

Sensitization of Tb³⁺ Luminescence with Ce³⁺ in LaOBr: Tb³⁺, Ce³⁺

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Luminescence emission and uv-excitation properties of LaOBr: Tb³⁺, LaOBr: Ce³⁺, and LaOBr: Tb³⁺, Ce³⁺ phosphors were studied. The visible emission spectra of La_{0.995}Tb_{0.005}OBr consists of ⁵D_{3,4} → ⁷F₃₋₈ transitions in the wavelength range of 410–630 nm. The excitation of the Tb³⁺ ion gives a broad 4*f* → 5*d* transition band at 254 nm and weaker 4*f* → 4*f* transition lines above 300 nm. The uv-excitation and emission of La_{0.995}Ce_{0.005}OBr at 290, 315, 355 (excitation), and 440 nm (emission) originate from transitions between the 4*f*-ground state and the four crystal field components of the 5*d* ²D excited state. The sensitization of Tb³⁺ luminescence in LaOBr with Ce³⁺ at varying concentrations is described and discussed. With increasing Ce³⁺ concentration the ⁵D₃ → ⁷F transitions of Tb³⁺ quench totally and the ⁵D₄ → ⁷F transitions begin to quench gradually. The excitation spectrum of the ⁵D₄ → ⁷F₅ transition of Tb³⁺ consists of four bands due to Tb³⁺ and Ce³⁺, of which the three Ce³⁺ bands increase in intensity and the Tb³⁺ band decreases as the Ce³⁺ concentration is increased.

Introduction

The two rare earth elements terbium and cerium, combined as activators in LaOBr-matrix, give an efficient green-emitting phosphor, which can be used for X-ray intensifying screens (1, 2). No full studies concerning the emission and excitation properties of the LaOBr: Tb³⁺, Ce³⁺ system have been published, and there are only a few, incomplete studies on the properties of separate LaOBr: Tb³⁺ (3–6) and LaOBr: Ce³⁺ phosphors (7, 8). The energy transfer in Tb³⁺, Ce³⁺ activated systems has been studied in various matrices, for example in YOCl, where the transfer was observed to be weak (9). The results for YOCl may not be compared with those for LaOBr, however, because of the strong dependence of Ce³⁺ luminescence on the host matrix (10).

The visible emission spectrum of the

Tb³⁺ ion in LaOBr-matrix consists of sharp peaks in the wavelength range of 400–700 nm originating from ⁵D_{3A} → ⁷F(4*f* → *f*) transitions (3). The uv-excitation spectrum contains a broad 4*f* → 5*d* transition band with a maximum at 258 nm (3).

According to Blasse and Brill (7) the broad band emission (λ_{max} 440 nm) of the Ce³⁺ ion in LaOBr-matrix originates from 5*d* → 4*f* transitions, while uv-excitation involves, as in Tb³⁺, 4*f* → 5*d* transitions from the ground 4*f* level ²F_{5/2} to the excited 5*d* levels ²D.

The aim of the present work was to study the effect of Ce³⁺ at various concentrations on the emission and uv-excitation spectra of LaOBr: Tb³⁺, Ce³⁺ phosphors.

Experimental

The lanthanum oxide (Kemira Oy, Oulu,

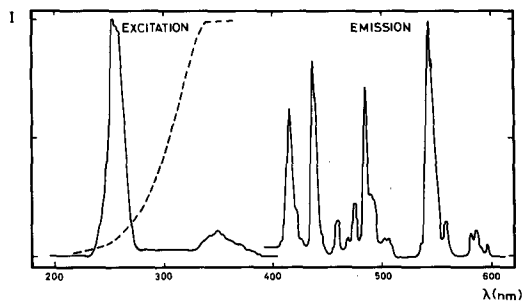


FIG. 1. Emission and uv-excitation spectra of Tb^{3+} -activated $LaOBr$ ($x_{Tb} = 0.005$, $\lambda_{em} = 543$ nm, $\lambda_{ex} = 260$ nm).

Finland) had a purity of 99.99%. The oxide was dissolved in nitric acid and the activators were introduced in such quantities that the terbium concentration was always 0.5% and the cerium concentration varied between 0.01 and 5%. RE ions were coprecipitated as oxalates which were ignited at 1050°C for 1 hr. The conversion of the oxide mixture formed during ignition to oxybromide was carried out as described earlier (11). The formation of oxybromide was verified for each sample by X-ray powder diffraction.

Luminescence spectra of the oxybromide were measured with a Hitachi Perkin-Elmer fluorescence spectrometer type MPF-3A. The excitation source was a xenon arc lamp. Filters UV-D25 (excitation) and UV-39 (emission) were used.

The wavelength dependence of Xe lamp intensity (Fig. 1; dashed curve) was measured with the aid of sodium salicylate (12). This curve can be used to correct the excitation spectra in Figs. 1–3 and 5. Decay times were not measured due to the short duration of cerium $5d \rightarrow 4f$ transitions ($< 10^{-7}$ sec) (7).

Results and Discussion

$LaOBr: Tb^{3+}$

The emission and uv-excitation spectra of $La_{0.995}Tb_{0.005}OBr$ are presented in Fig. 1.

The broad excitation band with a maximum at 254 nm originates from the spin allowed ${}^7F \rightarrow {}^7D$ ($4f \rightarrow 5d$) transitions or the spin forbidden ${}^7F \rightarrow {}^9D$ transitions (3). The much weaker peaks in the long wavelength range are due to $4f \rightarrow 4f$ transitions.

The ${}^5D_3 \rightarrow {}^7F_{4,5}$ (440 and 420 nm) and ${}^5D_4 \rightarrow {}^7F_{5,6}$ (540 and 485 nm) transitions dominate the visible emission spectrum of $LaOBr: Tb^{3+}$ but other ${}^5D_3 \rightarrow {}^7F$ and ${}^5D_4 \rightarrow {}^7F$ transitions can be observed, too (Fig. 1).

$LaOBr: Ce^{3+}$

According to Prather (13) the excited $5d$ state 2D of the Ce^{3+} ion splits into four states in a crystal field of C_{4v} symmetry. Transitions to or from all of these states can be observed in the uv-excitation and emission spectra of $La_{0.995}Ce_{0.005}OBr$ (Fig. 2). The presence of three excitation bands (290, 315, and 355 nm) in Fig. 2 is in disagreement with a previous study (7) where only two bands were found.

The Ce^{3+} emission usually shows two bands (8) due to the duplet character of the $4f$ ground state (${}^2F_{5/2}$ and ${}^2F_{7/2}$ states) but splitting is not observed either in $LaOBr$ -matrix or in $LaOCl$ -matrix (8).

$LaOBr: Tb^{3+}, Ce^{3+}$

Typical emission and uv-excitation spectra of $LaOBr: Tb^{3+}, Ce^{3+}$ phosphors are

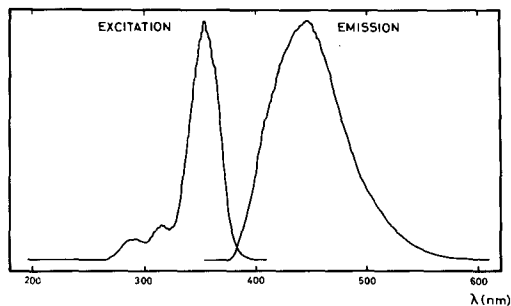


FIG. 2. Emission and uv-excitation spectra of Ce^{3+} -activated $LaOBr$ ($x_{Ce} = 0.005$, $\lambda_{em} = 440$ nm, $\lambda_{ex} = 350$ nm).

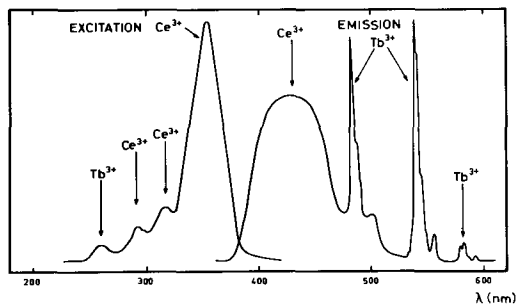


FIG. 3. Emission and uv-excitation spectra of Tb³⁺- and Ce³⁺-activated LaOBr ($x_{Tb} = x_{Ce} = 0.005$, $\lambda_{em} = 543$ nm, $\lambda_{ex} = 313$ nm).

shown in Fig. 3. The excitation spectrum of Tb³⁺ $^5D_4 \rightarrow ^7F_5$ transition at 543 nm consists of four bands due to the $4f \rightarrow 5d$ transitions of Tb³⁺ and Ce³⁺ as indicated in Fig. 3. The presence of Ce³⁺ excitation bands at 290, 315, and 355 nm suggests energy transfer from Ce³⁺ to Tb³⁺.

In LaOBr: Tb³⁺, Ce³⁺ the Ce³⁺ emission band overlaps the forbidden $4f \rightarrow 4f$ transitions of Tb³⁺ allowing resonance energy transfer from Ce³⁺ to Tb³⁺ (9). Accordingly, the $^5D_3 \rightarrow ^7F$ transitions can be observed, together with the $^5D_4 \rightarrow ^7F$ transitions, in the emission spectrum of LaOBr: Tb³⁺, Ce³⁺. With increasing Ce³⁺ concentration, however, the $^5D_3 \rightarrow ^7F$ transitions quench totally (Fig. 3), while the Ce³⁺ emis-

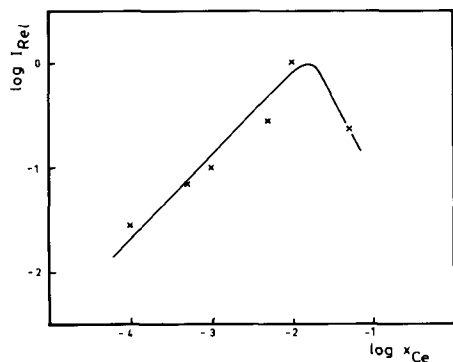


FIG. 4. The effect of Ce³⁺ concentration on the intensity of emission from terbium $^5D_4 \rightarrow ^7F_5$ (543 nm) transition ($\lambda_{ex} = 315$ nm (Ce³⁺), $x_{Tb} = 0.005$).

sion at 440 nm gains strength. Evidently the emission from Ce³⁺ becomes more favorable than the energy transfer Ce³⁺ \rightarrow Tb³⁺ and emission for 5D_3 states of Tb³⁺.

Possible energy transfer from the lowest 2D level of Ce³⁺ to the 5D_4 levels of Tb³⁺ is indicated by the overlap of emission and excitation bands (Figs. 1 and 2). Unlike the $^5D_3 \rightarrow ^7F$ transitions the $^5D_4 \rightarrow ^7F$ transitions are not totally absent but quench gradually above the Ce³⁺ concentration of 1% when the Ce³⁺ band excitation wavelength is 315 nm (Fig. 4). At this Tb³⁺ concentration (0.5%) self-quenching does not play a role as seen in pure LaOBr: Tb³⁺ phosphors where a much higher concentration of Tb³⁺ (>5%) is needed for quenching of $^5D_4 \rightarrow ^7F$ transitions (6). This phenomenon is most likely due to Ce³⁺ self-quenching.

The influence of Ce³⁺ concentration on the uv-excitation of the $^5D_4 \rightarrow ^7F_5$ transition of Tb³⁺ in LaOBr: Tb³⁺, Ce³⁺ phosphors can be seen in Fig. 5. With increasing Ce³⁺ concentration the intensity of the Tb³⁺ excitation band at 254 nm decreases, while at the same time the intensities of the Ce³⁺ excitation bands at 290, 315, and 355 nm increase. At the Ce³⁺ concentration of 5% the excitation spectrum of

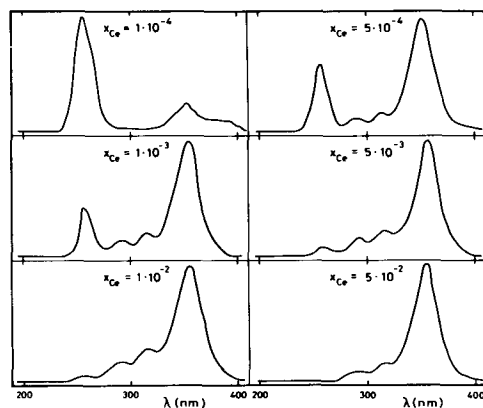


FIG. 5. The effect of Ce³⁺ concentration on the uv-excitation spectra of LaOBr: Tb³⁺, Ce³⁺ ($x_{Tb} = 0.005$, $\lambda_{em} = 543$ nm).

$\text{La}_{0.945}\text{Tb}_{0.005}\text{Ce}_{0.05}\text{OBr}$ is identical to the excitation spectrum of $\text{La}_{0.995}\text{Ce}_{0.005}\text{OBr}$ (Fig. 2), which suggests that the excitation of Tb^{3+} then occurs totally through the excitation of Ce^{3+} and the energy transfer $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$.

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References

1. J. G. RABATIN, U.S. Pat. 3 617 743 (1971).
2. K. NOMOTO AND R. KUBO, Japan Kokai 76 37 883 (1976).
3. G. BLASSE AND A. BRIL, *Philips Res. Rep.* **22**, 481 (1967).
4. J. G. RABATIN, U.S. Pat. 3 666 676 (1972).
5. J. G. RABATIN, Ext. Abstr. 102, *Electrochem. Soc.*, Spring Meeting, May 12–17, San Francisco 1974.
6. J. HÖLSÄ, M. LESKELÄ, AND L. NIINISTÖ, *Mater. Res. Bull.* **14**, 1403 (1979).
7. G. BLASSE AND A. BRIL, *J. Chem. Phys.* **47**, 5132 (1967).
8. R. A. BUCHANAN, T. G. MAPLE, AND A. F. SKLENSKY, *Ger. Offen.* 2 815 679 (1978).
9. G. BLASSE AND A. BRIL, *J. Chem. Phys.* **47**, 1920 (1967).
10. G. BLASSE AND A. BRIL, *Philips Techn. Rev.* **31**, 304 (1970).
11. J. HÖLSÄ, M. LESKELÄ, AND L. NIINISTÖ, *Thermochim. Acta* **35**, 79 (1980).
12. A. BRIL AND A. W. DE JAGER-VEENIS, *J. Electrochem. Soc.* **123**, 396 (1976).
13. J. L. PRATHER, *NBS Monograph.* **19**, (1961).