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Thin Solid Films 434 (2003) 55–61

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Synthesis of cadmium tungstate films via sol–gel processing

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Received 16 August 2002; received in revised form 15 February 2003; accepted 28 February 2003

Abstract

Cadmium tungstate is a scintillator material with excellent intrinsic photoluminescent properties. It is highly resistant to gamma radiation, has an almost non-existent afterglow and is highly efficient. Cadmium tungstate is also non-hydroscopic, unlike the more prevalent thallium-doped alkali halide scintillators. In order to create thin films of cadmium tungstate with precise stoichiometric control, a sol–gel processing technique has been applied to produce this material for the first time. In addition to lower processing temperatures, sol–gel-derived cadmium tungstate is cheaper and easier than other technologies, particularly for thin films. Furthermore, it has the potential to produce nanostructured materials with good optical quality. X-Ray diffraction results of sol–gel-derived materials fired at various temperatures imply crystallization of cadmium tungstate without the intermediate formation of either tungsten oxide or cadmium oxide. Scanning electron microscopy analysis shows the formation of nano-sized particles prior to heat treatment, which form meso-sized particles after the heat treatment. Photoluminesce analysis indicates emission of derived films at 480 nm, which agrees with other published data. Finally, the efficiency of derived films was approximately 6% ± 1.8%.

Keywords: Sol–gel; Fluorescence; Luminescence; Tungsten oxide; Light scattering

1. Introduction

Due to its inherent optical and physical properties, cadmium tungstate ($CdWO_4$) is a desirable material for various scintillation applications. These properties include high emission efficiency (~40% that of NaI [1]), high radiation stability, little afterglow [2] and high density (7.9 g/cm^3). $CdWO_4$ is also non-hygroscopic and has high thermal stability. With absorption near 325 nm and emission near 480 nm [3], $CdWO_4$ can be coupled with a photomultiplier tube and photodiode for use in many applications, including nuclear spectroscopy [4], dosimetry [5], oil-well logging [6] and computed tomography [7]. Conventional polycrystalline $CdWO_4$ ceramics are not suitable for these applications due to light scattering at grain boundaries. Therefore, $CdWO_4$ single crystals are used for the above-mentioned applications. $CdWO_4$ single crystals, however, have several inherent limitations:

- $CdWO_4$ crystals of high quality are characterized by rather low technological output in mass production. Typically, the Czocharalski method is used to grow $CdWO_4$ single crystals.
- Large $CdWO_4$ crystals are not attainable. Typical boules are of the order of mm^3.
- Machining of $CdWO_4$ is rather difficult due to its intrinsic (010) cleavage plane.
- It is difficult to eliminate all defects from $CdWO_4$ single crystals. Typical defects in $CdWO_4$ crystals include macroinclusions, light scattering centers (LSC), blocks, twins and deviations from the stoichiometric composition [8]. The loss of one of the crystal constituents, namely CdO, is found to be very high at the growth temperature, and this gives rise to compositional changes and the presence of a defective core in the crystal grown. These growth imperfections adversely affect the optical transmission characteristics, and hence the scintillation output of the crystal.
- It is rather difficult to use single-crystal $CdWO_4$ in fabricating micro- and nano-scale devices such as micro-electro-mechanical systems (MEMS) and nano-electro-mechanical systems (NEMS).

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0040-6090/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6090(03)00485-1

- Thin films are not easily attainable through Czocharalski techniques.

Nanostructured polycrystalline $CdWO_4$ materials, with suitably designed processing methods, could conceivably overcome the above-mentioned limitations. One approach to producing nanostructured material is through thin film technology. In general, there are two possible film deposition methods: vapor-phase and liquid-phase deposition. The former includes chemical vapor deposition and physical vapor deposition; sol–gel processing is a typical liquid-phase deposition method. Tanaka and co-workers [9,10] are the only group so far that has reported deposition of polycrystalline $CdWO_4$ films in the literature. They studied the feasibility of the pulsed laser ablation method, one of the physical vapor deposition methods, for depositing nanostructured polycrystalline $CdWO_4$ films. $CdWO_4$ films with desired stoichiometric composition and photoluminescence similar to single-crystal $CdWO_4$ were deposited by carefully selecting an appropriate Cd/W ratio (0.56) for the mixed CdO and WO_3 target. It was found that Cd is enriched in the pulsed laser-deposited films. Such enrichment of Cd in the deposited film would result in depletion of Cd from the target, and would eventually lead to deviations from the desired stoichiometric composition. In addition, pulsed laser deposition requires an ultra-high vacuum (UHV; $\sim 1.33\times 10^{-5}$ Pa) system and complicated geometric design of the deposition chamber to achieve a uniform film. Currently, no other publications have focused on developing cadmium tungstate nanostructured thin films.

Solution processing has several advantages for the synthesis of complex oxides. Liao et al. [11] developed a successful hydrothermal processing technique to produce nanorod powder of crystalline cadmium tungstate. To date, no attempt at using the sol–gel process to produce cadmium tungstate has been made. Although the typical sol–gel process does not have advantages for producing defect-free material, it does have several innate advantages for producing oxide materials over traditional mixed-powder techniques. Heterogeneous condensation between differing alkoxides allows for the formation of appropriate precursors of complex oxide materials at relatively low temperatures. This can be effectively employed, through manipulation of processing conditions and procedures, to achieve homogenous xerogels of complex oxide materials. One key advantage with sol–gel processing is the lower processing temperatures required to produce crystalline material. This is particularly advantageous in this system because CdO is so volatile. Sol–gel processing can therefore maintain precise stoichiometric and phase control far more easily than other crystal growth techniques. Also, since sol–gel processing is a solution technique, it can easily deposit thin films through spin or dip coating. Finally, sol–gel processing does not require expensive equipment, precursors are easily obtained, the process is not labor-intensive and the resulting material is environmentally benign [12]. In this paper, the application of sol–gel technology to the cadmium tungstate system is presented for the first time. The films and powders deposited were analyzed via X-ray diffraction to determine the extent of crystallization. Scanning electron microscopy (SEM) analysis of $CdWO_4$ films and powders is presented to show the presence of nanocrystallites. Subsequently, photoluminescence (PL) data were obtained for cadmium tungstate deposited on quartz. Finally, the relationship between chemical composition, crystallinity, microstructure and luminescence for this material is discussed.

2. Experimental details

The precursors used in the preparation of $CdWO_4$ sol were tungsten (VI) chloride (WCl_6, Alfa-Aesar) and cadmium acetate [$Cd(OOCCH_3)_2\cdot 6H_2O$, Alfa-Aesar]. The materials used were not modified prior to precursor synthesis. First, the WCl_6 precursor was converted to tungsten alkoxide using the process described by Nishio et al. [13]. WCl_6 was dissolved in 100% ethanol (C_2H_5OH) at a molar ratio of 1:6 with flowing dry nitrogen in a glovebox; the following chemical reaction was expected to occur:

$$WCl_6 + 6C_2H_5OH \rightarrow W(OC_2H_5)_6 + 6HCl$$

First a yellow solution was formed, which quickly turned dark blue. The solution was then diluted to a 0.2 M $W(OC_2H_5)_6$ solution in ethanol, and refluxed with minimal air contact at 50 °C for 24 h to remove hydrogen chloride from the solution. The final alkoxide solution was clear and colorless, but highly acidic due to incomplete removal of hydrogen chloride.

The sol–gel processing procedure used in this research was developed by modifying the sol–gel process for the individual alkoxides for cadmium oxide [14,15] and tungsten oxide [13]. The $CdWO_4$ sol was prepared by dissolving a stochiometrically equivalent amount of cadmium acetate in a reaction kettle containing the tungsten ethoxide solution to produce a solution with a Cd/W molar ratio of 1:1. The mixture was then ultrasonicated at room temperature for 1 min to dissolve the cadmium acetate. The resulting sol was clear and yellowish and appeared to be stable, although the gelation time was found to be relatively short, approximately 1 h at room temperature. For making $CdWO_4$ films, the sol was spin-coated onto various substrates, including fused quartz, alumina and borosilicate glass, at a speed of 2000 rev./min. Powders were obtained by allowing the sol to gel at room temperature. The gel was then allowed to dry at 100 °C. The films and powders were

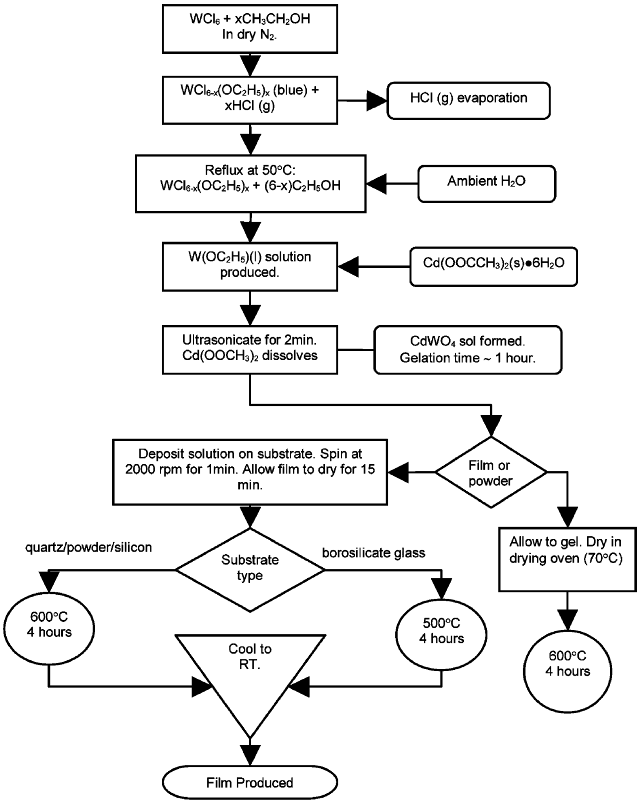

Fig. 1. Flow chart for the formation of cadmium tungstate ($CdWO_4$) sol.

sintered at 400, 500 and 600 °C in air. These temperatures were selected based on the annealing temperatures used for films prepared by Tanaka et al. [9,10]. The samples were typically fired for 4 h at these temperatures, with a ramping rate of 3 °C/min to minimize cracking. In all cases, the sintering temperature is far below the melting temperature of $CdWO_4$, which is approximately 1100 °C [16]. Fig. 1 is a flow chart, schematically summarizing the sol–gel process described above for producing $CdWO_4$ powders and films.

All X-ray diffraction (XRD) data were obtained using a Phillips PW1830 X-ray diffractometer. Micrographs of sol–gel-derived $CdWO_4$ powder and films on various substrates were obtained using a JEOL 840A SEM. The PL spectra were obtained with an Oriel Instaspec IV charge-coupled device camera using a mercury lamp for excitation. The samples for PL analysis were prepared as described above onto a fused quartz substrate. The absorbance was used to determine the best excitation wavelength. The film was then subjected to 300-nm light to promote excitation, which was subsequently recorded. The relative intensity was normalized for comparison purposes.

3. Results and discussion

The sol–gel process developed in this study appears to result in the formation of a single-phase crystalline $CdWO_4$ upon sintering, which is supported by the XRD results and is discussed later. Throughout the sol–gel process, no water was explicitly added to the system; however, ambient water, as well as associated water in cadmium acetate, was believed to drive the hydrolysis and condensation reactions. Although dissolution of WCl_6 in ethanol was carried out with flowing dry nitrogen gas in a glovebox, some moisture is present and presumably reacted with the tungsten precursor. With a relatively low concentration of water present in the tungsten ethoxide solution, it is reasonable that homogeneous hydrolysis and condensation reactions were greatly slowed. This is evidenced by the high stability of the tungsten precursor solution, which was independent of the concentration and never gelled at room temperature when sealed. This result implies that the condensation between (fully or partially) hydrolyzed tungsten precursors was slow. When cadmium acetate was dissolved in pure ethanol alone, the cadmium alkoxide was substantially stable and solution took 24 h to gel at room temperature. Each cadmium acetate molecule has six associated water molecules, so it seems reasonable to assume that the cadmium acetate underwent hydrolysis and condensation reactions with the associated water upon dissolution in ethanol. The long gelation time for cadmium alkoxide solution suggested that the hydrolysis and condensation reactions were slow. However, upon introduction of cadmium acetate into the tungsten precursor solution, subsequent hydrolysis and condensation reactions proceeded very rapidly. The gelation of resulting sols was strongly dependent on the precursor concentration and the solvent type. With precursor concentrations exceeding 0.3 M in ethanol, the sol immediately gelled upon introduction of cadmium acetate. The significantly differing gelation times or reaction rates found for tungsten, cadmium and tungsten–cadmium sols could be attributed to two possible mechanisms. One is that tungsten and cadmium alkoxides acted as catalysts for the hydrolysis and condensation reactions, as found in the silica–titania and silica–zirconia systems [17]. The other is that the condensation reaction between tungsten and cadmium precursors was far faster than the condensation reactions between tungsten precursors or between cadmium precursors, i.e. heterocondensation proceeded much faster than homocondensation. With the present data, it is impossible to ascertain whether heterogeneous condensation predominates within the solution, but it is reasonable to assume that predominant homocondensation reactions would result in the formation of a mixed gel or a composite of cadmium oxide (or hydroxide) and tungsten oxide (or hydroxide); while predominant heterocondensation like-

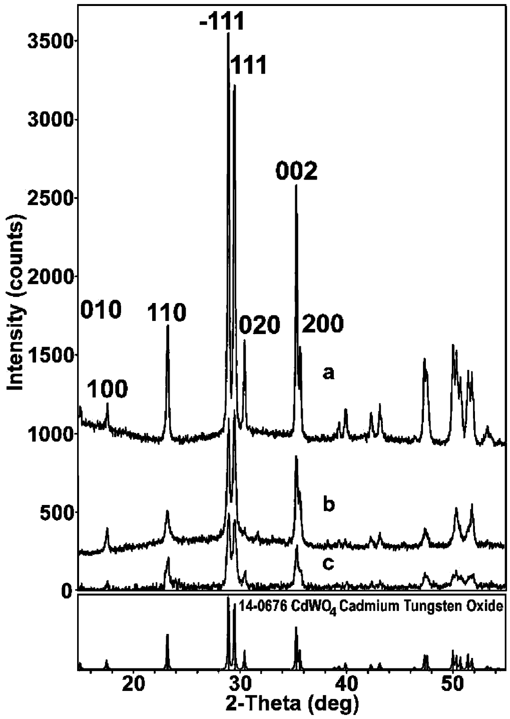

Fig. 2. Comparison of the X-ray spectra for: (a) powder sintered to 600 °C for 4 h; (b) film deposited on borosilicate glass, sintered to 400 °C for 4 h; and (c) film deposited on fused silica quartz, sintered to 600 °C for 4 h. Crystalline orientation of peaks at $2\theta > 40°$ were all identified as peaks for $CdWO_4$, but are not indicated for clarity.

ly results in a single-phase gel with homogeneously mixed cadmium oxygen and tungsten species. In the latter case, crystallization of cadmium tungstate occurs immediately upon heat treatment of the derived gel at low temperatures, without crystallization of either cadmium oxide or tungsten oxide. On the contrary, crystalline CdO and/or WO_3 are most likely found prior to the formation of cadmium tungstate in a composite gel derived from predominant homocondensation reactions, upon firing or even without heat treatment. XRD analyses revealed that the sol–gel-derived powder and films coated on various substrates were amorphous prior to heat treatment at elevated temperatures. It was found that no intermediate crystalline phase was formed prior to the crystallization of $CdWO_4$ phase when fired at temperatures above 500 °C. It is arguable that XRD results do not provide direct evidence supporting the hypothesis that heterocondensation occurred during the sol preparation in this study. However, the crystallization of $CdWO_4$ at a relatively low temperature (500 °C) without the formation of an intermediary phase does indicate that cadmium and tungsten components were homogeneously mixed within the gel prior to heat treatment. It is also noted that limited texturing occurred on the films. This is indicated by the absence of the (020) peak in both films. Although it is not known what exactly contributed to the texturing of the films, texturing was also observed in $CdWO_4$ boules grown by Sabrawaal and Sangeeta [18].

Fig. 2 shows typical XRD spectra for $CdWO_4$ powders and films deposited on both fused quartz and borosilicate glass substrates after heat treatment. XRD analyses revealed that the films deposited on different substrates showed different crystallization temperatures. Table 1 summarizes these results. It is evident that the formation of crystalline $CdWO_4$ on borosilicate substrate occurred at a temperature as low as 400 °C, whereas crystallization of $CdWO_4$ powder and films on other substrates occurred at 600 °C or higher. It is not known why the crystallization of $CdWO_4$ film on borosilicate substrate is appreciably lower than powder and films on other substrates. It is speculated that a crystallization activation energy exists, which is catalyzed by the borosilicate glass. Perhaps this catalytic activity is due to the lower melting temperature of the borosilicate glass over quartz. This hypothesis requires further research for confirmation.

Fig. 3a,b show SEM micrographs of a $CdWO_4$ film, whereas Fig. 3c,d show SEM micrographs of $CdWO_4$ powder. Fig. 3a,b show the surface morphology of $CdWO_4$ film on fused silica quartz before and after sintering at 600 °C for 4 h, respectively. Particles are approximately 1 μm in diameter and show clear crystal facets. It should also be noted that no continuous $CdWO_4$ films were formed before or after sintering at elevated temperatures (up to 750 °C) on all the substrates studied. In addition, the films did not exhibit the desired nanostructure to eliminate grain-boundary light scattering. The reason for the poor contiguity is not known. A low content of solid in the sol may be responsible. This is a difficulty for most sol–gel-derived films since the precursors contain organic solvents. The gelation time for the 0.2 M sol is very short, approximately 1 h at room temperature; it is very difficult to increase the concentration of solid in experiments without loss of sol stability. It is also possible that the low pH of the sol may catalyze the reaction, resulting in faster gelation. However, attempting to increase the sol

Table 1
Substrates tested and resulting successful sintering temperatures for forming crystalline cadmium tungstate

Substrate	Sintering temperature (°C)			
	RT	400	500	600
Borosilicate glass	X	O	O	NA
Fused quartz	X	X	X	O
Silicon	X	X	X	O
Alumina	X	X	X	O
Powder	X	X	X	O

X indicates crystallization did not occur, whereas O indicates that crystallization did occur.

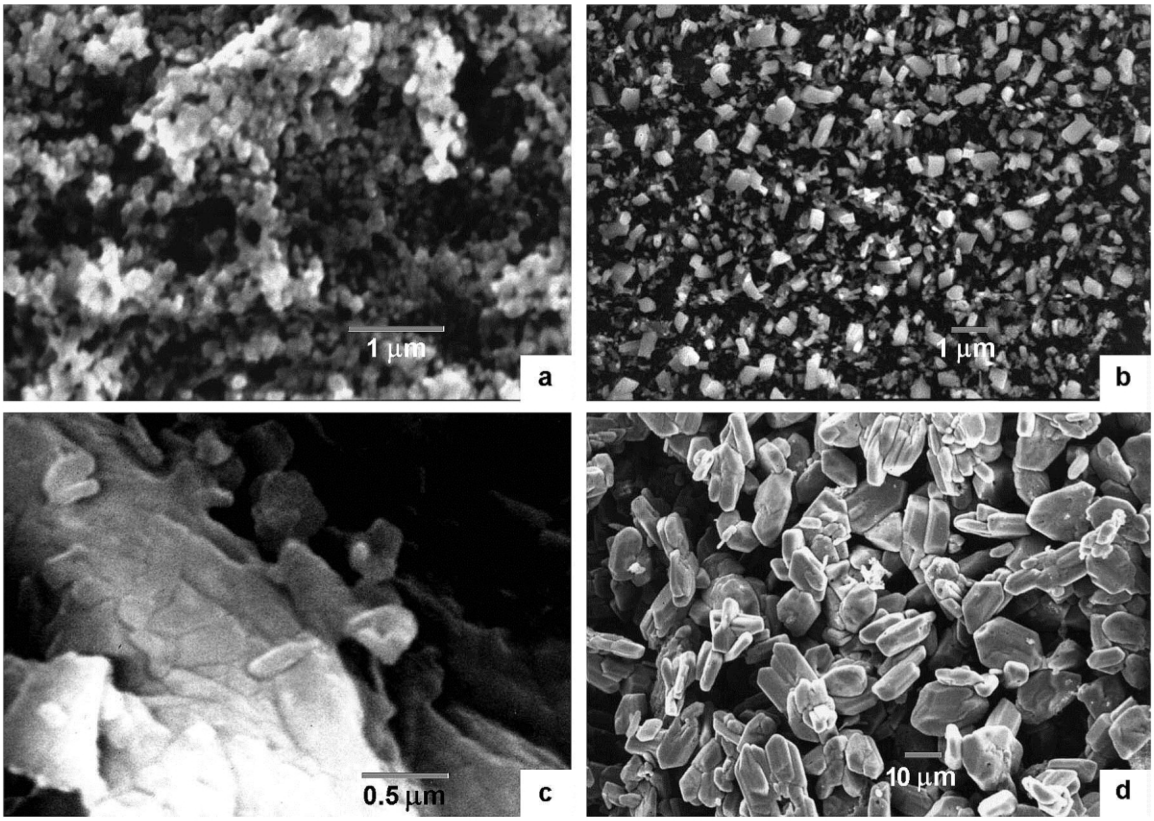

Fig. 3. (a) Thin film of cadmium tungstate gel as deposited on borosilicate glass. The open pore structure likely results from the short gelation time. (b) Thin film of cadmium tungstate deposited on borosilicate glass and sintered at 500 °C for 4 h. The resulting film consists of individual crystals of approximately 1 μm in diameter. (c) Bulk powder of dried cadmium tungstate gel. Agglomerates are thought to have formed, as indicated by fine lines bordering the grains. (d) Bulk powder of cadmium tungstate after sintering at 600 °C for 4 h. The micrograph indicates crystallization of large grains of the order of 10 μm in diameter.

pH by adding ammonium hydroxide resulted in immediate precipitation. Another possibility for the open structure is the volatile nature of the cadmium oxide during sintering, which may inhibit full densification of $CdWO_4$ films during this process. Fig. 3c shows the morphology of sol–gel-derived $CdWO_4$ powder prior to heat treatment at elevated temperatures and shows outlined particle agglomerates of approximately 500 nm in diameter with a relatively broad size distribution. Fig. 3d shows the powder upon sintering at 600 °C for 4 h. The particles are highly faceted and are approximately 10 μm in length and 5 μm wide. The reason for the lack of nanostructure is also not known. However, it is speculated that the heat treatment method is partially responsible. From Fig. 3a, it is clear that the films prior to heat treatment exhibit particles within the desired nanometer range. Upon crystallization, however, the particles grow to sizes approaching the micrometer range. A similar phenomenon was observed by Tang et al. [19] in $PbZrO_3$ films derived through a similar sol–gel spin-on process onto a $Pt/Ti/SiO_2/Si$ substrate. In this study, the authors attribute rapid grain growth at 550 °C to island coalescence within the film. Another study on the sol–gel development of zirconia films on MnO Guinebretiere et al. [20] seemed to show yet another similar phenomenon. In this study, thin films of sol–gel-derived zirconia developed into epitaxial single-crystal islands on the MnO substrate at high annealing temperatures. In each case, heterogeneous nucleation at lower temperatures between the substrate and the film was attributed to the formation of such islands. One issue that is not consistent between these studies and the current study, however, is that the cadmium tungstate films were not deposited onto single-crystal substrates. Thus, another driving force for heterogeneous nucleation prior to annealing must have been present. One possibility for heterogeneous nucleation is a reduction in thermal stresses between the film and substrate, or in high-energy facets during grain growth, or a combination thereof. Despite this, other groups have shown nanostructured material derived from sol–gel precursors [21,22], and thus it seems reasonable that the precursors developed in this research can be applied in such a way that nanostructured films would be attainable with more appropriate heat treatments. Differential thermal analysis or scanning calorimetry measurements have not yet been

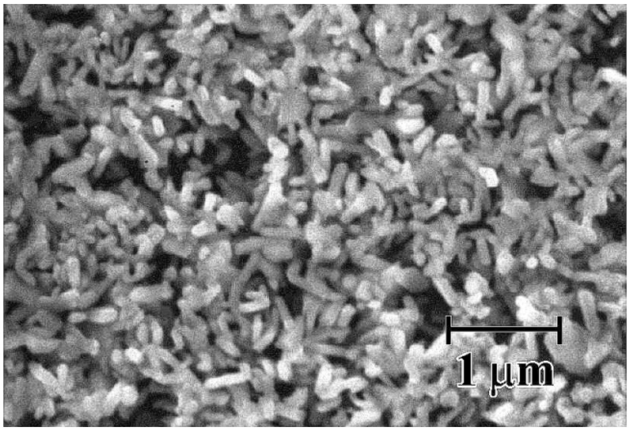

Fig. 4. Film deposited on borosilicate glass, sintered at 500 °C for 4 h. The film was derived from a sol–gel with butanol as a solvent instead of ethanol. The resulting morphology implies that the solvent has the desired effect of increasing the film density.

conducted for this system to determine the crystallization temperature of the films. This information would likely aid in determining the ideal heat treatment conditions to produce crystallites at the nanometer range. Of course, obtaining nanostructured grains is only half of the issue to obtain optically transparent films. The pore structure must also reside within the nano-scale. This gives rise to a two-fold challenge, which must be dealt with in order to obtain functional films: first, to control the porosity of the derived films to be low and of nanoscale dimension; and second, to control the processing conditions to promote adequate crystallization with limited grain growth. This may be possible without the need for annealing temperatures. Shimooka et al. [23] were able to produce optically clear, crystalline $BaTiO_4$ xerogels through pure control of hydrolysis and condensation reactions. They did this through control of sol concentration and H_2O concentration to result in an optimal condensation rate, which allowed for crystallization in situ during sol–gel processing without additional heat treatment. It seems reasonable that similar films of cadmium tungstate are attainable, but additional modification of the sol chemistry would be required to ensure sol stability. The 0.2 M (in ethanol) precursor sol used for the above films was rather reactive; any additional incorporation of water would result in immediate gelation. Using a less reactive solvent than ethanol could conceivably improve the sol stability. Using butanol as a solvent was found to greatly increase the gelation time of the sol, and thus seemed a reasonable solvent. Fig. 4 shows a crystallized film deposited on borosilicate glass using the butanol solvent. The heat treatment used to crystallize the film was identical to that used for films derived from ethanol-based sols. The figure clearly shows an improvement in contiguity over ethanol solvent films; moreover, the film approaches the desired nanocrystalline structure. This suggests that the solvent type alone can be an effective variable for modifying film morphology. It is clear that more than one variable must be adequately controlled to obtain the desired film morphology. Future experiments will be carefully designed to incorporate solvent, water and precursor concentration considerations, as well as heat treatment considerations, to determine effective variables for controlling the crystallinity and optical quality of sol–gel-derived films.

Nanorod-shaped $CdWO_4$ particles with an aspect ratio of 5 were also observed in the sol–gel-derived film coated on a fused silica quartz substrate and fired at 600 °C for 4 h; however, no correlation between the crystal shape, substrate and firing temperature could be established at this stage. The formation of $CdWO_4$ nanorods was reported by Liao et al. [11] using direct solution synthesis. The formation of $CdWO_4$ nanorods in sol–gel films occurs during crystallization, while the films were fired at elevated temperatures.

Fig. 5 shows the absorbance and photoluminescence spectra obtained from a sol–gel-derived film deposited on a fused quartz substrate, which was then heat-treated at 600 °C for 4 h. The results show a PL peak at 480 nm and agree well with data published in the literature. The presence of a characteristic PL peak at 480 nm further confirms that well-crystallized stoichiometric cadmium tungstate was formed by firing at 600 °C. This photoluminescence can also be visually observed upon irradiation with a UV lamp or electron bombardment during sputter coating. Samples that had not crystallized showed no visible photoluminescence. This confirms the notion that the sol–gel-derived powder and films are amorphous prior to firing. In addition, it is known

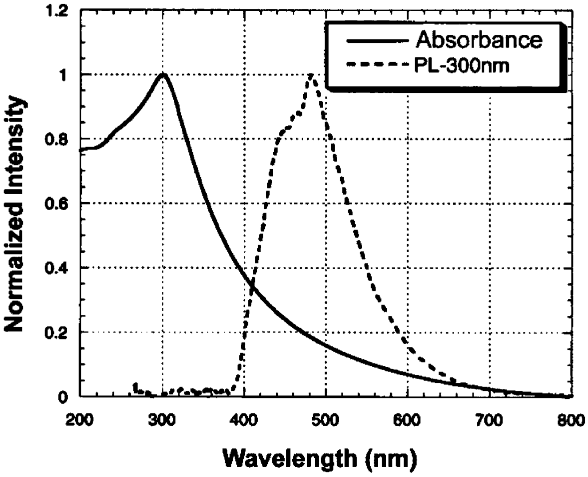

Fig. 5. Absorption and photoluminescence data for sol–gel-deposited cadmium tungstate on fused silica quartz. The intrinsic absorbance peaks at 300 nm, which in turn leads to excitation and emission at approximately 480 nm. The solid line indicates the absorbance and the dashed line indicates the emission.

that the photoluminescence is associated with only the crystal structure of $CdWO_4$, and thus no photoluminescence would be expected from either amorphous $CdWO_4$ or a mixture of CdO and WO_3. The efficiency of the films was investigated by Sol M. Gruner and colleagues at the synchrotron facility at Cornell University. They found the efficiency of films derived using butanol as the solvent to be approximately $6\pm1.8\%$. A large-grained microstructure and porosity would certainly exert a negative impact on the photoluminescence and optical transparency. To obtain maximum photoluminescence, it is necessary to eliminate all light scattering by grain boundaries and porosity. This, in turn, demands the films consist of particles and pores in the nanometer range. However, the photoluminescence spectra demonstrated by the $CdWO_4$ films obtained in this research, which have micrometer-sized pores and grains, serves as an important indicator that sol–gel processing is a promising approach for the preparation of $CdWO_4$ films for various scintillation applications.

4. Conclusions

A sol–gel process has been developed to form $CdWO_4$ powder and films on various substrates. It is believed that either amorphous $CdWO_4$ gel or highly mixed amorphous WO_3 and CdO gel formed during hydrolysis and condensation reactions. Single-phase crystalline cadmium tungstate powder and films were readily obtained by firing at temperatures above 600 °C for 4 h in air. The resulting powder and films consist of uniformly sized and well-faceted crystal grains of approximately 1 μm in diameter. Such $CdWO_4$ films show characteristic photoluminescence and absorption spectra and would suit applications requiring miniaturized scintillators. The formation of nanostructured $CdWO_4$ materials through sol–gel synthesis remains a challenge, however. Given the functionality of sol–gel processing, further research in this system this will likely realize this goal.

Acknowledgments

The authors would like to acknowledge the technical assistance and valuable advice from Michelle Liu and Prof Alex Jen. In addition, they acknowledge Prof Sol M. Gruner and colleagues at Cornell University for their valuable contributions to the efficiency data. K.L. acknowledges the Lewis and Katharine Marsh Fellowship, S.J.L. acknowledges the Ford Motor Company fellowship and partial support from the Joint Institute for Nanoscience funded by the Pacific Northwest National Laboratory (operated by Battelle for the US Department of Energy).

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