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Fabrication of an alpha particle counter: spin coated films of synthesized nanocrystalline cadmium tungstate powder

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ABSTRACT

Background: $CdWO_4$ is a scintillator with some unique properties. For example, high density, thermal and chemical stability and so on. Different applications of this scintillator such as X-ray scintillator has been investigated thoroughly so far. However, there is limited number of studies reporting the characteristics of $CdWO_4$ as an alpha counter. ***Materials and Methods:*** The $CdWO_4$ powder was synthesized by a simple co-precipitation method. Then, the $CdWO_4$ films with different thicknesses were prepared by spin coating method on glass substrates. The $CdWO_4$ powder and films were characterized by X-ray diffraction, photoluminescence, scanning electron microscopy, Fourier transformed-infrared spectroscopy, and ion beam induced luminescence. Finally, the response of samples with different thicknesses was measured using a ^{241}Am alpha source with 1860 Bq activity. ***Results:*** The analyses revealed that the nanocrystalline $CdWO_4$ with about 30 nm size was successfully synthesized without any impurity. Besides, the $CdWO_4$ films had the same luminescence emission peak characteristics as $CdWO_4$ powder had. ***Conclusion:*** It was observed that the sample with 2.9 mg/cm^2 thickness had the best counting efficiency (over 2π geometry) among the others.

Keywords: *$CdWO_4$, spin coating, alpha counter, co-precipitation.*

INTRODUCTION

Significant attention has been paid to tungstates for their unique luminescence and structure properties. One of the well-known and most practical tungstates is cadmium tungstate ($CdWO_4$). It is well known $CdWO_4$ with a monoclinic wolframite structure has high average refractive index, thermal stability, high density (7.9 g/cm^3), low afterglow to luminescence, low radiation damage and high X-ray coefficient. At room temperature, $CdWO_4$ single crystal shows photoluminescence (PL) at 460 nm which is routinely used as X-ray scintillator [1, 2]. As a scintillator, its advantages such as high efficiency, high chemical stability, and high stopping power makes $CdWO_4$ irreplaceable. Besides, it has a promising application as an advanced medical X-ray detector in computerized tomography, detection of high sensitivity double beta decay [3], and α decay of ^{180}W [4]. To date, $CdWO_4$ has been synthesized by various methods such as co-precipitation [1], sol–gel [5], reverse-micelle [6], solvothermal [7], solid-state metathetic reaction [8], spray pyrolysis [9], molten salt [10], and hydrothermal [11].

Most of $CdWO_4$ applications are based on crystal growth of $CdWO_4$.. However, it faces with some serious problem such as cracking along the cleavage plane (0 1 0) during and after pulling and evaporation of CdO during the growth. As a result, we propose new simple way to produce alpha particle counter from $CdWO_4$ film which is more convenient than crystal growth of $CdWO_4$.

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MATERIALS AND METHODS

CdWO4 Synthesis

The synthesis of $CdWO_4$- powder was synthesized by co–precipitation, based on the recipe of Priya and coworkers [1]. In this method only 5 g of $CdWO_4$- was synthesized per run [1], while in the present study by modifying synthesis parameters, we increased the amount of synthesized powder up to 100 g per run. For this purpose, sodium tungstate ($Na_2WO_4.2H_2O$) and cadmium acetate ($Cd(CH_3CO_2)_2.2H_2O$) were used as a precursors. 91.56 g of sodium tungstate and 73.96 g of cadmium acetate with analytical grade were dissolved in 1000 ml of distilled water individually. Afterward, the sodium tungstate solution was added drop-wise to cadmium acetate solution. At this step, the precipitate was formed. The precipitate was washed several times with distilled water and finally with ethanol in order to remove the impurities. It is worthy to mention that all the process was done at room temperature. Subsequently, the powder was dried at 80 ^{0}C for 24 hours in air. Finally, the powder was calcinated at 600 ^{0}C for 3 hours in air. pH of synthesizing solution has an imperative role in synthetic of $CdWO_4$. It has been reported that an optimal range of the pH value of $CdWO_4$ solution lies in the range of 3-8 [11]. In this study the final pH solution was 4.5.

Film preparation

In order to measure the response of $CdWO_4$- to alpha particles, $CdWO_4$- films were prepared by spin coating technique on glass substrates. At first, 1 g $CdWO_4$- powder was added to 20 ml ethanol with analytical grade. This solution was stirred for 24 hours at room temperature. To determine the optimum rate and time of spin coating process different experiments were carried out. The optimum speed and time for spin coating were 1000 rpm and 30 s, respectively. To produce a film with desired thickness, the process of spin coating has been repeated several times. After each coating, the samples were placed in an oven with 130 ^{0}C for 10 minutes. Five samples were prepared named as samples A, B, C, D, and E with thicknesses of 0.8, 1.3, 2.9, 4.5, and 10.4 mg/cm^2, respectively.

Characterization

The phase identification was carried out by using powder X-ray diffraction (XRD, PANalytial) with Cu-Kα1 radiation (λ=1.5406A˚) and 2θ from 10 to 70˚ at a scanning rate of 0.5˚/min. The stretching and bending vibrations of $CdWO_4$ were examined by Fourier transformed-infrared spectrometer (FT-IR, Nicolet 560). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were done by VEGAII TESCAN. PL characteristics of films were studied by Perkin Elmer LS55 at the room temperature. The ion beam induced luminescence (IBIL) and particle induced X-ray emission (PIXE) experiments were performed at the room temperature. Proton beam of 2.7 MeV energy and a current of about 4 nA were employed for the external IBIL experiments. The PIXE analyses of samples were performed in a vacuum reaction chamber, using 2 MeV proton beam of 10 pA. The size of the beam was a small spot of 10×10 μm^2, which scanned a 2×2 mm^2 area of each sample surface. To measure scintillation properties, the $CdWO_4$- films on glass substrate were optically connected to a Photonis XP2020 2” photomultiplier tube (PMT). The measurements were carried out with IAP NIM modules set-up consist of a high voltage power supply (IAP 8100), preamplifier (IAP 3001), amplifier (IAP 3600) and an ADC-multichannel analyzer (IAP 4110) (figure 1). The $CdWO_4$- films were irradiated by alpha particles from ^{241}Am source.

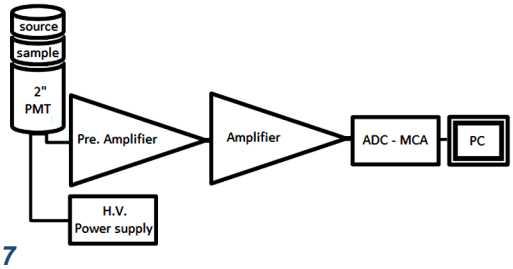

Figure 1. Experimental set-up to measure the response of films to the alpha particles.

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RESULTS AND DISCUSSION

XRD pattern of the $CdWO_4$ powder is presented in figure 2a. All the diffraction peaks can be exclusively indexed as the monoclinic $CdWO_4$ with unit cell parameters of a = 4.99, b = 5.2, c = 4.99 Å, which are well consistent with the reported data (JCPDS card no. 14-0676). Moreover, according to Scherer's equation ($D=0.9\lambda/\beta\cos\theta$) and based on (-111) and (111) peaks, average size of crystallites is about 30 nm. In Scherer's equation D, l, β, and θ are the grain size, wavelength of x-ray radiation, full width at half maximum (FWHM) and diffraction angle of (-111) and (111) peaks, respectively.

Figure 2b shows the FT-IR spectrum of $CdWO_4$ powder measured in the wave number region of 400-4000 cm^{-1}. A symmetrical stretching vibrations of W-O-W bond in WO_4^{-2} group is represented by the band at 813 cm^{-1} .The bands at 455 and 609 cm^{-1} are assigned to the in-plane deformation of the WO_4^{-2} group [7]. The band centered at 1514 cm^{-1} is assigned to the symmetrical and asymmetrical vibrations of the carboxylate group [12]. The bands located at 2923 cm^{-1} are due to the stretching modes of CH_2 group of CH_3CH_2OH [12]. The broad absorption bands centered at 3868 cm^{-1} is attributed to the vibration of H-O bonds for surface hydration films [17]. The band centered at 3444 cm^{-1} exhibits a strong absorption band, which is assigned to the H-stretching vibrations. The bands absorbed at 1635 cm^{-1} are assigned to the H-O-H bending vibrations [12].

Figures 2c and 2d show scanning electron microscope (SEM) images of $CdWO_4$ powder and lateral view of sample C, respectively. Figure 2c shows the morphology of $CdWO_4$ powder. According to EDS analysis (inset in figure 2c) weight percent of Cd, W and O were 28%, 49% and 23% respectively. Besides, to verify the values of obtained weight percent, PIXE is employed according to [13]. Interestingly, the PIXE analysis results are consistent with EDS results (table 1). Two layers can be seen in figure 2d. The top layer is $CdWO_4$ film which is coated on a glass substrate (bottom layer). It goes without saying that the thickness of $CdWO_4$ film is nearby monotonous.

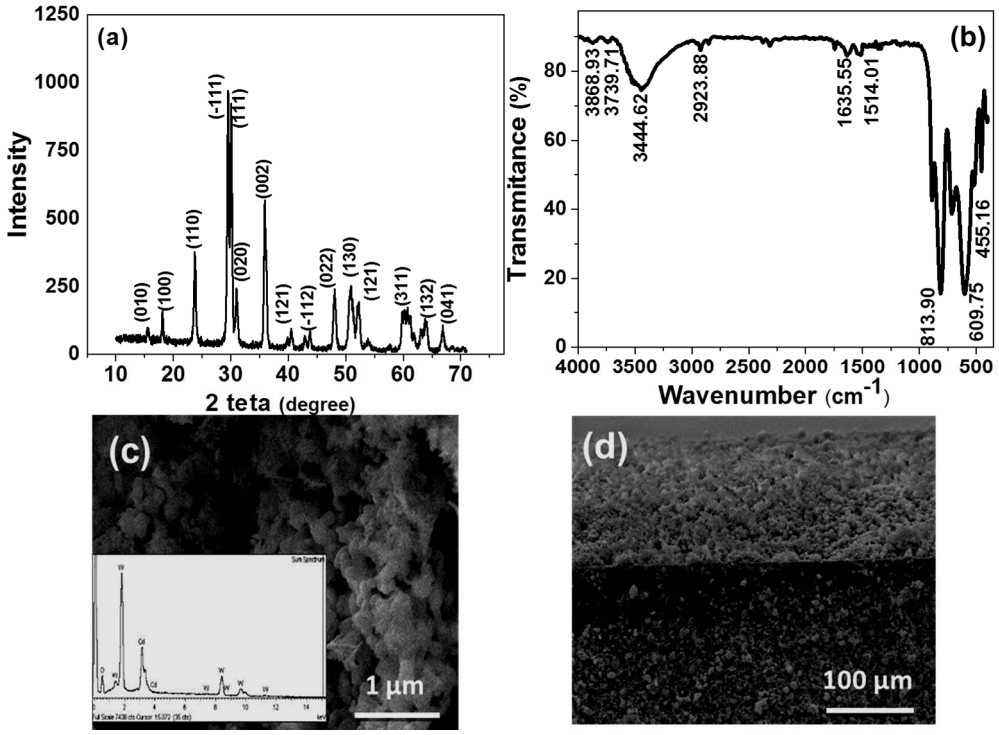

Figure 2. Structural properties of the synthesized CdWO4 powder. (a) XRD pattern, (b) FT-IR spectrum, (c) SEM of the powder (inset: EDS analysis of CdWO4 powder), and (d) lat-eral section view of sample C.

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Table 1. Weight percentage of Cd, W and O.

	Cd (%)	W (%)	O (%)
PIXE	27	51	22
EDS	28	49	23

The photoluminescence properties of sample C are also studied (figure 3). The PL spectrum is measured at room temperature. Sample C presents an emission peak at 454 nm corresponding to an excitation peak of 283 nm. Although the single crystal of cadmium tungstate at room temperature shows an emission peak at 460 nm [14], our result is consistent with the reported data [8, 10]. The structural differences between polycrystalline film and single crystal of cadmium tungstate can be the reason of 6 nm difference in emission peak [15]. Polak et al. [16] has reported that the PL emission of CdWO4 is caused by 1A1 3T1 transitions within the complex. In addition, the effect of morphology and size on PL spectrum of CdWO4 has been studied in other work [8].

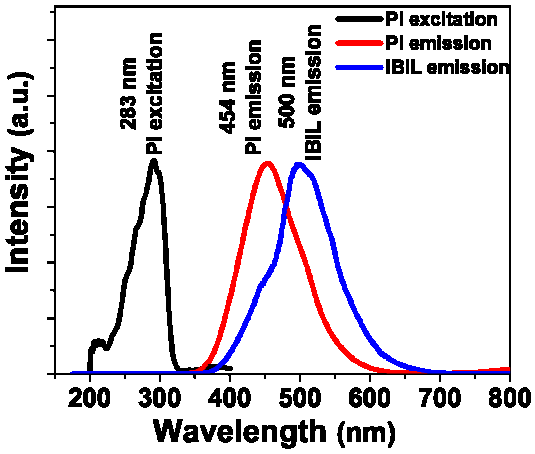

Figure 3. PI and IBIL spectra of sample C at the room temperature.

Ionoluminescence spectrum of sample C is also depicted in figure 3. The sensitivity of IBIL to various emission bands is different from PL method. As a result, it can identify different luminescence activators of samples (17). Obviously, sample C had ionoluminescence peak at 500 nm which was attributed to the optical transitions within the oxyanionic octahedral WO6 group [18]. A shoulder at 450 nm of ionoluminescence spectrum can be attributed to the PL emission peak of CdWO4. It is worthy to mention that based on our knowledge, it is the first report of CdWO4 emission peak using IBIL technique.

Figure 4a shows height pulse spectra of all samples. Although by increasing film thickness up to 4.5 mg/cm2 (sample D) the position of central peaks increases, their intensity decrease. As it is known, counting efficiency of alpha particles depends mainly on absorption alpha energy and the scintillation light which is collected by PMT. On the one hand, increase of film thickness results in absorption of a considerable part of alpha particles' energy. On the other hand, it could lead to a significant reduction in scintillation light. Based on the above explanation, the optimum thickness is determined to be 2.9 mg/cm2. Counting efficiency for sample A, B, C, D, and E were 34.67%, 46.39%, 48.09, 39.89, and 36.58%, respectively (figure 4b). This efficiency is comparable with the other alpha counter such as ZnS:Ag with 44% efficiency [19]. It is clear that the thickness plays an important role in counting efficiency of CdWO4 films. As it can be seen in figure 4b, by increasing the thickness of samples up to 2.9 mg/cm2 (sample C), counting efficiency of samples increases and after that, it starts to reduce. In fact, by increasing the thickness of films a considerable part of alpha particles' energy absorbed by films, while for thin films some of the alpha particles' energy is transmitted without complete interaction with CdWO4 particles. Indeed, transmittance of films is reduced by increasing the thickness of films. As a result, a considerable part of scintillation light absorbs by films.

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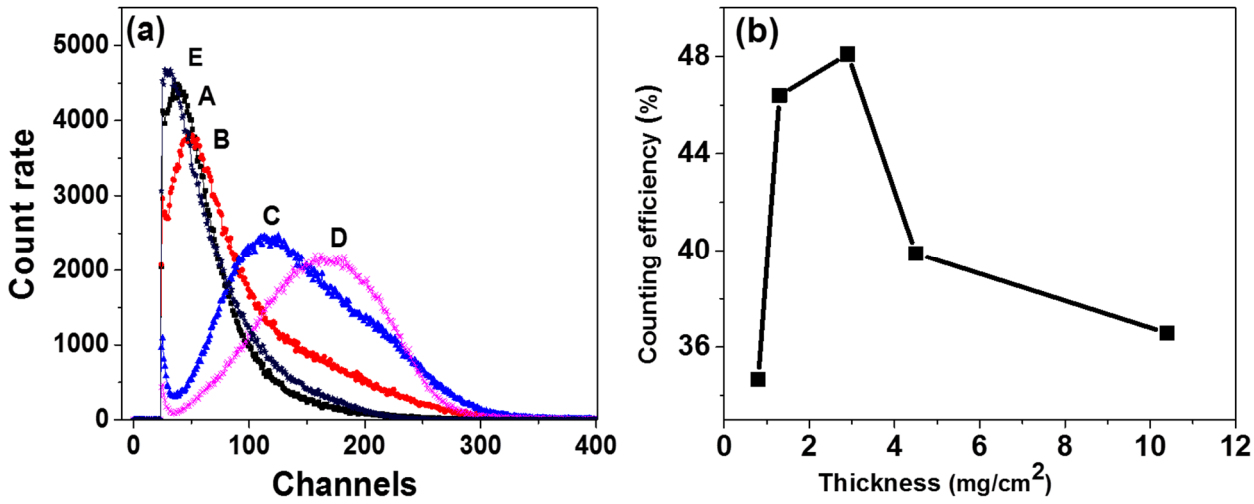

Figure 4. (a) Height pulse spectra (b) counting efficiency of all samples with 241Am source.

CONCLUSION

In conclusion, $CdWO_4$ films with different thicknesses were produced by spin coating method. XRD analysis proved that $CdWO_4$ powder with monoclinic wolframite structure was well synthesized. Besides, No peaks for other phases or impurities were observed in XRD patterns showing an acceptable purity level of prepared $CdWO_4$ powder. The PL spectrum of sample with 2.9 mg / cm^2 thickness had 454 nm emission peak at room temperature which is consistent with the PL spectrum of $CdWO_4$ single crystal. Ionoluminescence analysis revealed $CdWO_4$ film had a peak at 500 nm at room temperature. Among the prepared samples, the sample whose thickness was 2.9 mg / cm^2 had the most efficiency for detecting alpha particles (48%). In fact, in film with small thickness, a part of alpha particles without any interaction with $CdWO_4$ particles passed through the film, however, in the thicker films some part of scintillation light is absorbed by films leading to a decrease of scintillation light efficiency.

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***Conflicts of interest*: Declared none.**

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