Synthesis and characterization of Ag doped $CaWO_4$ powder phosphors for optical blue emission

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This paper reports on the synthesis of $Ca_{(1-x)}WO_4$: Ag_x ($0 \le x \le 0.05$ mol %) powder phosphors by a hydrothermal method and followed by calcinations. The effect of Ag-content on photoluminescence (PL) spectra of $CaWO_4$ was investigated. The phase nature of the synthesized powder phosphors have been examined from X-ray diffractometry. Thermal decomposition behaviors of the dried $CaWO_4$ powder phosphors have been studied from TG/DTA profiles and thus noticed that there exists a polymorphic transition at 800 ^oC. Based on the PL results, the dopant Ag content in the phosphors has been optimized to be 0.001 mol %, displaying a prominent *blue* emission from the phosphor. From the FT-IR spectrum, a strong peak at 845 cm^{-1} has been obtained due to the stretching vibration of WO_4^{2-} in scheelite structure, and a weak but sharp band at 445 cm^{-1} has also been noticed due to the metal, oxygen (Ca-O) band. Scanning Electron Microscopic (SEM) studies reveal that the synthesized $CaWO_4$ and Ag-doped $CaWO_4$ particles are in plate shape in the range from 400 nm to 1 micron. From SEM images, it has been noted that the agglomeration of synthesized powder phosphors has been increased with the change in Ag content, owing to the density variation.

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1. Introduction

Multi-metal oxide ceramics are found to be more promising materials for different optical and electronic applications [1-2]. Such oxides based phosphors have widely been used in the development of CRTs (Projection TVs), field emission vacuum fluorescent, electroluminescent displays and scintillators in X-ray and positron emission tomographs [3]. The specific luminescent properties of metal oxide ceramics are highly influenced by the host material, dopant ion concentration, chosen stoichiometry and also the preparation conditions [4]. Rare earth ions doped tungstate crystals prepared by different methods have received a great deal of attention as promising laser materials, due to their attractive third order nonlinear dielectric susceptibilities. Tungstates are divided into two groups as Scheelites ($CaWO_4$, $BaWO_4$, $SrWO_4$ and $PbWO_4$) and as Wolframites ($MgWO_4$, $ZnWO_4$ and others). As a representative example, $CaWO_4$ with the scheelite structure, containing Ca^{2+} ions and $WO_4^{\ 2-}$ groups with the coordination no of eight for Ca^{2+} and four for W^{6+} is considered to be highly functional material due to its intriguing luminescence properties. It mainly shows an efficient blue emission when excited by UV, X-rays and cathode rays. Owing to its wide variety of applications, several new routes of synthesis of pure and homogenously doped calcium tungstates are found to be significantly relevant [5-12]. Zhang et. al have reported that, ZnS: Ag at high current densities could show brightness saturation due to the ground state depletion or to non radiative Auger process at low Ag content. It has also been reported that activator recycling may not be possible due to its relatively high decay time ($\tau_{1/e\ \sim\ 25}$ μs) [13]. Kransnov et. al have noticed that the presence of Ag as a co-dopant has improved the luminescence efficiency in the case of ZnS: Mn phosphors by reducing the Mn clustering effects [14]. Mostly $CaWO_4$ synthesis has been carried out in the form of single crystal powders and films [8], by precipitation method [15], traditional solid state reaction [16], and spray pyrolysis route [17-18]. In the present paper, we report on yet another method of synthesis, characterization and the influence of dopant Ag content on the blue emission performance of $Ca_{(1-x)}WO_4$: Ag_x ($0 \le x \le 0.05$ mol %) powder phosphors.

2. Experimental

$CaWO_4$: Ag powder phosphors were prepared by a hydrothermal method with the following possible chemical reaction:

$CaCl_{2\,(1-x)} + Na_2WO_4 + x\ AgNO_3 \rightarrow CaWO_4{:}\ Ag + 2\ NaCl + NO_2\uparrow$(Where x = 0, 0.001, 0.005, 0.01 and 0.05 mol %) → {1}

The precursor solutions of the $CaCl_2$, Na_2WO_4 and $AgNO_3$ were prepared by dissolving (in mol %) the respective G.R grade chemicals. Sodium tungstate solution was added to the $CaCl_2$ solution under a vigorous stirring. Ethylene glycole was used as a dispersing media. To prepare Ag-doped $CaWO_4$ powder phosphors, $AgNO_3$ solution was added by a drop wise to the above $CaWO_4$ resultant dense media with continuous stirring by magnetic stirrer. The P^H of the above resultant dense liquid was maintained at 6.5 – 7.0 by using HNO_3 and NaOH with stirring for 3 hrs. The resultant precipitated mass was transferred into a 100 ml capacity teflon lined SS made auto-clave, which was heated in a electrical oven at 175 ^oC for 24 hrs under a self generated pressure. After a 24 hrs heating of the autoclave vessel without any stirring or disturbance, it was gradually cooled down to the room temperature. The resultant precipitated mass was separated centrifugally and washed thoroughly with DI water to remove the traces of NaCl and ethylene glycole. It was later dried at 120 ^oC for few minutes in an electrical oven. Thus the obtained fluffy powder was taken into a quartz boat and calcined in a resistance heated tubular furnace starting from room temperature to 800 ^oC and was kept at this temperature for 2 hrs under ambient atmosphere. The body colour of the synthesized powder phosphors were observed to be changing from white to magenta colour with an increased silver content. The synthesized powder phosphors were displaying blue emission under an UV source. The crystalline and phase purity of the synthesized $CaWO_4$: Ag powder phosphors were studied on a Phillips, X-Ray Diffractometer. XRD pattern of each phosphor sample was recorded in the range of diffraction angle 2Θ = 5 – 80 ^{o}. Thermal decomposition behaviour of $CaWO_4$ powder phosphor was studied by using Mettler Toledo Star SW 9.01, TG/DTA. The dried 3.4688 mg of $CaWO_4$ powder was heated from room temperature to 1100 ^oC @10 ^oC per minute under argon atmosphere. FT-IR spectrum of the synthesized powder phosphor was measured on a Perkin Elmer, FT-IR spectrometer by KBr pellet technique. Particle shape, size and surface morphology of the obtained powder phosphors were studied on a Phillips XL 30, scanning electron microscope (SEM). Photoluminescence spectra of the synthesized powder phosphors were measured by using an excitation wavelength, λ_{exc} = 261 nm, on a Hitachi, 650-10S Spectrofluorimeter.

3. Results and discussion

Based on d-spacing (Å), relative intensity and diffraction angle (2Θ) of XRD profile (Fig.1), it is conformed that the obtained powders were in scheelite structure i.e. JCPDF: 41-1413. TG/DTA curves (Fig. 2) show that the decomposition starts below 300 ^oC with a loss of water from the coordination sphere of the sample. The thermal decomposition behaviour has been attributed to the endothermic and exothermic effects in the DTA curve. A weak exothermic peak at 340 ^oC indicates the total decomposition of the traces of the solvent ethylene glycole. It is clear to realize that TG curve shows a 10 % of weight loss in the sample while heating from room the temperature to 500 ^oC under an Ar gas atmosphere. From 500 – 900 ^oC there has not been any change in the weight of the sample. A weak exothermic peak at 800 ^oC could possibly because of a polymorphic transition of $CaWO_4$. Thus, the thermal characterization of $CaWO_4$ provides information on the mechanism involved in the thermal decomposition of the Ca – W – O precursor and the optimum conditions for the final annealing can also be determined. According to the TG/DTA analysis data, the final annealing temperature for the preparation of $CaWO_4$ could be around 800 ^oC [19].

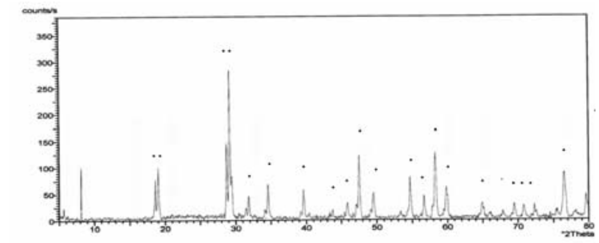


Fig. 1. XRD pattern of $CaWO_4$ powder phosphor.

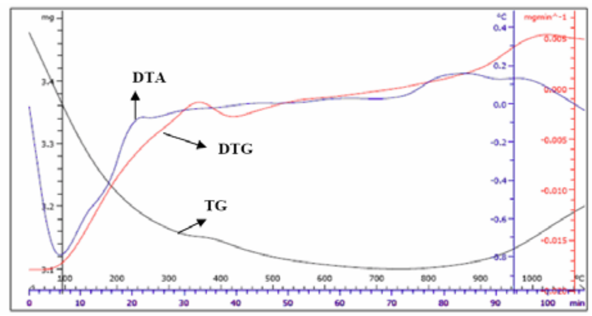


Fig. 2. TG/DTA/DTG profiles of $CaWO_4$ powder phosphor.

FT-IR spectrum (Fig. 3), shows a strong peak at 845 cm^{-1} which is due to the characteristic stretching vibration of WO_4^{2-} in scheelite. A sharp peak at 445 cm^{-1} indicates the bending vibration of metal-oxygen (Ca – O) bond. Two weak peaks at 1170 and 1370 cm^{-1} are due to the H-OH stretching vibration [20]. Scanning electron micrographs (Fig. 4) of Ag: $CaWO_4$ and $CaWO_4$ powder phosphors are revealing that the synthesized grains are in plate type structures with particle size ranging from 400 nm to 1 µm. SEM images also demonstrate the agglomeration of the particles due to an increase in Ag content in the phosphor studied due to density differences. A small amount of phosphor powder was dispersed in acetone solvent in an agate mortar with a pestle. A drop of acetone containing the sample was placed on a SEM sample holder, as soon as the solvent acetone evaporates most of the phosphor particles were found to be agglomerating, thus an increase of Ag-content increases the agglomeration.

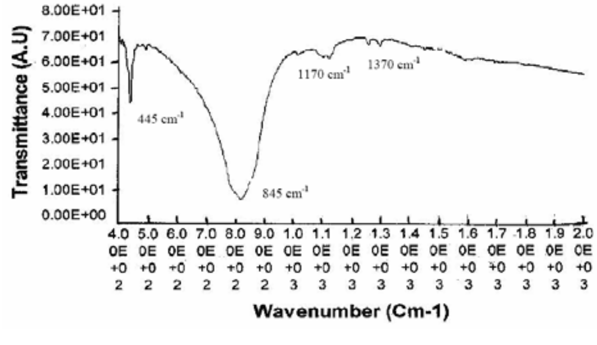
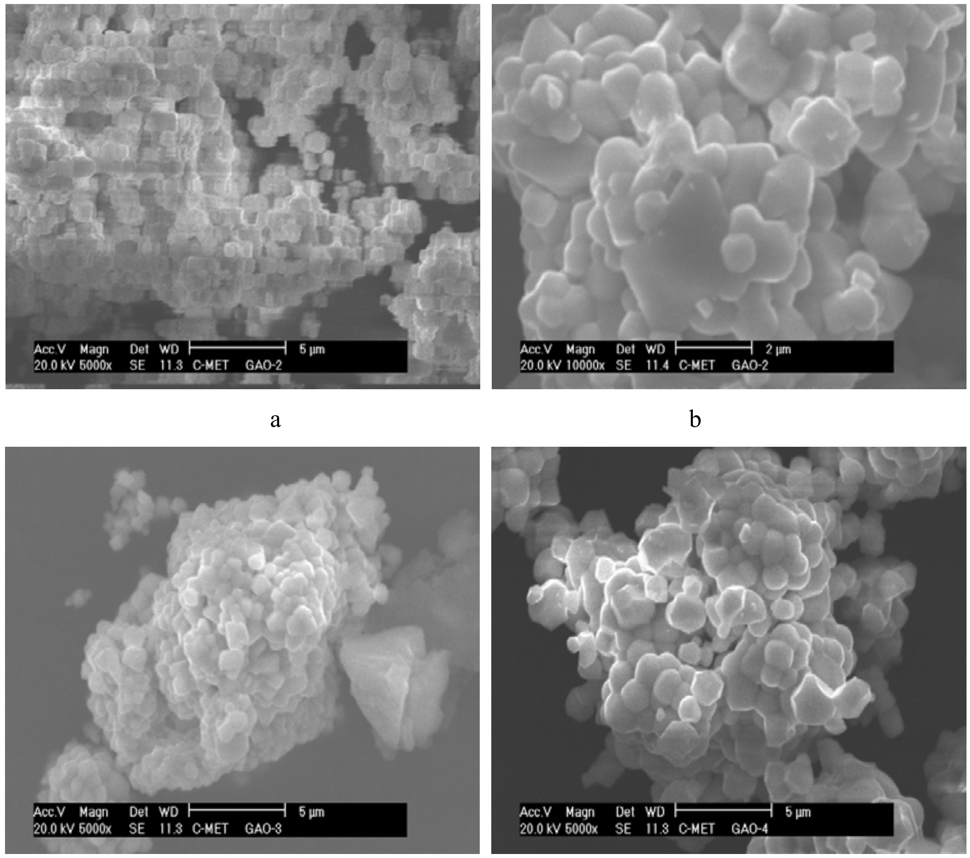


Fig. 3. FT- IR spectrum of $CaWO_4$ powder phosphor.



a b

c d

Fig. 4. SEM images of (a) $CaWO_4$: Ag (0.005 mol %), (b) $CaWO_4$: Ag (0.01 mol %), (c) $CaWO_4$: Ag (0.05 mol %), and (d) $CaWO_4$: Ag (0.0 mol %) powder phosphors.

The excitation spectrum (Fig.5) of the synthesized powder phosphor shows a broad band from 240-280 nm with a band maximum at 261 nm, which corresponds to the charge transfer transition in WO_4^- groups in which an oxygen (O) 2P electron goes into empty tungsten (W) 5d orbital [20].

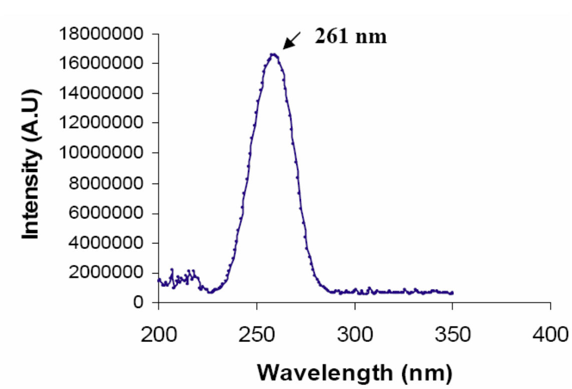


Fig. 5. Excitation spectrum of $CaWO_4$: Ag (0.001 mol %) powder phosphor.

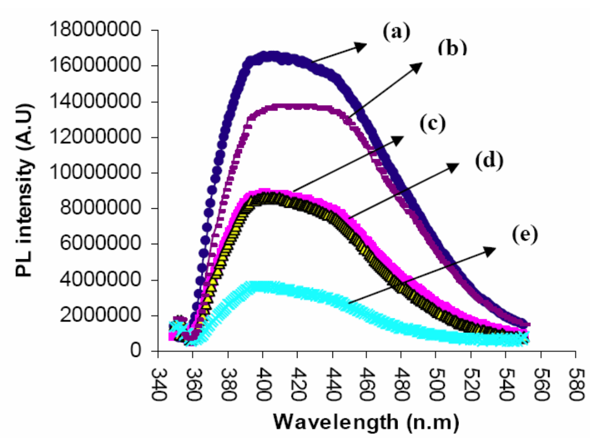


Fig. 6. Photoluminescence spectrum of (a)$CaWO_4$: Ag (0.001 mol %), (b) $CaWO_4$: Ag (0.005 mol %), (c) $CaWO_4$: Ag (0.01 mol %), (d) $CaWO_4$: Ag (0.05 mol %), and (e) $CaWO_4$: Ag (0.0 mol %) powder phosphors.

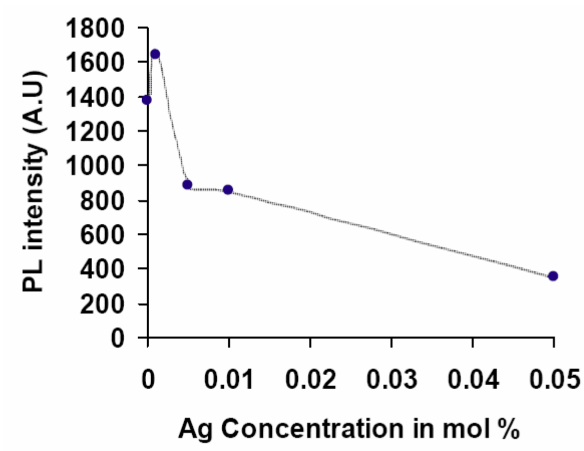


Fig. 7. The graphical representation of the effect of Ag - dopant ion concentration on photoluminescence intensity.

The emission spectrum shows a broad emission between the wavelength ranges of 360-550 nm revealing a peak position at 420 nm due to the WO_4^{2-} ion. From the molecular orbital theory the excitation and emission bands can be ascribed to transitions from the $^1A_1$ ground state to the high vibrational level of ^1B ($^1T_2$) and from the low vibrational level of ^1B ($^1T_2$) to the $^1A_1$ ground state within the WO_4^{2-} ion, respectively. From the emission spectrum (Fig. 6) of the Ag: $CaWO_4$ and undoped $CaWO_4$ powder phosphors, it is observed that emission band shifts towards the lower wavelength for the Ag: $CaWO_4$ compared with the undoped $CaWO_4$ phosphor. Silver at lower concentration levels has been showing a sensitized luminescence. Dopant ion (Ag) concentration quenching effect in $CaWO_4$ scheelite type powder phosphor has been noticed [21]. Fig. 7, shows a relationship between the fluorescence intensity and the dopant Ag ion concentration. Based on the fluorescence properties of the phosphor $CaWO_4$: 0.001 (mol %) Ag, which could be suggested as a novel optical material of technological importance in the progress of phosphor coated screens of certain electronic systems.

4. Conclusions

By employing the hydrothermal method followed by calcination, a strongly *blue* luminescent Ag-doped $CaWO_4$ powder phosphor has successfully been synthesized and carried out a systematic analysis based on the features obtained from the XRD, TG/DTA, FT-IR and photoluminescence spectra. Thus the results obtained in the present study clearly demonstrate the luminescent potentiality of the optical material. Since the results are encouraging to suggest that $CaWO_4$: Ag (0.001mol %), as a promising *blue* light emitting phosphor optical system for its application in certain electronic displays.

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