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$Ca_{1-x-y}Dy_xK_yWO_4$: A novel near UV converting phosphor for white light emitting diode

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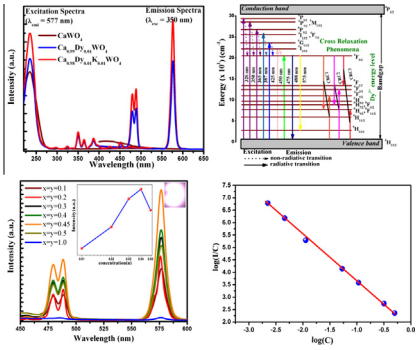
HIGHLIGHTS

- This paper reports structural and luminescence properties of calcium tungstate phosphors.
- Color tunability and white light emission was achieved from these phosphors.
- These indicate possible applications of these phosphors in phosphor converted w-LEDs.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of Dy^{3+}/K^+ doped calcium tungstate phosphors were synthesized by solid state reaction method. The crystal structure, surface morphology, chemical composition and photoluminescence properties of the prepared phosphors were investigated. The luminescence decay curves of doped/codoped phosphors were recorded. The X-ray diffraction analysis shows that the phosphors are of tetragonal structure. SEM studies confirm the particle size in the micro-meter (μm) range. The photoluminescence results indicate that these phosphors could be efficiently excited by the near-ultraviolet radiation which causes the emission in the blue and yellow regions. The white light was achieved by tailoring this yellow to blue ratio varying the Dy^{3+}/K^+ dopant concentration. The quality of emitted white light was checked by calculating different CIE parameters of these phosphors. Decay kinetics studies confirms the life time of activator ions in micro-second (μs) range.

Introduction

Recently, the study of optical spectra of scheelite type (AXO_4, A = Ca, Sr and Ba; X = Mo, W and V) materials attract intensive research attention owing to their good thermal and chemical properties. High melting point (~1450 °C), high refractive index (~1.98) and low vibrational frequency (~850 cm^{-1}) make these materials as the promising candidates in light emitting diodes (LEDs) [1,2]. Now a days, white light-emitting diodes (w-LEDs) have attracted increasing attention due to the advantages of long lifetime, high luminescence efficiency and environmental-friendliness [3]. w-LEDs based on phosphors have been produced by a combination of a blue LED coated with a yellow phosphor. Recently, another approach to generate white light has been suggested which utilizes Red/Green/Blue tri-color phosphors excited by near UV (n-UV) light [4]. n-UV phosphor converted LEDs are expected to have many potential applications due to their excellent optical stability, high color tolerance and high conversion efficiency. So, a careful selection of phosphors that are efficiently excited by near-UV light are highly desirable.

The luminescence properties of Dy^{3+} ions have attracted much research attention due to the existence of two intense bands in

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the blue and yellow wavelength regions [5]. It provides an excellent opportunity to produce white light by adjusting the yellow to blue (Y/B) intensity ratio. So, using Dy^{3+}, it is possible to achieve white light. Lot of research work is being carried out to achieve new tungstate materials with trivalent rare earth (RE^{3+}) ion due to their potential applications in solid state lighting devices [1–4]. But, till date no work has been reported on the white light emission from Dy^{3+}/K^{+} activated $CaWO_4$ phosphors. Keeping this in view, XRD and PL characterization of Dy^{3+}/K^{+} activated $CaWO_4$ phosphors were carried out first time. An attempt was made to investigate the quality of white light by calculating the various CIE parameters.

Experimental

Synthesis of calcium tungstate phosphors

A series of Dy^{3+}/K^{+} activated calcium tungstate phosphors were prepared by conventional solid state reaction method [1] taking $CaCO_3$, K_2CO_3, Dy_2O_3 and WO_3 as starting raw materials. All the ingredients were taken according to the formula $Ca_{1-x-y}Dy_xK_yWO_4$ ($x = y = 0$, 0.01, 0.02, 0.03, 0.04, 0.045, 0.05, 0.1, $x = 0.01$, $y = 0$) and then pulverized properly to achieve uniform mixture. This mixture was annealed for 3 h at 500 °C in an alumina crucible and then it was re-annealed for 3 h at 1000 °C. The obtained material was crushed in a mortar-pestle to achieve the desired phosphors.

Characterization of calcium tungstate phosphors

X-ray diffractogram of prepared phosphors were recorded in a wide range of Bragg angle 2θ ($20° \leqslant 2\theta \leqslant 90°$) using Bruker D8 advance XRD measuring instrument with Cu target radiation ($\lambda = 0.154056$ nm). The Fourier Transform Infrared spectra were studied in the wavelength range 4000–400 cm^{-1} using Perkin Elmer make Spectrum RX-I Spectrometer. Scanning electron microscope images were obtained using a Hitachi S-3400N scanning electron microscope to examine the crystallinity and surface morphology of the prepared phosphors. The photoluminescence studies were carried out on Hitachi Fluorescence Spectrometer F-2500 in the range 220–650 nm. The decay kinetics was studied on Quanta Master 40 fluorometer. All the studies were carried out at room temperature.

Results and discussion

Phase identification and morphology

XRD studies

XRD studies were performed in order to investigate the structure of $CaWO_4$ phosphors and are shown in Fig. 1. The sharp and single diffraction peaks of the XRD spectrum of undoped $CaWO_4$ (JCPDS pdf number 41-1431) confirm the formation of single phase tetragonal compound having lattice parameters $a = b = 5.242$ Å and $c = 11.37$ Å. After Dy^{3+} or Dy^{3+}/K^{+} doping no significant changes in the crystal structure was observed, suggesting that these dopants might have occupied the cationic sites in the host lattice structure, following the charge balancing: $2Ca^{2+} = Dy^{3+} + K^{+}$ [6].

FTIR studies

Fig. 2 shows the FTIR spectra of doped/codoped $CaWO_4$ phosphors. The broad absorption band at 3438 cm^{-1} and 1726 cm^{-1} are assigned to O–H stretching vibration and H–O–H bending vibration, respectively [7,8]. These two bands are the characteristic vibration of water absorbed from air on the sample surface, which is completely different from coordinated water in compounds. The

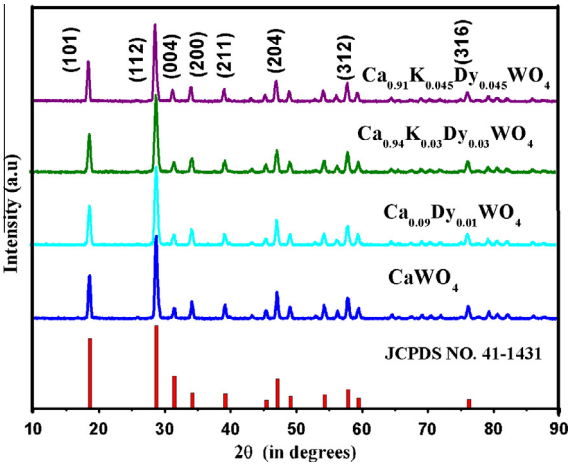

Fig. 1. XRD patterns of undoped/doped/codoped $CaWO_4$ phosphors.

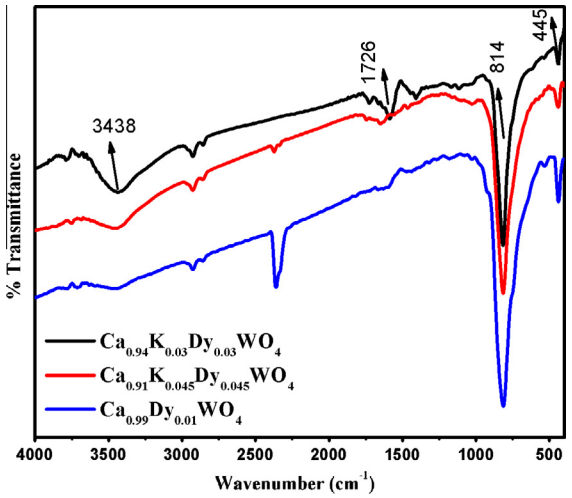

Fig. 2. FTIR Spectra of doped/codoped $CaWO_4$ phosphors.

set of bands below 1000 cm^{-1} are characteristic vibrations of W–O bands. The strong absorption band at 814 cm^{-1} is related to O–W–O stretching vibration of WO_4 tetrahedron. The band detected at 445 cm^{-1} is assigned to the stretching vibration of W–O [7]. The presence of these two bands confirms the formation of $CaWO_4$ compounds.

SEM–EDX studies

SEM and EDX studies were carried out in order to obtain information about morphology, grain size, shape and chemical composition of the synthesized phosphors. Figs. 3, 4 and 5(a–b) show the SEM micrographs of undoped, Dy^{3+} doped and K^{+} codoped $CaWO_4$ phosphors with different magnifications, confirming that the particles are grown with a very high density. A closer examination of microphotographs of undoped $CaWO_4$ shows the weakly agglomerated octahedral particles with size ranging from 0.5 μm to 2.5 μm. Non-uniform distribution of particles was observed consisting of either single particle or cluster of particles. Doped and codoped phosphors show strong agglomeration resulting lose in particles octahedral structure and formation of polygons of different shape and size. The agglomeration of particles is a common practice and expected in phosphors prepared by solid state reaction method. Diameter of particle size varies from 0.6 μm to