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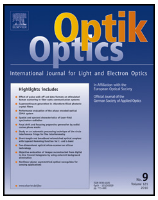

Original research article

VUV-UV photoluminescence properties of Ce^{3+} doped Ca_2SnO_4 phosphor for PDP application

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ABSTRACT

Calcium stannate oxide (Ca_2SnO_4) compound doped with Ce^{3+} rare earth ion was synthesized by conventional solid state synthesis method at 1300 °C. Phase confirmation and crystal structure analysis was done by obtaining its X-ray diffraction (XRD) pattern. The vacuum ultraviolet (VUV) – visible spectroscopic properties were investigated. Ca_2SnO_4:Ce^{3+} phosphor possesses broad and strong absorption in VUV and UV region. Excitation peaks are present at 140 nm, 174 nm, 200 nm and 261 nm. Ca_2SnO_4:Ce^{3+} exhibits intensive photoluminescence (PL) emission centered at 430 nm and 467 nm under VUV excitation. CIE chromaticity co-ordinates were calculated. The luminescence properties of Ca_2SnO_4:Ce^{3+} compound make it good candidate as a blue phosphor for mercury-free lamps and plasma display panel (PDP) applications.

1. Introduction

Plasma display panels (PDP) are widely used as large flat panel display in home theatre industry due to its absolute quality and size of the image they can produce. PDP is made up of number of pixels that create images when voltage is applied [1]. Neon/xenon gas discharge is used as source for illumination in the pixels. Pixel is made up of three primary color emitting phosphors (Red, green and blue). After passing a voltage pulse between two electrodes, the gas breaks down and produces weakly ionized plasma, which emits vacuum ultraviolet light (VUV, wavelength $\lambda < 200$ nm and energy $E > 50{,}000\ cm^{-1}$) radiation which activates phosphors. Xenon (Xe) gas is mostly used for this purpose and discharge of Xe gives two emissions at 147 nm and 172 nm. Moreover, by increasing the content of Xe gas, the light intensity of Xe2 molecular emission (172 nm) band becomes intense while that of the Xe resonance emission line (147 nm) becomes weaker [2]. There is a trend to use high Xe content gas discharge in PDPs in order to get high light conversion efficiency from Xe gas discharge, and high Xe content discharge has been applied in PDP and mercury-free fluorescent lamps [3]. So if Xe gas discharge is at high content level, the 172 nm band emission will dominate. Hence, there is a need to develop phosphor that is excited by VUV light. In addition, though tricolor luminescence lamps are widely used in lighting industry, but electric discharge of mercury (Hg) atoms is used as excitation source, and the mercury is harmful to the environment. In order to avoid the use of harmful mercury, mercury-free lamps are proposed. The development of phosphors that are efficiently excited by such a 172 nm band emission is significant.

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Ternary tin-based oxides (i.e. stannates) gained huge attraction of researchers from different fields owing to their unique properties as well as high thermal and chemical stability [4]. These compounds can be kept for many years in a perfect state of crystallinity and they are not water soluble. Among the stannates group, Ca_2SnO_4 compound is investigated and found to be applicable as growth inhibitor in SnO_2 for gas sensor applications, as an anode for Li-ion batteries and as a host material of phosphors [5,6]. It is reported that Ca_2SnO_4 is a self-luminescent compound [7]. It is stated that it is very easy to implant rare earth impurities in Ca_2SnO_4 since this compound possess one dimensional chain structure [8]. Ca_2SnO_4:Eu^{3+} phosphor is highly studied than other rare earth ion doped Ca_2SnO_4 compound. Wet chemical methods are useful in synthesis of nano and micro size inorganic compounds [9]. Various synthesis methods were applied for the synthesis of Ca_2SnO_4:Eu^{3+} such as solid state synthesis [10], co-precipitation method [11], sol-gel [12] and vibro-mill method [13]. Photoluminescence (PL) properties of Ca_2SnO_4 doped with Ce^{3+}/Eu^{3+}/Sm^{3+}/Tb^{3+}/Tm^{3+}/Pr^{3+} phosphors are also studied by researchers [14,15].

Ce^{3+} emission and excitation varies from host to host as it shows host dependent photoluminescence properties [16]. It can show blue, green or red emission in different hosts [17]. In this paper, we demonstrated that intense blue light emission is obtained when the phosphor Ca_2SnO_4:Ce^{3+} is irradiated under 147/172 and 270 nm excitations. The CIE color coordinates are improved relative to that of the commercial phosphor BAM, the present phosphor can be considered to be a potential blue phosphor for mercury-free lamps and PDPs application.

2. Experimental

2.1. Synthesis

$Ca_{1.94}SnO_4$:$0.06Ce^{3+}$ compound was synthesized by the two step solid state synthesis method. SnO_2, $CaCO_3$, and Ce_2O_3 (99.99% Sigma Aldrich Chemicals) chemicals were used as starting reagents. In our work we have represented PL results of 6 mol% doping of Ce^{3+}. For Cerium ion concentration quenching occurs at very high mol% such as 10 mol% or 20 mol% and at lower mol% emission intensity is not enough; therefore, we have chosen 6 mol% concentration of Ce [18]. Initially, stoichiometric quantities of the reactants were weighed and thoroughly mixed for 4 h in ethanol medium. After drying at 80 °C for 1 h, samples were heated upto 1300 °C in an alumina boat in air for 3 h. Later, the temperature is decreased to 950 °C and the samples were kept at that temperature for 1 h in air. These samples were cooled to room temperature and its characterisation was done.

2.2. Characterisation

X-ray diffraction study was carried out to confirm formation of compound on X'pert PANalytical X-ray diffractometer using Nickel filtered Cu-Kα radiation with a step size of 0.04°/s. Wavelength of Cu-K_α line used is 1.5406 Å. Energy dispersive spectrum (EDS) was recorded by using a Hitachi S-3700N (Hitachi) scanning electron microscope. VUV luminescence studies were performed using synchrotron radiation facility (National Synchrotron Radiation Research Center, Taiwan) using beam line 03 A. VUV excitation was given by beam line attached to the 1.5 GeV storage ring with a cylindrical-grating monochromator (CGM, 6 m). Its intensity was monitored using gold mesh transmitting about 90% recorded by electrometer (Keithley 6512). For the detection of PL of the sample, photomultiplier (Hamamatsu R943-02), monochromator (Jobin – Yvon HR320) equipped with a diffraction grating (1200 lines/mm) is used. All PLE spectra were normalized with respect to the spectral response of the CGM beamline. Details of this set-up are given by Lu et al. [19]. All measurements were performed at room temperature. VUV excitation spectra in the range 125–300 nm and VUV-excited emission spectra in the range 300–800 nm were measured.

3. Results and discussion

3.1. X-Ray diffraction analysis

The formation of the $Ca_{1.94}SnO_4$:$0.06Ce^{3+}$ compound was confirmed by obtaining the x-ray diffraction (XRD) pattern of the as-prepared sample. Fig. 1 shows the XRD pattern with hkl plane indexing of each peak of the as-synthesized sample along with standard JCPDS data. The diffraction pattern of the $Ca_{1.94}SnO_4$:$0.06Ce^{3+}$ sample matches the diffraction pattern given in JCPDS No.46-0112. Extra peak exist at 23.33° which may be due to presence of impurity in starting materials. This shows the formation of a highly homogeneous phase of Ca_2SnO_4 compound when prepared using the solid state diffusion method.

Fig. 2 shows crystal structure of Ca_2SnO_4 compound modelled by using Visualization for Electronic and Structural Analysis (VESTA) program, version 3.1.8 for Windows [20]. Ca_2SnO_4 compound crystallizes in orthorhombic crystal structure with space group *Pbam* (space group no. 55). Values for crystallographic constant are a = 5.75 Å, b = 9.70 Å and c = 3.27 Å, $\alpha = 90°$, $\beta = 90°$ and $\gamma = 90°$. Crystal structure of Ca_2SnO_4 compound was reported by Tromel [21]. Ca_2SnO_4 is isostructural with Sr_2PbO_4-type structure. The Ca atom is at the 4h site (x, y, 1/2) and coordinated by seven oxygen atoms and therefore, effective coordination number is 7 for Ca, the Sn atom of the 2a site (0, 0,0) is coordinated by six oxygen atoms forming SnO_6 octahedra as shown in Fig. 2. Coordination number of Sn is 6. SnO_6 octahedra are linked by sharing edges with each other,