



Luminescence properties of europium–terbium double activated calcium tungstate phosphor[☆]

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Abstract

Double incorporation of Eu^{3+} and Tb^{3+} ions into a CaWO_4 crystalline lattice modifies the luminescence spectrum due to the formation of new emission centers. Depending on the activators concentration and nature, as well as on the interaction between the activators themselves, the luminescence color can be varied within the entire range of the visible spectrum. Variable luminescence was obtained when $\text{CaWO}_4:\text{Eu,Tb}$ phosphors with 0–5 mol% activator ions were exposed to relatively low excitation energies as UV (365 and 254 nm). Under high energy excitation such as VUV (147 nm) radiation or electron beam, white light has been observed.

This material with controlled properties seems to be promising for the applications in fluorescent lamps, colored lightning for advertisement industries, and other optoelectronic devices.

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1. Introduction

Calcium tungstate phosphor ($\text{CaWO}_4:\text{W}$) was used for a very long time (75 years is an absolute record for a luminescent material!) for the manufacture of X-ray intensifying screens. Self-activated $\text{CaWO}_4:\text{W}$ is an efficient material emitting blue luminescence related to some tetrahedral WO_4 groups of the scheelite host lattice [1,2]. However, the luminescence properties of this classic phosphor could be varied by doping with rare-earth (RE)

ions, and therefore, some new applications could be proposed.

The incorporation of Eu^{3+} or Tb^{3+} ions into the CaWO_4 crystalline lattice modifies the luminescence spectrum, due to the created emission centers that generate the specific red and green light, respectively [3–8]. The simultaneous incorporation of Eu^{3+} and Tb^{3+} ions could permit us to obtain different luminescence colors on the entire visible spectrum. It is also possible that, in certain energy conditions, a process of energy transfer appears because of the proximity of the $^5\text{D}_4$ (Tb^{3+}) and $^5\text{D}_1$ (Eu^{3+}) energy levels. In this case, the Eu–Tb activator couple could work as donor–acceptor pair.

The aim of this work is to synthesize and characterize a $\text{CaWO}_4:\text{Eu,Tb}$ phosphor with variable colors, on the entire

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visible range. Moreover, one attempt will be made to explain quantitatively the cathodoluminescence (CL) and photoluminescence (PL) experimental data, by proposing a mathematical approach based on two- and three-level models.

The interesting properties of $\text{CaWO}_4:\text{Eu,Tb}$ phosphor samples recommend this material for the manufacture of fluorescent lamps for advertising signs, or other color rendering devices.

2. Experimental

$\text{CaWO}_4:\text{RE}$ phosphor samples were prepared by solid state reaction from homogeneous mixtures consisting of luminescent-grade CaWO_4 as host lattice, WO_3 and Eu_2O_3 (99.99% Jansen Chemical) and/or Tb_4O_7 (Johnson Matthey 'Specpure') as activating system, and alkaline salts as flux. CaWO_4 used as precursor in phosphor synthesis was prepared from highly purified CaCl_2 and Na_2WO_4 solutions [9].

The synthesis mixtures containing flux and equivalent amounts of WO_3 and Eu_2O_3 or Tb_4O_7 were homogenized and fired at 900°C . The prepared powders were carefully washed, dried, and sieved.

The incorporation of trivalent RE ions into the CaWO_4 crystalline lattice could proceed in two major ways. Either 2RE^{3+} replace 3Ca^{2+} ions, or a pair of RE^{3+} and M^+ replace 2Ca^{2+} ions (where M^+ = alkaline ion). In our sample preparation conditions, alkaline salt acts as a mineralizing agent and also as a source of compensating ion. Based on this principle, a series of synthesis mixtures was prepared according to the general phosphor formula $\text{Ca}_{1-2x-2y}\text{Eu}_x\text{Tb}_y\text{M}_{x+y}\text{WO}_4$.

PL characteristics were estimated on the basis of emission and excitation spectra registered at room temperature (Xe 500 W lamp) with DARS PRO 5100 PL System (Professional Scientific Instrument Co., Korea). The excitation was performed with a 254 nm UV radiation as well as 365 nm. Low temperature PL measurements (15 K) were also used to explain the energy transfer mechanism. He–Cd laser with excitation wavelength of 325 nm (55 mW) was applied as a light source.

To verify the luminescence properties of synthesized $\text{CaWO}_4:\text{Eu,Tb}$ phosphor in large range of excitations, low voltage CL was carried out at excitation energy of 0.5–1 keV by using a Kimball Physics FRA2X1-2/EGPS-2X1 electron gun system. High voltage 5–40 keV local CL measurements were performed with a special CL spectrometer, combined with a standard 'Camebax' [10].

3. Results and discussion

The dependence of the CL emission intensity on the

activator concentration is shown in Fig. 1. The variation of the main emission peaks of Eu and Tb with their concentration is clearly seen. As a result, the overall chromaticity also changes, strongly depending on the activator ratio and concentration.

Special attention was given to the CL and PL emissions of samples prepared with equal amounts of Eu and Tb. PL spectra illustrating the main peaks of Eu^{3+} ($\lambda = 612$ nm) and Tb^{3+} ($\lambda = 543$ nm) in $\text{CaWO}_4:\text{Eu}(2.5\%),\text{Tb}(2.5\%)$ (sample code F 73) are shown in Fig. 2.

It is well known that luminescence originating from transitions between 4f levels is predominantly due to electric dipole or magnetic dipole interactions [3,11–14]. When RE ions are incorporated into the host crystalline lattice, electric dipole f–f transitions become partially allowed because of an odd crystal field component. The intensity of electric dipole transitions strongly depends on the site symmetry of the host crystal accommodating the RE ions. On the contrary, magnetic dipole f–f transitions are only in a little measure affected by the site symmetry, because they are parity-allowed. If RE ions occupy sites with inversion symmetry, optical transitions inside $4f^n$ configuration are strictly forbidden as electric dipole transition. They can only occur as magnetic-dipole transition,

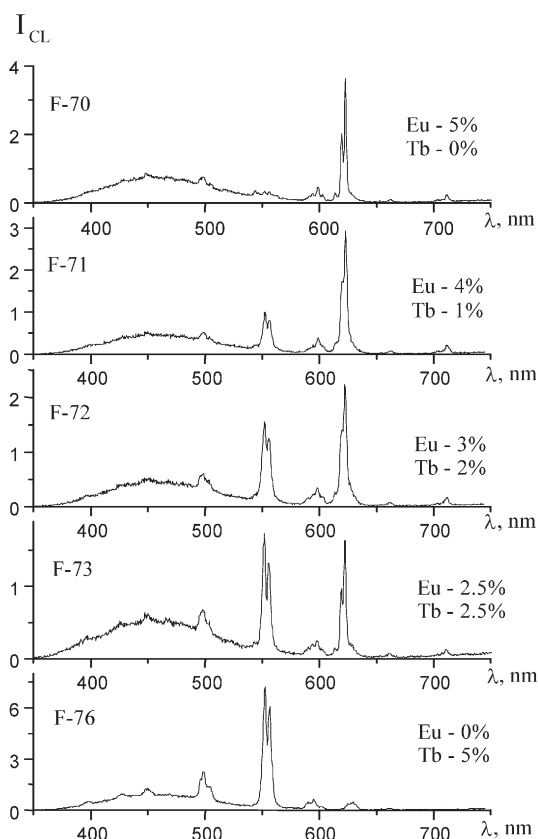


Fig. 1. CL spectra of $\text{CaWO}_4:\text{Eu,Tb}$ samples (codes F70–F76) prepared with different activator concentrations.

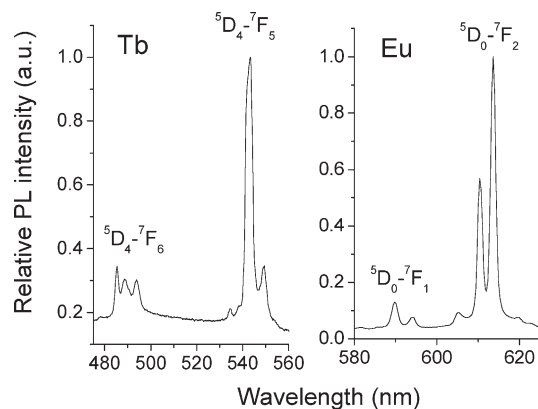


Fig. 2. Fragments of normalized PL spectra of $\text{CaWO}_4:\text{Eu}(2.5\%),\text{Tb}(2.5\%)$ phosphor (excitation with 325 nm laser radiation at 15 K).

which obey the selection rule $\Delta J = 0, \pm 1$. If there is no inversion symmetry at the sites of the RE ions, the electric dipole transitions are no longer strictly forbidden and the transitions with $\Delta J = 0, \pm 2$ are hypersensitive to this effect.

The specific green emission band of Tb centers that is situated at 543 nm is due to electronic transition ${}^5\text{D}_4-{}^7\text{F}_5$ inside Tb^{3+} ion with $4f^7$ configuration. In order to obtain an efficient green luminescence, the activator concentration has to be at least 2.5 mol%.

Emission lines of Eu^{3+} ion correspond to transitions from the excited ${}^5\text{D}_0$ level to the ${}^7\text{F}_J$ ($J = 1, 2, \dots$) levels of the $4f^6$ configuration (transition from $J = 0$ to $J = 0$ being forbidden, because the total orbital momentum is not changed). The weak emission in the vicinity of 590–600 nm is due to the magnetic dipole transition ${}^5\text{D}_0-{}^7\text{F}_1$. The strong emission around 610–630 nm is due to the hypersensitive electric dipole transition of ${}^5\text{D}_0-{}^7\text{F}_2$, induced by the lack of inversion symmetry at the Eu^{3+} site. In order to obtain an efficient red luminescence, the activator concentration of Eu has to be at least 2.5 mol%.

PL spectra and CL spectra are very similar, thus indicates that the mechanism of energy transfer is the same, whatever the excitation is (Fig. 3).

Both investigation methods, namely PL and CL spectroscopy, put in evidence a continuous increase in the red emission band and a considerable decrease in the green emission band. Our previous results showed that no activator quenching effect could be noticed in this concentration range, so that the possible effect of concentration quenching is not to be taken into consideration [15]. To explain the experimental PL and CL results, two- and three-level models taking into account an interaction between Tb^{3+} and Eu^{3+} are proposed (Fig. 4).

For the two-level system (one excited state, namely ${}^5\text{D}_4$ for Tb^{3+} or ${}^5\text{D}_0$ for Eu^{3+} ions and the ground state) the CL intensity from excited level (1) is determined by the population of this level. The population of the excited

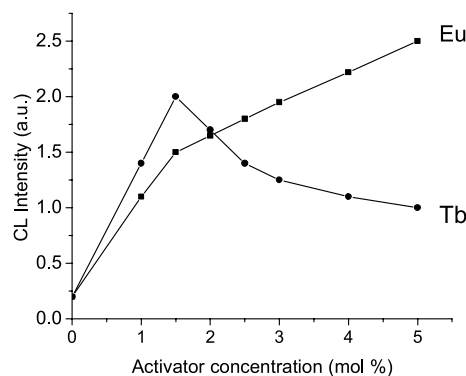
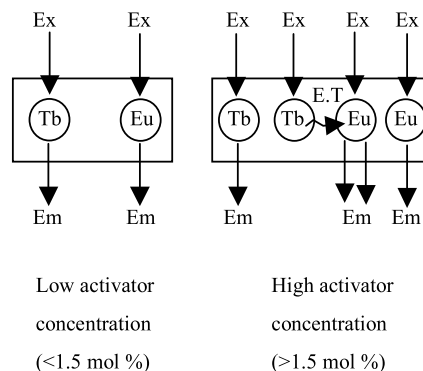


Fig. 3. Dependence of the CL intensity of the specific Eu^{3+} red band at 612 nm and Tb^{3+} green band at 543 nm on activator concentration.

state decreases according to Eq. (1):

$$\frac{dn_1}{dt} = LJn_0 - \tau^{-1}n_1 \quad (1)$$

where n_0 and n_1 give the number of luminescent ions in the ground (0) and excited (1) state, respectively, τ^{-1} is the probability for spontaneous emission $1 \rightarrow 0$, J is an electron beam density, and L is a quantum yield of CL. Taking into account that for the stationary conditions of excitation $dn/dt = 0$, and that the total number of luminescent ions $N = n_1 + n_0$, Eq. (1) becomes:

$$n_1 = \frac{LJN}{LJ + \tau^{-1}} \quad (2)$$

Expression (2) explains the linear dependence of CL intensity on the activator concentration when the concentration is low and the interaction between ions is not to be considered.

At relatively high activator concentration, when different ions are present, e.g. Tb^{3+} and Eu^{3+} , a more complicated three-level model (with two excited states, namely ${}^5\text{D}_4$, ${}^5\text{D}_0$, and the ground state) could be proposed. In this situation, the non-radiative transitions ${}^5\text{D}_4-{}^5\text{D}_1$ and ${}^5\text{D}_1-{}^5\text{D}_0$ are possible. In this case, Tb^{3+} ion serves as donor and Eu^{3+} ion serves as acceptor, and one additional channel for the population of acceptor level appears. Eu^{3+} and Tb^{3+}

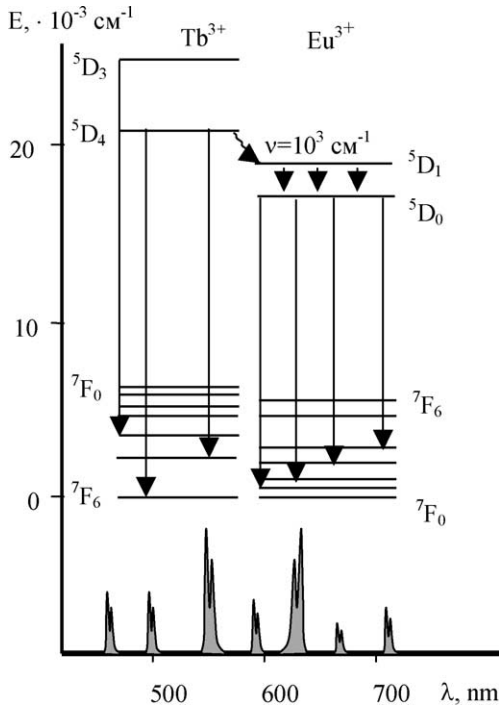


Fig. 4. Schematic representation of the energy transfer in CaWO_4 , double activated with Tb^{3+} and Eu^{3+} ions.

concentration determine the probability of energy transfer. The most probable energy transfer corresponds to the case when the activators concentrations are equal. One can assume that the probability of this process could be given by relation (3):

$$K = \frac{N_{\text{Tb}}N_{\text{Eu}}}{N^2} \quad (3)$$

where N is the sum of Eu^{3+} and Tb^{3+} concentrations.

The additional energy transfer from excited $^5\text{D}_4$ level of Tb reduces the life time of this excited state. For the stationary conditions of excitation, the following expression could be applied:

$$LJn_0 - [\tau^{-1} + (1/N^2)N_{\text{Tb}}N_{\text{Eu}}]n_1 = 0 \quad (4)$$

where n_0 and n_1 are populations of ground state and excited state of Tb ions, respectively. Considering that $n_0 + n_1 = N_{\text{Tb}}$, and $N_{\text{Tb}} + N_{\text{Eu}} = N$, the expression for Tb^{3+} excited level could be given by Eq. (5):

$$I \sim n_1 = \frac{LJN_{\text{Tb}}}{LJ + \tau^{-1} + (1/N^2)N_{\text{Tb}}(N - N_{\text{Tb}})} \quad (5)$$

For Eu^{3+} ions the energy transfer from Tb^{3+} means that one additional channel becomes available. When the stationary conditions of excitation are satisfied, expression (6) could be written as:

$$LJn_0 - [\tau^{-1} - (1/N^2)N_{\text{Tb}}N_{\text{Eu}}]n_1 = 0 \quad (6)$$

where n_0 and n_1 are populations of ground state and excited

state of Eu ions, respectively. Taking into account that $n_0 + n_1 = N_{\text{Eu}}$, and $N_{\text{Tb}} + N_{\text{Eu}} = N$, the equation for excited Eu^{3+} level could be given by

$$I \sim n_1 = \frac{LJN_{\text{Eu}}}{LJ + \tau^{-1} - (1/N^2)N_{\text{Eu}}(N - N_{\text{Eu}})} \quad (7)$$

Comparing Eqs. (5) and (7), one can conclude that when the interaction between Tb^{3+} and Eu^{3+} is taken into consideration, the luminescence intensity from Eu centers is higher than from Tb ones.

If the condition $LJ \gg \tau^{-1} - (1/N^2)N_{\text{Eu}}(N - N_{\text{Eu}})$ is satisfied, the luminescence intensity could be described as:

$$I \sim n = N_{\text{Eu}} \quad (8)$$

Hence, according to the proposed model, the Tb^{3+} emission intensity decreases non-linearly, whereas the Eu^{3+} emission intensity increases linearly with activator concentration.

These calculations are in agreement with our experimental data, as shown in Fig. 3. When Eu^{3+} and Tb^{3+} were simultaneously introduced in equal amounts at relatively low concentration (up to 1.5%), the linear dependence can be noticed and the mutual activators interaction need not be accounted. The simple two-level model could be used in this case (Eqs. (1) and (2)). At higher concentration the activators interaction has to be taken into consideration to explain the results, and Eqs. (5)–(8) are to be applied.

The proposed models are confirmed by numerous measurements with different excitations such as high and low voltage CL or PL, including VUV.

In addition, other interesting properties of $\text{CaWO}_4:\text{Eu},\text{Tb}$ phosphors were revealed by CL and PL measurements. The chromaticity coordinates of luminescence shown by our samples under different excitations were determined. The chromaticity CIE diagram presented in Fig. 5 shows the various luminescence colors of some of our samples.

Every natural color could be identified by (x, y) coordinates that are disposed inside the ‘chromatic shoe’ representing the saturated colors. Luminescence colors of self-activated ($\text{CaWO}_4:\text{W}$), terbium-activated ($\text{CaWO}_4:\text{Tb}$) and europium-activated ($\text{CaWO}_4:\text{Eu}$) phosphors are placed in the blue, green or red corner, respectively. The chromatic co-ordinates of the luminescence of these ‘simple’ phosphors are in a little measure affected by the energy of exciting radiation.

Different situation occurs when calcium tungstate is double activated with terbium and europium ions. In this case, the luminescence color position depends not only on the activator concentration and ratio, but also, on the excitation energy. When excitation is performed with radiation whose energy is not high enough to excite the host lattice ($\lambda_{\text{exc}} = 365$ nm, for example), the interaction between Eu^{3+} and Tb^{3+} follows the proposed model and PL colors are located between the two extreme points corresponding to F70 and F76 samples. For high excitation energy such as VUV ($\lambda_{\text{exc}} = 147$ nm) radiation and cathode-ray, PL and CL color co-ordinates are disposed

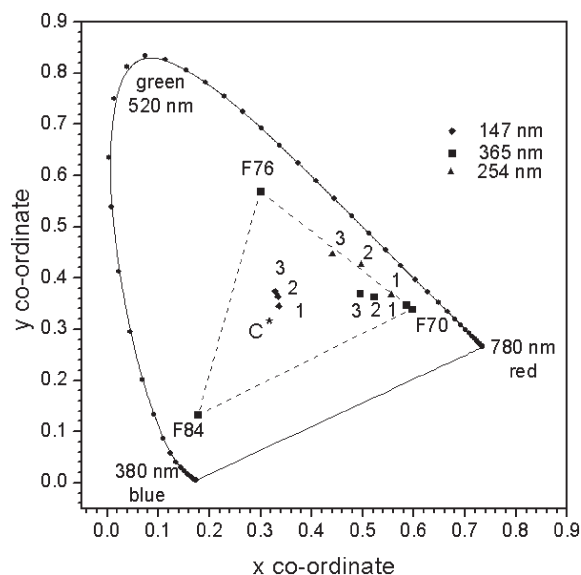


Fig. 5. Chromatic map of some double activated samples (1–3) under different PL excitations, in comparison with self- and single activated calcium tungstate under 254 nm excitation. 1—F83 [$\text{CaWO}_4\text{:Eu}(5\%),\text{Tb}(5\%)$]; 2—F73 [$\text{CaWO}_4\text{:Eu}(2.5\%),\text{Tb}(2.5\%)$]; 3—F85 [$\text{CaWO}_4\text{:Eu}(1.5\%),\text{Tb}(1.5\%)$]; F70— $\text{CaWO}_4\text{:Eu}(5\%)$; F76— $\text{CaWO}_4\text{:Tb}(5\%)$; F84— $\text{CaWO}_4\text{:W}$.

well inside the F70–F76–F84 triangle, and a more complicated process of energy transfer with the host–lattice participation, could be envisaged. In certain conditions, white light can be observed.

4. Conclusion

The double activation of CaWO_4 with Tb^{3+} and Eu^{3+} , in the presence of alkaline salts as flux, permitted us to synthesize phosphors with variable chromatic emissions. CL and PL spectroscopy put in evidence the mutual interaction between the two activating ions. The proposed method and compositions offers a simple, rapid, and effective way to change the emitting colors of phosphors in all visible range by changing the activator concentration or excitation energy.

Variable luminescence colors could be obtained when calcium tungstate phosphors containing 0–5 mol% activator ions were exposed to relatively low excitation energies, such as 365 or 254 nm ultraviolet radiations. Under high-

energy excitation such as VUV (147 nm) radiation or electron beam, white light could be observed. Due to this chromatic variability, $\text{CaWO}_4\text{:Eu,Tb}$ powders are potentially utilizable in the manufacture of fluorescent lamps for advertising signs, or other color rendering devices.

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