



LUMINESCENCE OF YTTRIUM TANTALATE DOUBLY ACTIVATED WITH EUROPIUM AND TERBIUM UNDER X-RAY AND ELECTRON BEAM EXCITATIONS

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Abstract

This paper reports the luminescence spectra of YTaO_4 activated with rare-earth ions, such as Eu^{3+} and Tb^{3+} . The effect of these rare-earth ions on the luminescence of yttrium tantalate phosphors is studied. The luminescent properties are studied under X-ray and electron beam excitations. It is found that, under these excitations, the emission centers of the rare-earth activators (Eu^{3+} , Tb^{3+}) efficiently contribute to the overall luminescence. Color cathodoluminescence images clearly show the dependence of chromaticity on the different activators. These rare-earth activated phosphors exhibiting various luminescence chromaticities are promising materials for optoelectronic applications and for X-ray intensifying screens in medical diagnosis, because they provide a broad variation of visible photoluminescence from blue to red.

Keywords: YTaO_4 , $\text{YTaO}_4:\text{Eu}^{3+},\text{Tb}^{3+}$, cathodoluminescence.

Rezumat

În această lucrare sunt prezentate spectrele de luminescență ale cristalelor de YTaO_4 activate cu ioni de pământuri rare, cum ar fi Eu^{3+} și Tb^{3+} . A fost investigată influența acestor ioni de pământuri rare asupra luminescenței fosforilor de tantalat de ytriu. Proprietățile luminescente au fost studiate la escitare cu raze X și fascicule de electroni. S-a constatat că centrele de emisie ale activatorilor de pământuri rare (Eu^{3+} , Tb^{3+}) contribuie eficient la luminescența generală. Imaginile de catodoluminescență color au arătat în mod clar dependența cromaticității de diferiți activatori. Datorită cromaticităților diferite de luminescență, acești fosfori activați cu pământuri rare sunt materiale promițătoare pentru aplicații optoelectronice, precum și pentru ecranele de intensificare a razelor X în diagnosticul medical, oferind o variație largă a fotoluminescenței vizibile de la albastru până la roșu.

Cuvinte cheie : YTaO_4 , $\text{YTaO}_4:\text{Eu}^{3+},\text{Tb}^{3+}$, catodoluminescență.

1. Introduction

Yttrium tantalate phosphors are of large interest for the manufacture of some medical imaging detectors, especially for conventional radiographic cassettes [1, 2]. These luminescent materials exhibit good X-ray absorption and emit in the ultraviolet and blue region of the electromagnetic spectrum [3]. Yttrium tantalate has three crystal structures: high-temperature tetragonal (scheelite, T-structure), low-temperature monoclinic (fergusonite, M-structure), and another monoclinic form, which is referred to as M' and can be synthesized at lower temperatures (below 1400°C) [1, 4]. In the M'-YTaO₄ structure, tantalum atoms are in a distorted octahedral coordination with six Ta–O bonds, whereas in M-YTaO₄ tantalum atoms are in a tetrahedral coordination. In addition, the unit cell volume of the M' phase is approximately two times smaller than that of the M phase, and the average Ta–O distances are relatively smaller [5, 6]. As a result, the M' phase presents a more efficient charge transfer process that determines superior luminescent emission.

In this paper, rare-earth activators Eu³⁺ and Tb³⁺ were simultaneously incorporated into M'-YTaO₄ structures. The luminescent properties of these phosphors under electron beam and X-ray excitation were studied. Color cathodoluminescence (CCL) images clearly showed the dependence of chromaticity on the different activators.

2. Experimental

2.1. Sample preparation

Samples of YTaO₄ doubly activated with Eu³⁺ and Tb³⁺ were prepared by the solid-state reaction method from a homogeneous mixture consisting of Y₂O₃ and Ta₂O₅. Europium oxide Eu₂O₃ and/or terbium oxide Tb₄O₇ were used in the activator system and Na₂SO₄ as a flux. The mixtures were homogenized in a ball mill in an acetone medium and dried at 70°C. The phosphor samples were baked at 1200°C for 4 h and slowly cooled to room temperature. Finally, the samples were water washed, dried, and then sieved.

2.2. X-ray excited luminescence (XEL) measurements

To study luminescence under X-ray excitation, the powder phosphor samples were illuminated with broadband X-ray radiation. Figure 1 shows that the samples were placed at a position of 45° from the incident X-rays and close to the exit of the Be X-ray window to minimize the loss of X-ray flux by scattering in air. Since the luminescence light spread out to all directions, a collimating lens system was used to effectively collect the light. The emission spectrum was recorded with a spectrometer (SM240, Spectral Products) in a wavelength range of 200–1200 nm.

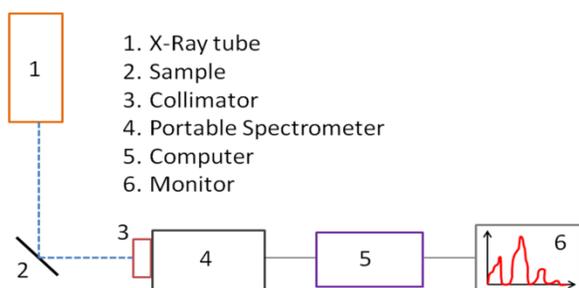


Fig. 1. Schematic diagram of the experimental configuration to study the luminescence of phosphors under X-ray excitation.

2.3. Cathodoluminescence (CL) studies

Sample characterization in CL under electron beam excitation was performed using a special spectrometer [7] installed on the optical microscope port of a standard Camebax electron microprobe. The samples in a powder form were pressed in indium. The CL spectra were recorded at an accelerating voltage of 15 kV and room temperature. The diameter of the beam on the samples was 1 μm . The beam current was 1.5 nA. The color images were recorded with a camera through an optical microscope with a defocused electron beam of about 200 μm .

3. Results and Discussion

3.1. X-ray excited luminescence characterization

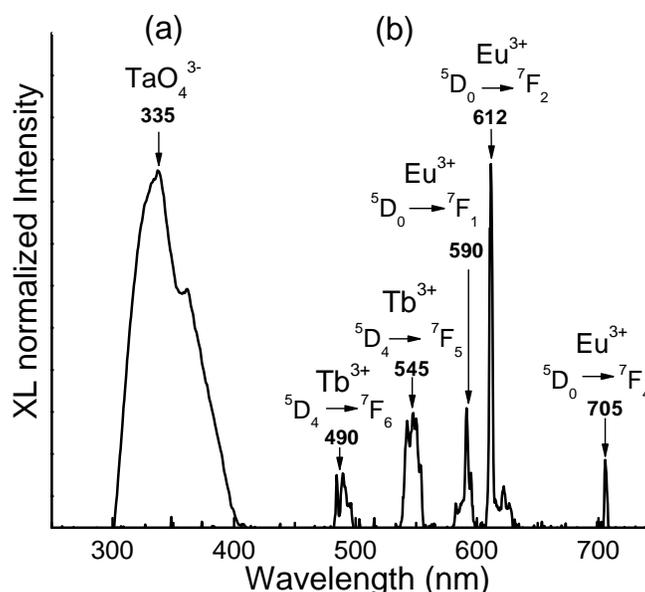


Fig. 2. X-ray emission spectra of the TaO_4^{3-} group in (a) the YTaO_4 and (b) $\text{YTaO}_4:\text{Eu}^{3+}, \text{Tb}^{3+}$ host lattices.

The XEL spectra of the host lattice doubly activated with Eu^{3+} and Tb^{3+} and without activators are shown in Fig. 2. Figure 2a shows the XEL of the YTaO_4 host lattice without activators. The emission peak is localized at 335 nm for YTaO_4 . Figure 2b shows the luminescence spectrum of the host lattices doubly doped with the rare-earth ions. The emission spectra were measured in a range of 200–1200 nm; the peaks were mostly detected in a range of 450–725 nm. The first two peaks at 490 and 545 nm correspond to Tb^{3+} , and the peaks at 590, 612, and 705 nm are the Eu^{3+} contribution to the luminescence.

Figures 2a and 2b (YTaO_4 and $\text{YTaO}_4:\text{Eu}^{3+}, \text{Tb}^{3+}$, respectively) clearly show that the simultaneous incorporation of rare-earth ions, such as Eu^{3+} and Tb^{3+} , which partly substitute the Y ions from the host crystalline lattice, leads to the formation of Eu^{3+} and Tb^{3+} emission centers (Fig. 3).

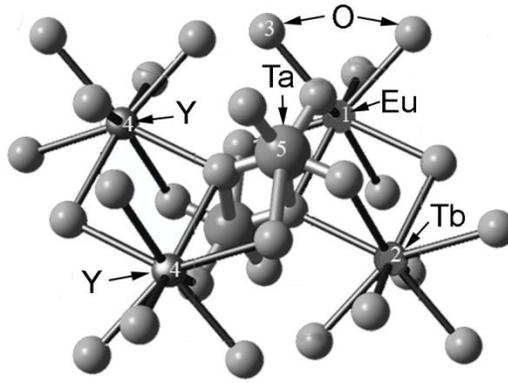


Fig. 3. Crystal structure of YTaO_4 with double activation with Eu^{3+} and Tb^{3+} .

In this case, the excitation energy is first absorbed by the host lattices; the process involves the transition between the 4d-like states of Y and the 2p-like states of O. The absorbed energy can be further transferred to the TaO_4^{3-} groups and at last transferred to the Eu^{3+} or Tb^{3+} centers. It is also possible that, under certain energy conditions, energy transfer between the activators takes place because of the proximity of the $^5\text{D}_4$ (Tb^{3+}) and $^5\text{D}_1$ (Eu^{3+}) energy levels [8]. In this case, the Eu–Tb activator couple can act as a donor–acceptor pair (Fig. 4).

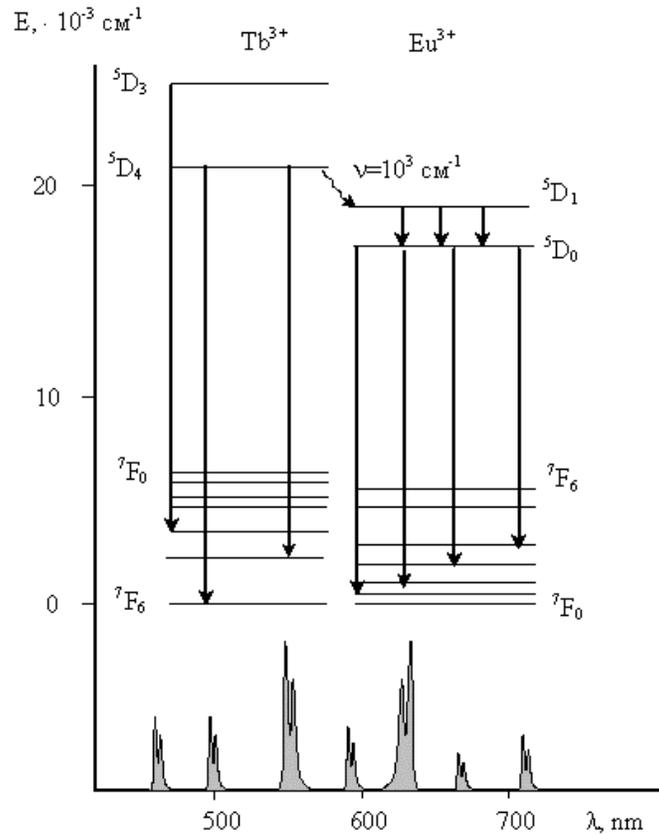


Fig. 4. Schematic representation of energy transfer in YTaO_4 double activated with Tb^{3+} and Eu^{3+} ions.

The molar concentration of the incorporated activators (Eu^{3+} and Tb^{3+}) can be varied to obtain a broad variation of visible photoluminescence.

3.2. Cathodoluminescence spectroscopy and CCL characterization

Under electron beam excitation (CL), the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 1, 2, 3, 4$) and ${}^5\text{D}_1 \rightarrow {}^7\text{F}_1$ emission peaks are observed (Fig. 5). Comparison of Fig. 2b and Fig. 5 shows that the CL and XEL spectra are similar.

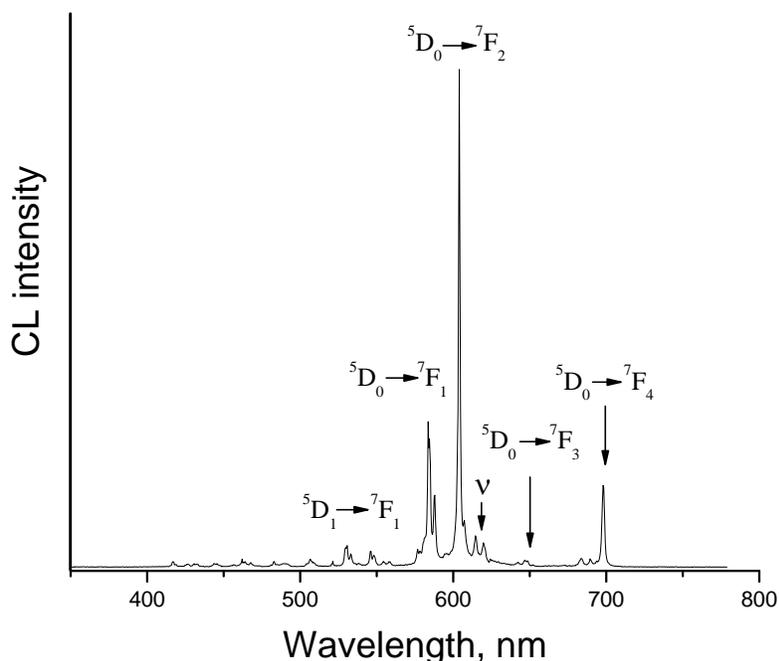


Fig. 5. Emission CL spectra under electron beam excitation of M^3 -type $\text{Y}_{0.95}\text{Eu}_{0.05}\text{TaO}_4$ (v -vibronic transitions).

For the phosphors activated with Eu^{3+} and Tb^{3+} (Figs. 2 and 5), the magnetic dipole transitions are weaker in intensity (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$, respectively). The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition intensity is clearly seen under X-ray and electron beam excitation. Typically, this emission is extremely weak and cannot be seen under UV excitation [9]. Under X-ray and electron beam excitation, the empty upper levels of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ emission can be readily filled. This factor is responsible for the appearance of a visible ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition and the increment of the luminescence intensity of Eu^{3+} and Tb^{3+} emission centers under these high-energy excitations.

Figure 6 shows CCL images (top) of the YTaO_4 host lattice due to the incorporation of europium and terbium activators and their CL spectra (bottom). The CCL image of the host (YTaO_4) lattice without activators is shown in Fig. 6a. A weak blue-violet color is seen due to the small tail of the spectrum after 400 nm in the XEL and CL spectra (Figs. 2a and 6e). Some green spots or speckles are also seen in this image; they suggest the presence of Tb^{3+} -containing particles in the sample. In the case of a heterogeneous material, the local cathodoluminescence

method can be used to avoid these admixtures. By choosing one or more spots in the sample and averaging them, it is possible to elude these undesired peaks, in our case, the ${}^5D_4 \rightarrow {}^7F_5$ and ${}^5D_4 \rightarrow {}^7F_6$ transitions (Fig. 2).

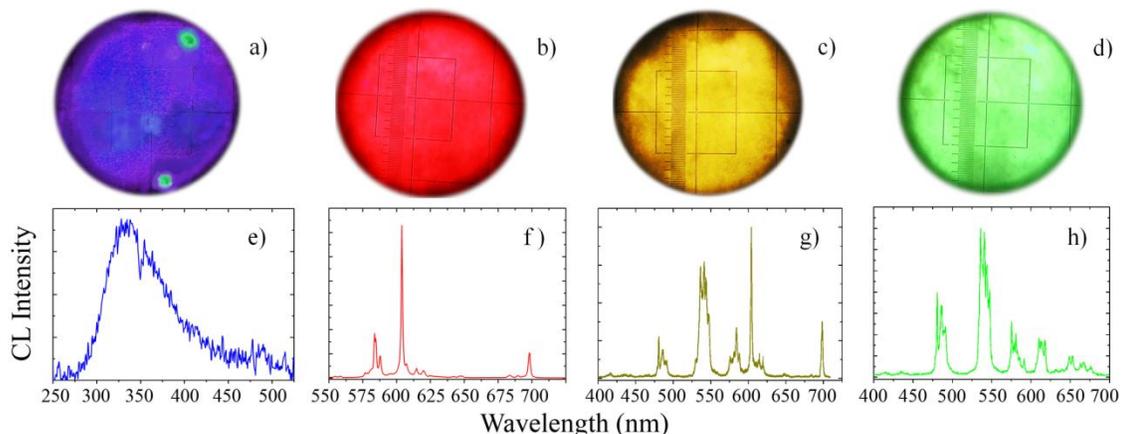


Fig. 6. Color cathodoluminescence images and CL spectra: (a, e) YTaO_4 ; (b, f) $\text{YTaO}_4:\text{Eu}^{3+}$; (c, g) $\text{YTaO}_4:\text{Eu}^{3+},\text{Tb}^{3+}$; and (d, h) $\text{YTaO}_4:\text{Tb}^{3+}$ (in original colors).

Figures 6b and 6d show the manifestation of bright red and green color chromaticity, which is the contribution of the Eu^{3+} and Tb^{3+} rare-earth activators, respectively. In the case of similar molar concentrations of Eu^{3+} and Tb^{3+} ($\text{Eu}^{3+} = 2.5 \text{ mol } \%$, $\text{Tb}^{3+} = 2.5 \text{ mol } \%$), the photoluminescence of the phosphor from the rare-earth ions exhibits a yellowish color in the CL image (Fig. 6c), which results from the mixing of green and red. The proportion of Eu^{3+} and Tb^{3+} in the host lattice can be varied from 0 to 5 mol % to obtain a broad range of different colors between red and green.

4. Conclusions

Owing to the partial substitution of Eu^{3+} and Tb^{3+} activators for Y ions, the emission centers are red-shifted toward longer wavelengths and both activators contribute to the overall luminescence. The molar concentration of the incorporated activators can be varied to obtain a broad variation of visible photoluminescence. This dependence of chromaticity on the concentration of incorporated activators is clearly seen in CCL.

These double activated phosphors can be applied in the X-ray intensifying screens for medical diagnosis with variable photoluminescence colors and in other optoelectronic devices.

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