

## Luminescent materials of red and green emission on the basis of calcium tungstate

*S.B.Meshkova, Z.M.Topilova, V.P.Dotsenko,  
I.P.Kovalevskaya, A.V.Kiriyak*

A.Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, 86 Lustdorfskaya Road, 65080 Odesa, Ukraine

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Co-precipitation conditions of scheelite tungstates have been studied as well as effect of the alkali-earth metal and anion nature and calcination temperature on the luminescence intensity of the compounds. The scheelite structure of the solid solutions obtained has been confirmed X-ray phase analysis. The excitation conditions, luminescence properties, and light-resistance of the compounds under continuous UV irradiation have been examined. The luminescence intensity of Eu doped calcium tungstate has been found to amount 33 % as compared to that of FL-612 luminophor ( $Y_2O_3:Eu$ ) while that of Tb doped one, 146% as compared to crystal luminophor  $Gd_2O_2S:Tb$ .

Исследованы условия совместного осаждения кальций-лантанид-вольфрамов, влияние природы щелочноземельного металла и анионов, а также температуры прокаливания соединений на интенсивность их люминесценции. Рентгенофазовым анализом подтверждено соответствие полученных твердых растворов структуре шеелита. Исследованы условия их возбуждения, люминесцентные свойства и фотостойкость при непрерывном облучении УФ-светом. Установлено, что интенсивность люминесценции вольфрамата кальция, допированного Eu, составляет 33 % от свечения фотолуминофора ФЛ-612 ( $Y_2O_3:Eu$ ), а допированного Tb — 146 % от свечения кристаллофосфора  $Gd_2O_2S:Tb$ .

Alkali earth tungstates and molybdates activated with lanthanide (Ln) ions are used widely in different fields of quantum electronics due to their high emission stability. Activation with double salts of  $MLn(WO_4)_2$  type ( $M = Li, Na, K$ ) having the same scheelite ( $CaWO_4$ ) structure as the matrix to be activated is of a special interest. In this case, not only the excess charge of the activator ion is compensated, but also, due to close sizes of all cations in the lattice, it becomes possible to increase the activator ion concentration without distortion of the matrix crystal structure and formation of heterogeneity. With Li, Na, K, a continuous series of compounds with the scheelite structure is formed due to that ionic radii of  $Li^+, Na^+, K^+, Ln^{3+}(Nd^{3+})$  and  $Ca^{2+}$  are close to each other as it is shown in [1]. The

$K^+$  ion radius has been found to be of critical importance for the scheelite type structure in compounds, e.g.,  $M^I Nd(WO_4)_2$  while when passing to  $Rb^+$  and  $Cs^+$ , the structure type of crystal lattice changes; in those cases, the X-ray examinations evidences the presence of two phases.

Double tungstates (molybdates) of  $M^I Ln^{III}(WO_4)_2$  composition exhibit the scheelite structure or a similar one with either statistical or ordered arrangement of  $M^I$  and  $Ln^{III}$  over the Ca sites. The mixed tungstates of mono- or trivalent metals retain the structure of bivalent metal ones not only with tetrahedral  $WO_4^{2-}$  ions but also when a transition to octahedral coordination occurs [2]. In most cases, the double tungstates are obtained by high temperature synthesis, as well as crystal lumino-

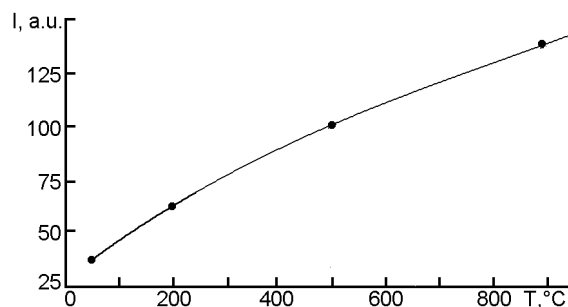


Fig. 1. Luminescence intensity of  $\text{CaWO}_4\text{-NaTb}(\text{WO}_4)_2$  as a function of the calcination temperature.

phors. The energy saving considerations, however, require development of cheaper low-temperature methods to prepare luminescent materials on the basis of various solid matrices. For example, in [3], a novel luminophor is described obtained using sorption of  $\text{Tb}^{\text{III}}$  ions with a zeolite (faujasite) followed by the sorbate treatment with benzoic acid. The luminophor is proposed for use in daylight lamps and to apply onto display screens.

Among the low-temperature synthetic methods, the co-precipitation from solutions [4–6] occupies a leading place. The method provides finely dispersed multicomponent precipitates by matching the precipitation conditions. The method advantages are high homogeneity of the product formed and the synthesis temperatures being several degrees lower as compared to crystal luminophor production [7, 8]. The low light resistance of Ln compounds with organic reagents require to use inorganic ones. Among the latter, it is just tungstates ( $\lambda_{\text{abs}} = 250$  to  $280$  nm) that answer to the highest extent to conditions of photoluminophor excitation ( $\lambda_{\text{ex}} = 254$  nm) in daylight lamps. This work is aimed at preparation of double tungstates  $\text{NaLn}(\text{WO}_4)_2$  co-precipitated with  $\text{CaWO}_4$ , study of their phase composition and spectral and luminescent properties as well as comparison of the emission intensity of the compounds obtained with that of industrial photoluminophors.

In the work,  $1 \cdot 10^{-2}$  mol/L solutions of europium (Eu) and terbium (Tb) chlorides were used prepared by dissolution of the appropriate weights of the oxides (99.9 %) in HCl. 1 mol/L aqueous solutions of Mg, Ca, Sr, Ba chlorides as well as of  $\text{Na}_2\text{WO}_4$  were obtained proceeding from precisely weighed preparations ("chemical purity" or "analytical purity" grades). At the co-pre-

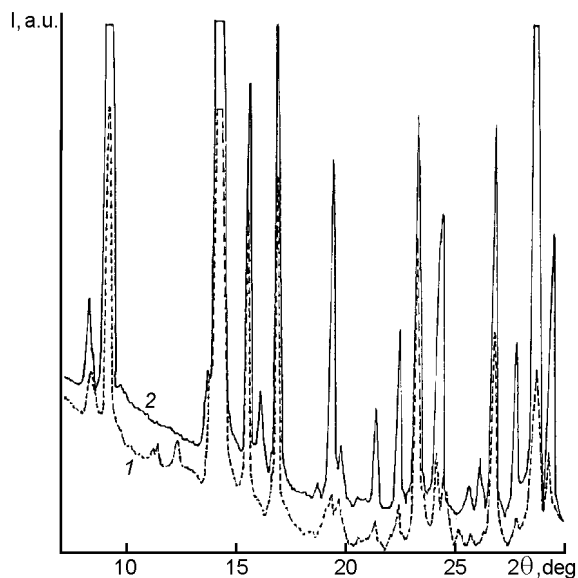


Fig. 2. Powder diffraction patterns of  $\text{NaEu}(\text{WO}_4)_2$  (1) and  $\text{CaWO}_4\text{-NaEu}(\text{WO}_4)_2$  (2) calcined at  $500^\circ\text{C}$  for 1 h (Ca:Eu = 10:1).

cipitation, the Ca:Ln molar ratio was 10:1, the  $\text{Na}_2\text{WO}_4$  excess was 10 % over the stoichiometry. After the co-precipitation, the solutions with precipitates were leaven to stand overnight, then the precipitates were filtered, washed with bidistilled water and dried at  $20$  to  $25^\circ\text{C}$ . Some samples were heat treated at  $50$ ,  $200$ ,  $500$ , and  $900^\circ\text{C}$ . All samples were stored in an exiccator over sulfuric acid. The phase composition of the samples was determined from X-ray diffraction patterns taken using a DRON unit in  $\text{Cu K}\alpha$  emission with Ni filter. ASTM and JCPDS data bases were used to identify the phase composition. The excitation and luminescence spectra were recorded using a SDL-1 spectrometer with a DKSSh-150 xenon lamp, a MSD-1 diffraction monochromator was used to filter the emission of desired wavelength. The excitation spectra were recorded in the luminescence maximum of the most intense lines of Eu ( $\lambda = 614$  nm,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition) and Tb ( $\lambda = 545$  nm,  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition) while the luminescence spectra of the samples, in  $580\text{--}630$  nm range for Eu and  $530\text{--}560$  nm for Tb ( $\lambda_{\text{ex}} = 254$  nm). The cell for solid samples ( $11 \times 11 \times 45$  mm<sup>3</sup>) had a cavity ( $d = 9$  mm) where the samples were placed after a thorough grinding.

Study of the macroscale component (alkali earth metal) nature has shown that, the experimental conditions being identical, the luminescence intensity ( $I$ ) of Eu in tungstates co-precipitated with Mg, Ca, Sr, and

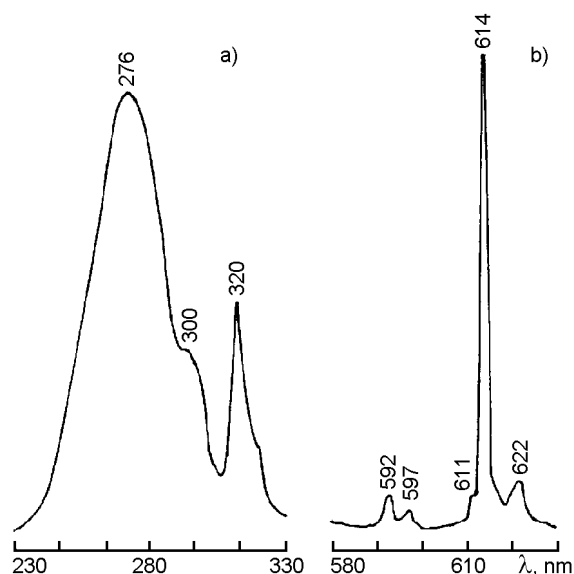


Fig. 3. Excitation ( $\lambda_{lum} = 614$  nm) (a) and luminescence ( $\lambda_{ex} = 254$  nm) spectra (b) of  $\text{CaWO}_4\text{-NaEu(WO}_4)_2$ .

Ba amounts 46, 114, 87, and 64 relative units (r.u.), respectively. At the same time, the effect of anions of the alkali earth metal and lanthanide is such that the emission intensity of the precipitated tungstates is 103, 37, and 10 r.u. for the chlorides, perchlorates, and nitrates, respectively. In this connection, the Eu (Tb) doped Ca tungstates co-precipitated from the chloride solutions were used in further studies.

The calcination temperature of the samples obtained influences considerably the luminescence intensity, as is seen in Fig. 1. The X-ray phase analysis (XPA) of samples obtained using different storage regimes of solutions with precipitates and heat treatment (50–900°C) has shown that all samples have the scheelite structure. Fig. 2 shows the X-ray diffraction patterns (XRD) for the double tungstate  $\text{NaEu(WO}_4)_2$  (1) and for that co-precipitated with Ca (2). The positions of the main lines are coincident while their intensities are increased considerably in the presence of the co-precipitating element. The presence of several weak unidentified lines may evidence a distortion of the scheelite lattice due to formation of  $\text{CaWO}_4\text{-NaEu(WO}_4)_2$  solid solution.

The excitation spectra of Tb and Eu double tungstates and those co-precipitated with Ca are identical and exhibit a maximum at 273–276 nm. It is seen from the excitation spectrum of Eu co-precipitated with  $\text{CaWO}_4$  (Fig. 3a) that the excitation at  $\lambda = 254$  nm amounts more than 50 % of

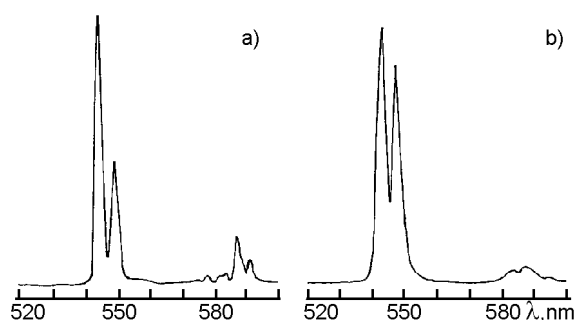


Fig. 4. Luminescence spectra ( $\lambda_{ex} = 254$  nm) of green emission luminophor (a) and  $\text{CaWO}_4\text{-NaTb(WO}_4)_2$  calcined at 900°C (Ca:Tb = 10:1) (b).

the maximum. The intensity ratio in the luminescence spectrum (Fig. 3b) is such that it is just the  $\lambda_{max} = 614$  nm answering to the supersensitive  ${}^5D_0 \rightarrow {}^7F_2$  transition (red emission of  $\text{Eu}^{3+}$  ion) that shows the highest intensity. As in the case of Eu, in the  $\text{CaWO}_4\text{-NaTb(WO}_4)_2$  luminescence spectrum, the line answering to the supersensitive  ${}^5D_4 \rightarrow {}^7F_5$  transition of  $\text{Tb}^{3+}$  ion shows the highest intensity. It splits into two lines peaked at 545 and 549 nm (Fig. 4b) due to influence of the ligand field. For comparison, Fig. 4a presents the luminescence spectrum of a green emission luminophor produced by industry. Even a visual comparison evidences an increased integral intensity for  $\text{CaWO}_4\text{-NaTb(WO}_4)_2$ .

Characteristics of the obtained  $\text{CaWO}_4\text{-NaEu(WO}_4)_2$  and  $\text{CaWO}_4\text{-NaTb(WO}_4)_2$  in comparison to those of industrial red (FL-612) and green ( $\text{Gd}_2\text{O}_2\text{S:Tb}$ ) luminophors are presented in the Table. It is seen that, the matrix being the same, the doping with Tb results in increased (almost by a factor of 1.5) luminescence intensity as compared to  $\text{Gd}_2\text{O}_2\text{S:Tb}$ . The Eu doped luminophor emission is as low as one third of the FL-612 one, perhaps due to a narrower (than in Tb) energy gap between the emitting level and

Table. Luminescence intensity ( $I$ , per cent) of Ca:Ln tungstates ( $T_{calc} = 900^\circ\text{C}$ ) and industrial photoluminophors ( $I = 100$  %). Eu (Tb) content 9 to 10 %

Sample	$I$ , %
Photoluminophor $\text{Gd}_2\text{O}_2\text{S:Tb}$	100
$\text{CaWO}_4\text{-NaTb(WO}_4)_2$	146
Photoluminophor $\text{Y}_2\text{O}_3\text{:Eu (FL-612)}$	100
$\text{CaWO}_4\text{-NaEu(WO}_4)_2$	33

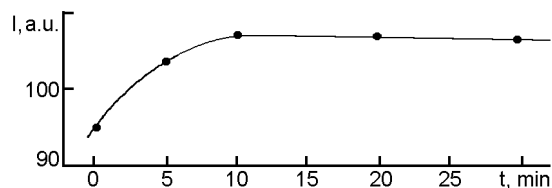


Fig. 5. Luminescence intensity of  $\text{CaWO}_4\text{-NaEu}(\text{WO}_4)_2$  as a function of the continuous UV irradiation time.

the sublevel of the ground level to which the transition occurs.

The obtained  $\text{CaWO}_4\text{-NaLn}(\text{WO}_4)_2$  compounds, as is expected, are characterized by a high light resistance. The plot of Fig. 5 shows that the luminescence intensity of  $\text{CaWO}_4\text{-NaEu}(\text{WO}_4)_2$  increases by about 14 % during the first 10 min of UV irradiation and then remains constant. Thus, the results of our study evidence that it is possible and advisable to use the co-precipitation of  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  with Ca (the major matrix component) with tungstate ion to produce photoluminophors as a more economical alternative to crystal luminophor production.

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## Люмінесцентні матеріали червоного та зеленого кольору світіння на основі вольфрамату кальцію

**С.Б.Мешкова, З.М.Топілова, В.П.Доценко,  
І.П.Ковалевська, Г.В.Кіріяк**

Досліджено умови співсадженьня кальцій-лантанід-вольфраматів, вплив природи лужноземельного металу та аніонів, а також температури пропікання сполук на інтенсивність їх люмінесценції. Рентгенофазовим аналізом підтверджено відповідність збуджених твердих розчинів структурі шееліту. Досліджено умови їх збудження, люмінесцентні властивості та фотостійкість при безперервному опроміненні УФ-світлом. Встановлено, що інтенсивність люмінесценції вольфрамату кальцію, допованого Eu, складає 33 % від світіння фотолюмінофора ФЛ-612 ( $\text{Y}_2\text{O}_3\text{:Eu}$ ), а допованого Tb — 146 % від світіння кристаллофосфора  $\text{Gd}_2\text{O}_2\text{S:Tb}$ .