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# Luminescence efficiency of calcium tungstate ($CaWO_4$) under X-ray radiation: Comparison with $Gd_2O_2S$:Tb

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ABSTRACT

The aim of the present study was to investigate the absolute luminescence efficiency (AE) of a $CaWO_4$ screen, under X-ray irradiation and to compare it with a custom made PMMA/$Gd_2O_2S$:Tb composite film screen. The emitted light was evaluated by performing measurements of the AE under X-ray exposure conditions, with tube voltages ranging from 50 to 125 kV. The spectral compatibility of the $CaWO_4$ screen, with various existing optical detectors, was investigated after emission spectra measurements. AE was found maximum at 50 kVp (2.34 Efficiency Units-E.U) which was slightly lower than the corresponding "gold standard" $Gd_2O_2S$:Tb (2.67 E.U), at the same X-ray energy. The emission spectrum of $CaWO_4$ is excellent matched with the spectral sensitivities of photocathodes and silicon photomultipliers often employed in radiation detectors, and with good matching with amorphous silicon photodiodes. Considering the adequate luminescence efficiency values and the spectral compatibility with various photodetectors, $CaWO_4$ could be also considered for use in X-ray imaging devices such as charged-coupled devices (CCD) and complementary metal oxide semiconductors (CMOS).

## 1. Introduction

After the discovery of X-rays by Roentgen various fields of research were emerged [1]. Photographic films were found inefficient to capture X-rays, thus research turned to the quest of efficient X-ray to light converting materials for coupling with films. These materials incorporated crystals of inorganic salts (called phosphors) made of calcium tungstate ($CaWO_4$) in the form of thin screens [2,3]. $CaWO_4$ along with zinc sulfide (ZnS), were used as radiation detectors, for more than eight decades [4,5].

$CaWO_4$ is a low cost, very stable material, with melting point ranging from 1570 to 1670 °C, molar mass of 287.9156 g/mol and an atomic number of 74 [4,6]. The density ranges from 6.06 to 6.1 g/cm$^3$, with afterglow, ranging from $5 \times 10^{-6}$ sec up to a few seconds, depending upon the synthesis method [4,7,8], refractive index of 1.94, a K edge of 69.5 keV and the decay time has been reported to range from 6 to $8 \times 10^3$ ns which is not ideal for applications that require high counting rate measurements [4–9].

$CaWO_4$ have reasonable X-ray absorption in the 20–100 keV range (at 50 keV, a 200 μm thick screen absorbs 35% of the X-rays), but rather low X-ray to light conversion efficiency ranging from 4 to 5% [4,5].

$CaWO_4$ emits light in the blue region of the spectrum which is well suited with the sensitivity of the first radiographic films and within the central part of the quantum efficiency curves of various photodetectors, such as photocathodes, photomultipliers (PMTs) and silicon photodiodes [10].

However these properties of $CaWO_4$ were moderate for medical imaging applications, therefore when rare earth phosphors appeared in the forefront the predominance of $CaWO_4$ was questioned [4]. Rare earths, such as, terbium-doped gadolinium oxysulfide ($Gd_2O_2S$:Tb) were also stable-low cost phosphors, with however higher absorption, density (7.3 g/cm$^3$), higher X-ray to light conversion efficiency (13–18%), superior imaging performance, properties that renders this material suitable for digital X-ray imaging devices such as charged-coupled devices (CCD) and complementary metal oxide semiconductors (CMOS) [2,4,5,11]. The K-edge for gadolinium, in $Gd_2O_2S$, is at 50.2 keV which is preferable for photon energies between 50 and 70 keV.

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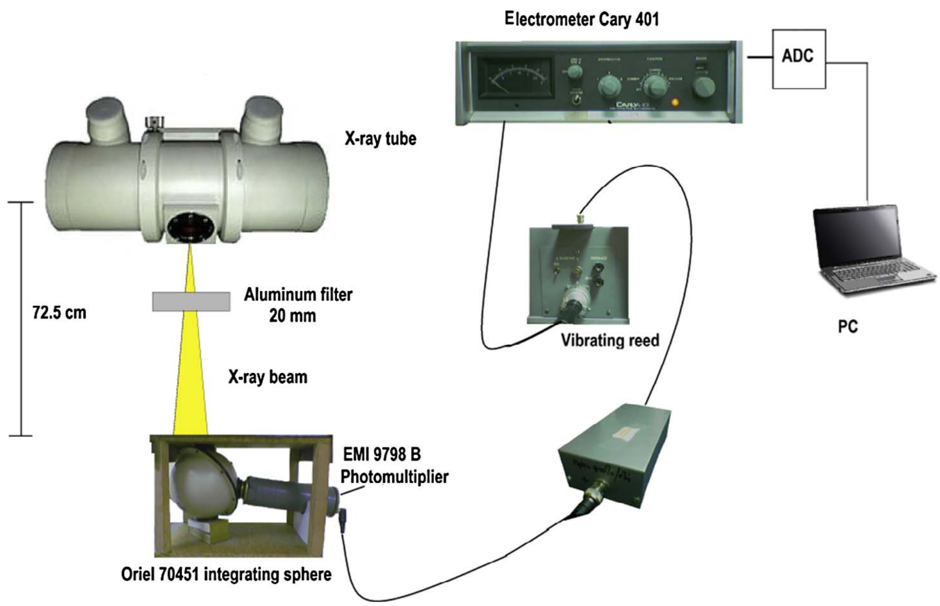


**Fig. 1.** Experimental set-up for the measurement of the emitted light energy flux comprising the integrating sphere, the PMT and the vibrating reed electrometer.

Nowadays $CaWO_4$ showed again in the spotlight of research due to the increasing interest of particle astrophysicists in the quest for dark matter in the universe [6,9,12–15].

In dark matter research, crystal form scintillators are used, in conjunction with photomultipliers to detect weakly interacting massive particles (WIMPs). The detectors operate in low temperatures, since WIMPs interact with ordinary matter extremely rarely, thus their observation requires a very low-background detector environment to determine precisely the energy of an event and the type of recoil (i.e. electron or nuclear) [13,16,17].

$CaWO_4$ is a favorable material for WIMP-nucleon elastic scattering interactions, since it meets the requirements for low intrinsic radioactivity, the ability to measure very small energy depositions, the high light yield in the cryogenic temperature range, the excellent spectral match of the emitted light of the scintillator and the photocathodes detection efficiency, along with the good temperature dependence of the scintillation decay constants of $CaWO_4$ [18–22].

Furthermore $CaWO_4$ has been also studied as a radiation detector for custom and border control, in which high density scintillators, with good energy resolution and high-detection efficiency are needed, such as sodium iodide activated with thallium (NaI:Tl) [9,23]. In this sense, $CaWO_4$ crystals were ranked among bright scintillators with good energy resolution, since they showed high light output of 15800 ± 1600 phe/MeV and good energy resolution of 6.6 ± 0.2% for 662 keV gamma rays from a $^{137}$Cs source [9].

Due to the renewed interest in calcium tungstate this study aiming to contribute in the luminescence properties of this compound. The novelty of this work resides in experimental measurements leading to the determination of physical parameters directly related to the overall X-ray to light conversion efficiency of a fluorescent material, in terms of absolute values. These parameters are (i) the absolute luminescence efficiency (light energy flux over exposure rate) under X-ray excitation in the radiographic energy range from 50 to 125 kVp, which represent the typical values adopted in practice in X-ray analysis [24], (ii) the X-ray luminescence efficiency (XLE) expressing the energy conversion properties of the material, useful for characterizing energy integrating detectors in X-ray imaging, (iii), the detector quantum optical gain (DQG), expressing the phosphor's photon creation properties traditionally employed for scintillator characterization and ranking in photon counting detection (for radionuclides) as well in counting and image statistics and (iv) the effective efficiency relating the light emission properties to particular phosphor-optical sensor couplings [25]. To our knowledge these quantities have not never been previously systematically investigated for the particular phosphor ($CaWO_4$) in the past. Comparisons with the "gold standard" $Gd_2O_2S$:Tb phosphor, under the same experimental conditions are presented. Moreover calculations regarding the attenuation coefficients of $CaWO_4$ compounds and the stopping power in terms of quantum detection efficiency (QDE) were illustrated.

## 2. Materials and methods

### 2.1. Phosphor sample preparation

Circular $CaWO_4$ samples, with diameter of 3 cm, were extracted from an Agfa curix universal screen. Parameters such as particle size and thickness of the $CaWO_4$ powder phosphor were verified via scanning electron microscope (SEM) micrographs using the Jeol JSM 5310 scanning electron microscope (SEM) collaborating with the INCA software. A flexible fluorescent $Gd_2O_2S$:Tb thin film sample, with coating thickness of 30.8 mg/cm$^2$, was produced by homogenously diluting $Gd_2O_2S$:Tb powder in 1 ml toluene and subsequently mixed into an organic transparent thermoplastic polymer, such as Poly(methyl methacrylate) PMMA/MMA (37.5% w/wo) solution to the final $Gd_2O_2S$:Tb/Toluene mixture, to obtain the final PMMA/ $Gd_2O_2S$:Tb composite film screen [26]. PMMA have distinct advantages, compared to silica glass, such as the higher light transmittance (including UV), lower weight and higher impact strength [27]. The $CaWO_4$ sample was exposed to X-rays on a BMI General Medical Merate tube with rotating Tungsten anode and inherent filtration equivalent to 2 mm Al, with energies ranging from 50 to 125 kVp. An additional 20 mm Al filtration was introduced in the beam to simulate beam quality alternation by a human body [28,25].

### 2.2. Absolute efficiency (AE)

The efficiency of a scintillator to emit light, upon X-ray irradiation can be experimentally determined by the absolute luminescence efficiency (AE). AE is defined as the emitted light energy flux $\dot{\Psi}\lambda$ per unit of incident exposure rate (2.1):

$$\eta_A = \dot{\Psi}_\lambda / \dot{X} \tag{2.1}$$

$\dot{X}$ is the exposure rate measured with a Piranha P100B (RTI) dosimeter. AE is expressed in efficiency units (E.U.) $\mu$ W× m$^{-2}$/(mR × s$^{-1}$). The