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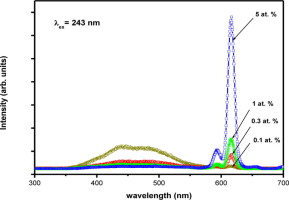
**Effects of annealing on luminescence of CaWO4:Eu3+ nanoparticles and its thermoluminescence study**

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**Abstract**

Eu3+ doped CaWO4 nano-sized phosphor powders with tunable optical properties were successfully prepared at comparatively low temperature (130 °C) in ethylene glycol (EG) medium and were further annealed to study heating effects in their luminescence properties. The particles exhibit the tetragonal scheelite structure. The luminescence study of the annealed nanoparticles leads to the confirmation that CaWO4:Eu3+ shows a strong red emission at 614 nm originating from 5D0 → 7F2 transition. The optimum concentration of Eu3+ for the highest luminescence is found to be 20 at.% and the luminescence intensities of the prepared nanoparticles increase with increasing annealing temperature from 500 to 900 °C. Thermoluminescence (TL) intensity of CaWO4:Eu3+with two prominent peaks at 393 and 514 K is found to be dependent on Eu3+concentration with highest TL intensity at 3 at.% of Eu3+.

**Graphical abstract**

The emission spectra of CaWO4:Eu3+ (very low concentration of Eu3+ ion) excited at 243 nm.

1. [Download : Download full-size image](https://ars.els-cdn.com/content/image/1-s2.0-S0925838812023110-fx1.jpg)

**Highlights**

► Highly luminescent CaWO4 : Eu3+ nanopartilces have been synthesized in ethylene glycol route and further annealed.►The luminescence intensity increased manifolds due to annealing at higher temperatures. ► [Thermoluminescence](https://www.sciencedirect.com/topics/materials-science/thermoluminescence) (TL) studies of CaWO4:Eu3+ (x at.%) samples show that the TL intensity depends upon the concentration of Eu3+. ► 3 at.% Eu3+ have the highest TL intensity.

**Introduction**

Rare-earth doped nanoparticles (NPs) have emerged as a new class of luminescence materials which find a wide variety of applications [1]. Such type of NPs has the advantage of high stability, brightness, and flexible industrial processing ability. They are commonly used in fluorescent lamps and luminescent displays [1] and have potential applications in lasers [2] and X-ray imaging [3]. Lanthanide doped nanophosphors with tunable optical properties are used in luminescent displays and investigations on color tunable nanophosphors of Y2O3 have been done very recently [4]. These materials have more than one component: one component being the host matrix and the lanthanide doping element being responsible for the radiation [5]. One of the most studied ceramics as host matrix for phosphors is calcium tungstate (CaWO4). CaWO4 is ablue-emitting luminescence material. It is an important member of metal tungstate families [6], which has generally been considered as a prototype scheelite compounds with a close structural link to many materials such as CaMoO4, PbMoO4, PbWO4, YLiF4, and high-pressure phases of TbVO4 and DyVO4. The rising need for high-performance phosphors renewed the interest in this luminescent material with more than a century of history. Improvement of the luminescence properties of scheelite based phosphors has become a primary focus in the luminescent materials science. Tungstate has broad and intense absorption bands due to charge transfer (CT) from oxygen to metal in the near-UV region. Many scheelite-related phosphors doped with Eu3+ have also been studied extensively and reveal a non-radiative mechanism for the energy transfer to the activator ion [7], [8], [9], [10], [11], [12], [13]. The luminescence properties of this superior phosphor could be enhanced by doping with lanthanide ions [14]. The incorporation of Eu3+ ions into the CaWO4 crystal lattice modifies the luminescence spectrum due to the formation of the emission centers that generate the specific red light when excited by UV wavelength light [7], [15], [16], [17], [18], [19]. As a self-activating phosphor, tungstate complexes have some advantages, e.g. high chemical stability, high X-ray absorption coefficient, and high average refractive index, which present efficient energy transfer from the tungstate host matrix to the localized states of the doping ions [20]. Consequently, Eu3+ doped tungstate materials may serve as efficient red phosphors.

A variety of preparation techniques have been proposed to produce low-dimensional materials with controlled morphology, including microemulsion reaction [21], hydrothermal process [22], molten salt reaction [23] pechini sol–gel method [24], sonochemical route [25] and the peptide-induced precipitation method [26]. However, preparation of lanthanide doped nanoparticles at high temperature results in clustering of optically active lanthanide ions. In general, the chemical synthesis routes results in agglomeration of particles, which in turn, reduces the luminescent intensity. However, use of suitable capping agents can remove this drawback [27], [28].

In our previous work, CaWO4 doped with Eu3+ has been successfully prepared in ethylene glycol (EG) medium and its luminescence properties were studied [29]. In the present work, investigations have been carried out on the optical properties, luminescence lifetime and particle structure upon heat treatment of nanoparticles prepared in EG. Specifically, polyol such as EG, has been widely used for synthesizing dispersible nanomaterials because of its ability to bind the OH on the surface of particle. Also, simultaneously EG can act as efficient solvent and stabilizer. The nanoparticles prepared in EG medium have significant advantage in the sense that organic part can be removed by heating at 500 °C. Thermoluminescence (TL) studies were also carried out for the prepared nanoparticles. TL is a very common technique used for dosimetry and radiation detection. In the last several years, many thermoluminescent materials have been produced and studied. A number of commercial thermolumionescent dosimeters (TLDs) are available [30], [31]. However, efforts are still being made to improve the thermoluminescence characteristics by preparing different phosphors and techniques. There have been reports of the photoluminescence and thermoluminescence of CaWO4 crystals excited by X-rays and UV-rays [32], [33]. Shmilevich et al. [34] reported phototransferred thermoluminescence (PTTL) and TL of CaWO4. In this paper TL characteristics of CaWO4 doped with different concentrations of Eu3+, irradiated with *γ*-rays are reported.

**Section snippets**

**Sample preparation**

The nanoparticles of CaWO4:Eu3+ (Eu3+ = 5, 7, 10, 15, 20, 30 at.%) were prepared at low temperature (130 °C for 3 h) in EG medium following our earlier report [29]. Finally, the as-prepared samples were annealed at 500 and 900 °C for 3 h and their photoluminescence properties were investigated. To study the TL properties, the samples were annealed at 600 °C and irradiated with *γ*-rays.

**Characterization**

X-ray powder diffraction (XRD) data for all the samples were examined using PANalytical powder diffractometer(X’Pert

**XRD study**

Fig. 1 shows the XRD patterns of 500 °C heated samples of 5, 7, 10, 15, 20 and 30 at.% Eu3+ doped CaWO4 nanoparticles. The pattern fits well with the tetragonal scheelite crystal structure of CaWO4 (JCPDS No. 01-077-2234) [35]. Fig. 2 shows the XRD patterns of 900 °C annealed Eu3+ doped CaWO4 nanoparticles. XRD patterns of different concentrations of Eu3+ doped in CaWO4 samples heated at 900 °C were also found to be similar to the tetragonal scheelite structure and no traces of additional peaks

**Conclusion**

CaWO4:Eu3+ nanoparticles were obtained via ethylene glycol route. Photoluminescence examination revealed bright red phosphorescence for CaWO4:Eu3 + nanoparticles. The highest emission is observed when doped with 20 at.% of Eu3+ for 500 and 900 °C heated samples. The PL emission intensity increased with increasing annealing temperature due to the decrease in the content of impurities, such as –OH, NO3-, and CH2 in the prepared nanoparticles. The emission color of the CaWO4 nanoparticles could be

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