quenching results have clearly shown that in some hosts, not only the ${}^3\text{P}_0$ level but also ${}^1\text{D}_2$ suffers from crossover quenching to the IVCT state. On the other hand, we have presented evidence that the IVCT mechanism effectively quenches the ${}^5\text{D}_3$ level of Tb^{3+} , and in some hosts also ${}^5\text{D}_4$. It has been possible to obtain information about the activation energies of the thermal quenching and therefore on the relative position of the IVCT potential curve with respect to the ones belonging to the $4f^n$ excited states. In the frame of the preliminary approach used in the current work, the situation appears to have some similarities for the two ions under investigation. In fact, the position of the IVCT band does not seem to be very different, and also two excited levels (${}^3\text{P}_0$ and ${}^1\text{D}_2$ for Pr^{3+} , ${}^5\text{D}_3$ and ${}^5\text{D}_4$ for Tb^{3+}) are affected by the quenching mechanism for both ions. However, the relatively high energy position of ${}^5\text{D}_3$ is such that this level is more efficiently quenched than ${}^3\text{P}_0$. Further experiments are under progress to estimate in more details the efficiency of the IVCT quenching of ${}^3\text{P}_0$ and ${}^5\text{D}_4$ levels, which have similar energy position in the same hosts.

In conclusion, the current results have clearly evidenced that detailed information about the IVCT states is necessary for the design of red-emitting and green-emitting phosphors respectively based on Pr^{3+} and Tb^{3+} ions doped into lattices such as titanates, vanadates, niobates, and tantalates. In this connection, additional thermal quenching experiments are being extended to other series of host materials.

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