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On the synthesis of europium or terbium activated calcium tungstate phosphors

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ABSTRACT

Utilisation of luminescent substances in various optoelectronic devices depends on their luminescent properties and sensitivity to various excitation radiation as well as on particle size distribution and crystalline structure of luminous powders. Calcium tungstate phosphors are well excited with roentgen radiation, so that they are largely used for manufacture of X-ray intensifying screens. Being sensitive to short UV-radiations as well, they could be utilised in Plasma Display Panels or in advertising signs fluorescent tubes. In order to diversify the utilisation possibilities of this tungstate class, luminescent powders based on $\text{CaWO}_4:\text{Eu}^{3+}$ and $\text{CaWO}_4:\text{Tb}^{3+}$ were synthesised and characterised. As compared with the starting self-activated phosphor, larger excitation wavelength domain and emission colours from blue-to-green-to-yellow-to-red were obtained. The good UV excitability and variable luminescence colour recommend these phosphors for optoelectronic device manufacture.

Keywords: phosphors, calcium tungstate, luminescent substances, europium, terbium, Eu^{3+} ions, Tb^{3+} ions.

1. INTRODUCTION

Utilisation of luminescent substances in various optoelectronic devices depends on their luminescent properties and sensitivity to various excitation radiation as well as on particle size distribution and crystalline structure of luminous powders. The well-known self-activated calcium tungstate ($\text{CaWO}_4:\text{W}$) is still an efficient material for X-ray image rendering (X-ray intensifying screens) and coloured lighting (advertisements). Its characteristic blue luminescence is related to some tetrahedral WO_4 groups of the scheelite host lattice.^{1,2}

In order to diversify the utilisation possibilities of this tungstate class, luminescent powders based on $\text{CaWO}_4:\text{Eu}^{3+}$ and $\text{CaWO}_4:\text{Tb}^{3+}$ were synthesised and characterised. Rare-earth ions are successful and still promising activating species.³ There are few information in the literature about rare-earth incorporation into the calcium tungstate powder lattice. The literature data refer mainly to the light emission of $\text{CaWO}_4:\text{RE}$ single crystals, that are materials of great interest for solid state lasers and masers.⁴

The incorporation of Eu^{3+} or Tb^{3+} -ions into CaWO_4 lattice modifies the luminescence colour by forming new luminescence centres. Consequently, these phosphor powders could be used for the manufacture of high and low pressure lamps or Plasma Display Panels.⁵ Our previous works showed that, depending on the activator nature and concentration, the colour of the apparent luminescence could be varied on the entire visible spectrum from blue-to-green-to-red.^{6,7}

This paper presents a comparison between luminescent properties of rare-earth activated calcium tungstate phosphors, namely $\text{CaWO}_4:\text{Eu}^{3+}$ or $\text{CaWO}_4:\text{Tb}^{3+}$ powder phosphors.

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2. EXPERIMENTAL PART

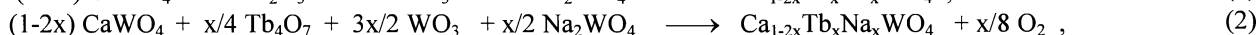
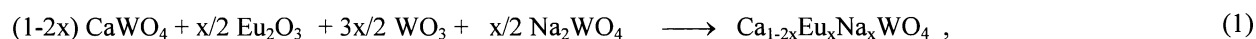
CaWO_4 :RE phosphor samples were prepared by thermal synthesis from homogeneous mixtures consisting of “luminescent grade” (l.g.) CaWO_4 , l.g. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ as flux and l.g. WO_3 and Eu_2O_3 (99,99% Jansen Chemical) or Tb_4O_7 (Johnson Matthey “Specpure”) as activating system. All luminescent grade substances were prepared in our laboratory by original procedures.

Calcium tungstate used as precursor in phosphor synthesis was prepared at room temperature, from highly purified CaCl_2 and Na_2WO_4 solutions.⁸ The synthesis mixtures contained 10wt.% flux and equivalent amounts of WO_3 and Eu_2O_3 or Tb_4O_7 corresponding to $0.0025 \div 0.05$ mole% $\text{RE}_2(\text{WO}_4)_3$. The thermal synthesis was conducted for 2 hrs at 1000°C , in covered alumina crucibles. After the thermal synthesis was over, all samples were washed, dried and sieved.

Phosphor samples were characterised by crystalline structure (Philips PW 1050 Diffractometer, $\text{CuK}\alpha$), and luminescent properties. These ones were estimated on the basis of emission and excitation spectra registered at room temperature (Xe lamp), on Perkin Elmer 204 Spectrofluorimeter. The excitation was performed with a 254 nm UV radiation and a self-activated calcium tungstate phosphor (N61, Bad Liebenstein) was taken as standard. Some cathodoluminescence defectoscopy (CL) measurements were performed by CL mode coupled with scanning electron microscopy (CL-SEM).

3. RESULTS AND DISCUSSIONS

The incorporation of trivalent rare-earth ions into the CaWO_4 crystalline lattice could proceed in two major ways. Either 2RE^{3+} replace 3Ca^{2+} ions, or a pair $\text{RE}^{3+} + \text{M}^+$ replace 2Ca^{2+} ions (where M^+ = alkaline ion). In our working conditions, sodium tungstate acts as mineralising agent and also as a source of compensating ion. As a result, one can assume that the formation of rare-earth activated phosphors proceeds during the thermal synthesis stage in the following manner:



Our previous works^{6,7} showed that rare-earth incorporation into calcium tungstate host lattice modifies the original calcium tungstate luminescent properties. In order to compare the luminescent properties of Eu- and Tb-activated phosphors, two samples series with equal activator concentration were prepared according to the formula:

Samples series #1: CaWO_4 : x Eu^{3+} (Na_2WO_4) where $x = 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0$ mole%;
 Samples series #2 : CaWO_4 : x Tb^{3+} (Na_2WO_4) where $x = 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0$ mole%.

Emission spectra were registered under 254 nm excitation in comparison with the standard. The spectral distribution curves i.e. the relative emission intensities versus wavelength of the emitted radiation of the two samples series are depicted in figure 1 and figure 2. Mention must be made that, in order to better put in evidence the specific activator contribution, only a restricted part of the visible domain was presented.

All phosphor samples show relative intense luminescence under short wave UV radiation ($\lambda_{\text{exc}}=254$ nm). Depending on activator ion nature, RE-concentration and incorporation degree, various narrow emission bands could be observed in the presented spectra.

CaWO_4 :W with no RE-addition, i.e. the self-activated calcium tungstate phosphor, exhibits the broad characteristic emission band centred at 400 nm. Incorporation of increasing Tb-ions amounts structures the broad emission self-activated band by generating new narrow emission bands situated in the blue part of the visible spectrum - centred at 346, 378, 410 and 433 nm- and in the green-yellow one, respectively - centred at 487 and 545 nm (Fig. 1). The specific green emission band of Tb-centres is situated at 545 nm and is due to an electronic transition $^5\text{D}_7 \rightarrow ^7\text{F}_5$ inside the Tb^{3+} . Samples with 0.5-2.5 mole Tb present the most structured spectra on blue part domain, whereas larger Tb amounts determine the diminution of this blue emission part and consequently the disappearance of the spectrum blue part structure. In order to obtain an efficient green photoluminescence, the activator concentration have to be at least 2,5 mole %Tb.

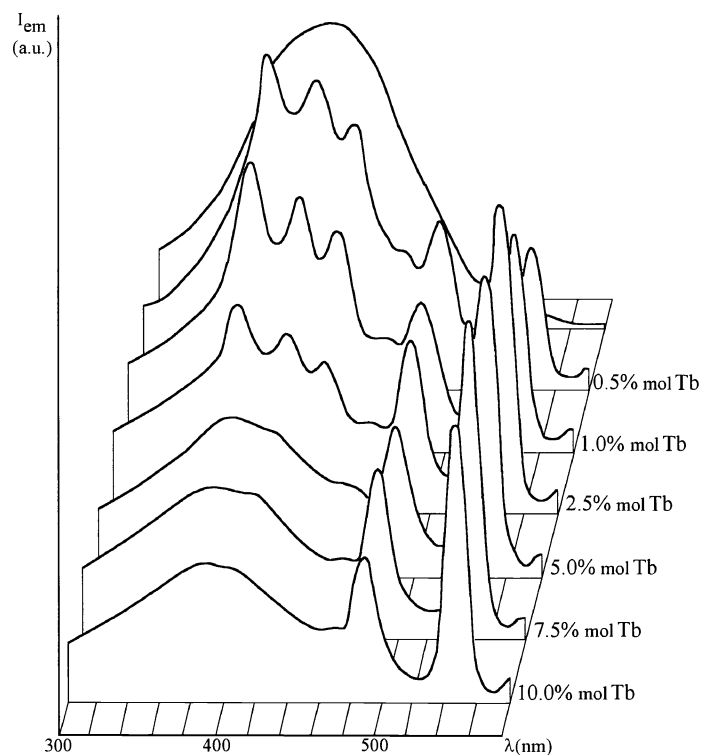


Fig. 1 Emission spectra of $\text{CaWO}_4:\text{Tb}(\text{Na}_2\text{WO}_4)$ phosphors

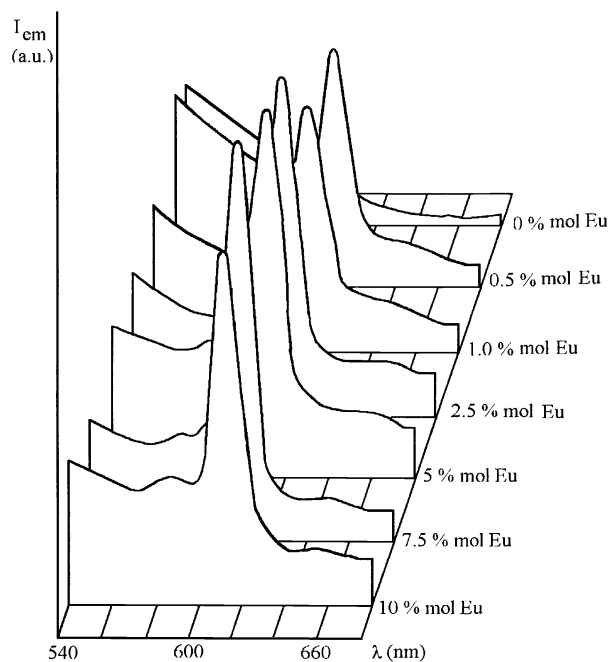


Fig. 2 Emission spectra of $\text{CaWO}_4:\text{Eu}(\text{Na}_2\text{WO}_4)$ phosphors

Incorporation of Eu-ions into the calcium tungstate host lattice produces weak narrow emission bands situated in the blue-green domain (355, 365, 395, 410 and 460 nm – these are not presented in Fig. 2) and relatively stronger ones in the red spectral domain, namely at 590, 615 and 650 nm (Fig. 2).

The specific red emission band is centred at 615 nm and is due to an electronic transition $^5D_0 \rightarrow ^7F_2$ inside the Eu^{3+} . In order to obtain an efficient red photoluminescence, the activator concentration have to be at least 2,5 mole% Eu. It seems that sample containing 7.5 mole% Eu exhibits the strongest red photoluminescence.

Our experimental results showed also that, when the synthesis conditions are not appropriate, the activator incorporation degree could be extremely low so that the concentration of efficient rare earth ions centres could be so diminished that the specific luminescence is masked by the broad host lattice band.

The XRD-patterns registered shows that all phosphor samples possess the expected well-formed scheelite structure. During the thermal synthesis stage, europium-sodium tungstate is formed and dissolved into the host CaWO_4 lattice. A solid solution $\text{CaWO}_4\text{-RENa}(\text{WO}_4)_2$ is formed. In our working conditions, no unreacted RE_2O_3 or WO_3 phases were observed.

In order to put in evidence the major changes produced by different activators-incorporation on the apparent luminescence colour and brightness, emission spectra of various calcium tungstate phosphors are presented on the entire visible spectral domain (Fig. 3). One can observe that $\text{CaWO}_4\text{:W}$ exhibits the characteristic *blue* luminescence. $\text{CaWO}_4\text{:Eu}$ show an intense *red* luminescence colour as a result of both contributions of blue and red part of the visible spectrum. In case of $\text{CaWO}_4\text{:Tb}$, there are two distinct situations namely: for a relatively lower Tb-content, the apparent luminescence colour is *blue-green*, resulting from almost equal contribution of blue and green emission bands; for relatively higher Tb-concentrations, the luminescence colour is *green-yellow* resulting from the more intense green bands contributions as compared with the blue ones. Mention must be made that for blue-green luminescence, the contribution of the lattice emission is significant.

In order to illustrate the chromatic possibilities in tungstate phosphor class, the luminescence emission of lead activated calcium tungstate is presented. By their luminescence properties, $\text{CaWO}_4\text{:Pb}$ phosphor is similar to self-activated tungstate phosphor. As in this case, the luminescent emission of $\text{CaWO}_4\text{:Pb}$ is due to WO_4 groups slightly perturbed by Pb-presence. As a result, the broad emission band is shifted from 400 nm (in the self-activated CaWO_4) to 425 nm (in 1 mole% Pb activated CaWO_4 phosphor). As a result, the apparent luminescence colour modifies from blue to *blue-greenish*.

In rare-earth activated calcium tungstate phosphors, the apparent luminescence is the contribution result of both tungstate lattice and metallic-ions emissions. Therefore, by varying the RE-activator type and concentration, white or blue-to-green-to-yellow-to-red luminescence could be obtained.

Supplementary information about the incorporation degree of activator ions and the contribution of different emission centres to the apparent luminescence could be obtained from the excitation spectra that are more sensitive to the presence of various centres implied into the luminescent process. Excitation spectra register the emission intensity at peak position versus the wavelength of the exciting radiation. Fig. 4 presents the excitation spectra of the same different activated phosphors based on calcium tungstate, namely: F3: $\text{CaWO}_4\text{:W}$; F17: $\text{CaWO}_4\text{:Pb}$ (1mole%); F51: $\text{CaWO}_4\text{:Eu}$ (1mole%) and F55: $\text{CaWO}_4\text{:Tb}$ (1 mole%). The spectra were registered for the emission maxima indicated in the brackets.

Excitation spectra of self-activated $\text{CaWO}_4\text{:W}$ shows that the blue characteristic emission ($\lambda_{\text{em}} = 400$ nm) is well excited into the 265 nm UV domain. As it was expected, the incorporation of Pb^{2+} -ions into the calcium tungstate host lattice shifts the phosphors excitability toward longer wavelengths i.e. 285 nm.

The similar spectra of rare-earth activated calcium tungstate consist in many narrower excitation bands whose relative intensity is variable. For $\text{CaWO}_4\text{:Tb}$ phosphor sample, the blue emission ($\lambda_{\text{em}} = 400$ nm) is well excited in only one band namely 265 nm. In fact, this short wave UV band corresponds to the excitation peak of the self activated $\text{CaWO}_4\text{:W}$ phosphor. The characteristic green emission ($\lambda_{\text{em}} = 545$ nm) is very sensitive in the same UV region (270 nm), but also in the near UV (365 and 375 nm) and in the Vis domain (475 and 495). In the case of $\text{CaWO}_4\text{:Eu}$ phosphors, the characteristic red emission ($\lambda_{\text{em}} = 615$ nm) is mostly excited with 315 nm.

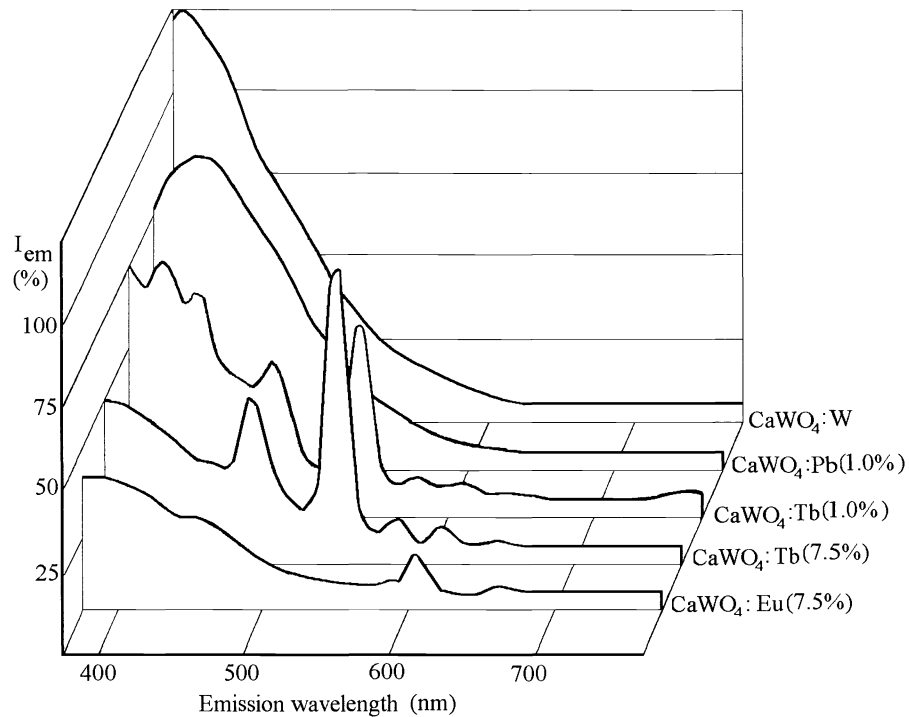


Fig. 3 Emission spectra of some calcium tungstate phosphors

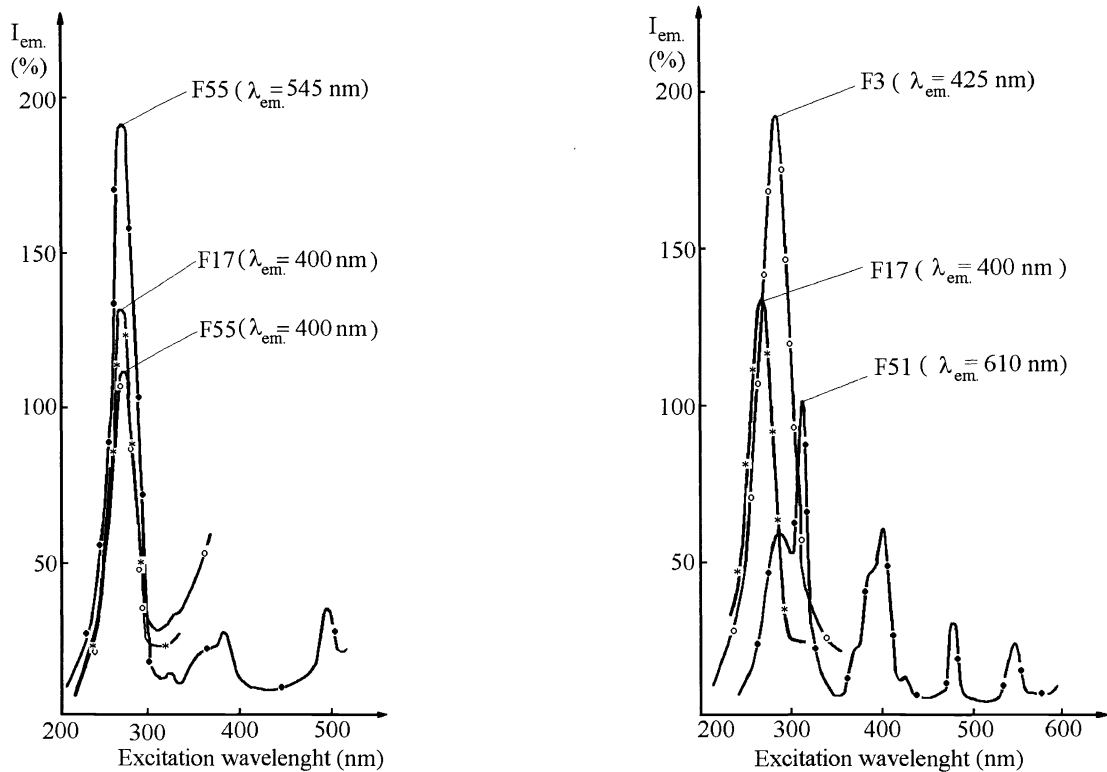


Fig. 4 Excitation spectra of some calcium tungstate phosphors

Supplementary excitations bands appear at 290, 370, 390, 400, 425, 470 and 540 nm situated into the visible part of the spectrum. One can see that, whereas the luminescence of WO_4 groups is excited by short UV radiation (below 300 nm), the

RE³⁺-centres could be excited by long UV radiation as well. RE³⁺-incorporation determines the increasing of UV sensitivity of tungstate phosphors towards longer wavelength.

The spectra from Fig. 4 illustrate also that three different excitation mechanisms are implied in RE-activated CaWO₄ phosphor luminescence. Excitation could be produced in the 4f-4f absorption bands of RE³⁺ (the long wave region of the spectrum), in the broad absorption band of the RE³⁺ (the short wave region of the spectrum) and finally, in the host lattice and followed by an energy transfer. The excitation into the broad RE³⁺ absorption band is proceeds differently for Eu³⁺ (charge transfer in the Eu³⁺-O centre) and correspondingly for Tb³⁺ ions (4f-5d transition inside Tb-centre).

The use of cathodoluminescence (CL) defectoscopy method could offer supplementary information about the defect state of the luminescent materials prepared in various conditions. The CL-images registered for self-activated CaWO₄ and RE-activated CaWO₄ reveal that, depending on synthesis conditions, the non-homogeneous luminescent materials could be prepared. Moreover, a variable incorporation degree of the rare-earth ions into the crystalline host lattice was observed.

4. CONCLUSIONS

New luminescent powders based on CaWO₄:Eu³⁺ and CaWO₄:Tb³⁺ phosphors with various luminescence colours and excitability could be prepared in the classic ceramic techniques.

Whereas CaWO₄:W could be excited only by short UV radiation (254 nm), the rare-earth activated tungstates became sensitive to long UV radiation (365 nm).

As compared with the starting self-activated phosphor, larger excitation wavelength domain and emission colours from blue-to-green-to-yellow-to-red were obtained. The good UV excitability and variable luminescence colour recommend these phosphors for optoelectronic device manufacture.

ACKNOWLEDGMENTS

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REFERENCES

1. F.Forgaciu, E.J.Popovici, C.Ciocan, L.Ungur and M.Vădan, "Calcium tungstate with well defined particle sizes", *SPIE Proceedings Series* **4068**, pp.124-129, 1999.
2. R.Grasser and A.Scharmann, "The Optical Properties of Extrinsic Anionic Oxo-Complexes in Tungstates", *Phys.Status Sol. (a)* **130**, K99-K105, 1990.
3. G.Blasse and B.C.Grabmeyer, *Luminescent Materials*, Springer Verlag, Berlin, 1994.
4. L.G.van Uitert, "Luminescence of Insulating Solids for Optical Massers" in *Luminescence of Inorganic Solids* (Ed.P.Goldberg), Academic Press, 1966.
5. W.Stern, "Colour plasma display by UV-excited phosphors", *Beitr. Plasmaphys.* **25(1)**, pp.57-75, 1985.
6. F.Forgaciu, E.J.Popovici and M.Vasilescu, "Study on the synthesis of rare-earth activated calcium tungstate phosphors", *Proceedings of SIOEL 98*, pp.80-82, Bucharest 1998.
7. E.J.Popovici, F.Forgaciu, M. Nemes and V.Ursu, "Study on the synthesis of europium activated calcium tungstate phosphor", *SPIE Proceedings Series*, **3405**, pp.292-296, 1999.
8. F.Forgaciu, M. Nemes, E.J.Popovici, V.Ursu and D.Macarovici, "Influence of precipitation conditions on the quality of calcium tungstate used in phosphor synthesis", *Studia Univer.Babes-Bolyai, Chemia*, **XL(1-2)**, pp.47-54, 1995.