Luminescence Properties Of Europium-Terbium Double Activated Calcium Tungstate Phosphor

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Blue-emitting calcium tungstate phosphor ($CaWO_4$:W) has been used for a very long time for the manufacture of X-ray intensifying screens. 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.

Double incorporation of Eu^{3+} and Tb^{3+} ions into $CaWO_4$ crystalline lattice modifies the luminescence spectrum due to 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 light emission was obtained when $CaWO_4$: Eu, Tb phosphors with 0-5 mole % activator ions were exposed to relatively low excitation energies as 365 or 254 ultraviolet radiation. Under high excitation energy such as VUV (147 nm) radiation or electron beam, white light could be observed. Cathodoluminescence (CL) spectra for several samples are shown in Fig.1.

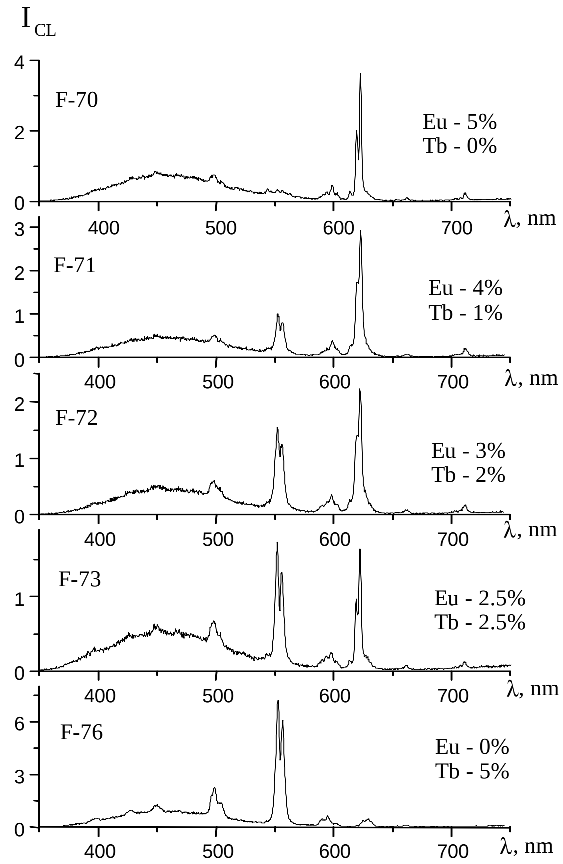

Fig.1. CL spectra of $CaWO_4$:Eu, Tb samples (codes F70-F76) prepared with different activator concentrations

An attempt was made to explain quantitatively the CL and PL experimental data, by proposing a mathematical approach based on two-and three-level models.

The selection rules for the optical transitions inside the RE ions, that in $CaWO_4$ host lattice occupy sites with S_4 point symmetry, are discussed and some results are presented in the table 1. Special attention is paid to the angular dependence of the two-photon absorption process that seems to be an effective tool approach for the optical pattern understanding. The paper presents the results of our theoretical analysis as well as some experimental data determined by low temperature PL measurements that sustain the theory.

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.

$CaWO_4:Eu^{3+},Tb^{3+}$ with controlled properties seems to be promising material for the applications in fluorescent lamps, colored lightning for advertisement industries, and other optoelectronic devices.

Terms *LSJ*	Eu^{3+}	Tb^{3+}	
	$^5D_0$	$^5D_4$	$^5D_3$
$^7F_6$	$3\sigma+7\pi$	$32\sigma+21\pi$	$26\sigma+16\pi$
$^7F_5$	$3\sigma+2\pi$	$25\sigma+18\pi$	$19\sigma+14\pi$
$^7F_4$	$2\sigma+2\pi$	$20\sigma+16\pi$	$16\sigma+12\pi$
$^7F_3$	$2\sigma+2\pi$	$14\sigma+12\pi$	$12\sigma+8\pi$
$^7F_2$	$\sigma+2\pi$	$11\sigma+10\pi$	$9\sigma+6\pi$
$^7F_1$	σ	$7\sigma+4\pi$	$6\sigma+4\pi$
$^7F_0$	-	$2\sigma+2\pi$	$2\sigma+2\pi$

*Table 1. Polarization rules for the allowed electric dipole intracenter transitions in Eu^{3+} and Tb^{3+} ions in **S_4** symmetry*