Dense and optical transparent $CdWO_4$ films by sol-gel processing for scintillation applications

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In this paper, we report the first successful fabrication of dense and optically transparent cadmium tungstate (CWO) films by sol-gel processing and the study of their optical and x-ray scintillation properties. A new sol-gel processing method was developed using tungstic acid and cadmium nitrate as precursors and hydrogen peroxide as solvent; homogeneous and stable CWO sols were aged at room temperature and used for the preparation of CWO films. A rapid sintering process was investigated and found to be necessary to make dense and optically transparent nanocrystalline CWO films. CWO films were uniform, fully dense, and crack-free, with CWO as the only detectable crystalline phase, as determined by x-ray diffraction. The thickness, density, grain size, and crystallinity of CWO films are all found to be strongly dependent on the sintering conditions and in turn impact the optical and x-ray scintillation properties. Sol-gel-derived dense CWO films demonstrated intense photoluminescence and x-ray excited optical luminescence intensity. The relationships between sol-gel processing, nanostructures, and optical and x-ray scintillation properties are discussed in detail.

I. INTRODUCTION

Cadmium tungstate ($CdWO_4$, CWO) is a luminescent material that absorbs the energy of high-energy radiation such as x-rays, γ-rays, and neutrons and then converts the energy to visible or near visible light within a short time of less than 10^{-8} s,[1] making it a valuable scintillation material. Due to its high emission efficiency (~40% that of sodium iodide),[2] high radiation stability, little afterglow, and high density, CWO has been widely used in high-energy radiation imaging and detection, spectrometry and radiometry of radionuclides in extra-low activities, and especially for computer tomography (CT).[3,4] Moreover, based on radiation capture reactions, CWO has been investigated for application in neutron detection.[5]

Although CWO has been widely used, most studies and applications of CWO were focused on single crystals synthesized by the Czocharalski method at high temperatures.[6] Single-crystal CWO is difficult to grow at a high temperature since stoichiometric control is difficult to maintain due to incompatible vapor pressures of the constituents during crystal growth. The maintenance of chemistry stoichiometry is critical because the scintillation properties of CWO are highly dependent on its chemical composition. Conventional ceramic processing is difficult to apply to the fabrication because CWO decomposes at 1100 °C and highly volatile CdO prevents densification at temperatures even far below 1100 °C.[6] It is also difficult to use single-crystal CWO in fabricating micro- and nanoscale devices that require films for high spatial resolution. Recent developments in film engineering have allowed more and more nanostructured polycrystalline CWO to be made by various methods including sol-gel processing,[7] pulsed laser deposition,[8] spray pyrolysis,[9] hydrothermal method,[10] polymer-controlled

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crystallization,[11] and liquid epitaxy growth.[12] Of these methods, sol-gel processing is particularly useful or the only choice for the formation of dense polycrystalline complex oxide films that decompose at elevated temperatures or consist of highly volatile constituent elements such as cadmium in CWO. Furthermore, the moderate sintering temperatures of sol-gel processing will also preserve nano-sized particles because grain growth becomes predominant at high temperatures[13]; large grains may cause unacceptable loss of luminescence by grain boundary scattering.

Previous sol-gel-derived CWO films have demonstrated photoluminescence and the capability to detect x-rays, γ-rays, and neutron emissions.[14] However, CWO films that are simultaneously transparent, thick, and dense have never been achieved despite various modifications and improvement reported in the literature. A common problem in sol-gel processing is the control of hydrolysis and condensation reactions and the prevention of precipitation or phase separation, particularly in complex oxide systems. For CWO sols, the stabilization of tungsten precursors is particularly difficult because most tungsten precursors are highly moisture sensitive. Many different tungsten precursors have been investigated to fabricate tungsten-related films by sol-gel processing, including tungsten alkoxide,[15] sodium tungstate,[16] tungsten chloride,[7] and tungsten oxychloride.[17] Tungsten alkoxide is arguably the standard sol-gel precursor for tungsten systems, but it is extremely moisture sensitive and difficult to deal with at ambient conditions. Sodium tungstate can be used but will introduce sodium into the sol as an impurity that is hard to remove from the film. The other frequently used tungsten precursors were those precursors with chlorine, such as WCl_6 and $WOCl_4$, because they were more stable and less expensive.[7,18] When these precursors react with alcohol, such as iso-propanol, the following reaction is expected to occur[19]:

$$WOCl_4 + 4(CH_3)_2CHOH \rightarrow WO[OCH(CH_3)_2]_xCl_{4-x} + x\mathrm{HCl} \quad . \qquad (1)$$

The byproduct of this reaction is hydrogen chloride, which decreases the pH value of sol, leading to a long gelation time, and leaves chloride as an impurity in CWO film after sintering. Hydrogen chloride in the sol will also lead to the formation of crystalline cadmium chloride upon the addition of cadmium nitrate during the sol preparation, resulting in the formation of milky and relatively unstable sols. These crystalline particles were easily observed by microscope in CWO sol and film without any thermal annealing; the results were confirmed by x-ray diffraction (XRD).[17] The presence of cadmium chloride crystals in the CWO film would effectively prevent the full densification by sintering at elevated temperatures; typically, the films will consist of large particles and many large open-voids that result in inhomogeneous morphology and low optical transparency. Multiple coatings did not improve the densification and the optical transparency. Other modifications in sol-gel preparation also failed to achieve uniform dense CWO films. The practical scintillation applications require thick, dense, and optically transparent films with desired stoichiometric composition and good crystallinity to capture as many of the incident high-energy particles as possible to generate the maximum number of photons; good optical transparency is desired to permit the resultant luminescent photons to come out of the scintillation films so that the photons can be detected by a charge-coupled device (CCD) or photomultiplier tube (PMT) and thus achieve high scintillation efficiency.

In this paper, we report our recent study on the synthesis of dense and optically transparent CWO films by a combination of a new sol-gel processing and rapid sintering, which effectively prevented the precipitation of an undesired parasitic phase during the sol preparation and the loss of volatile CdO during sintering at elevated temperature. A systematic study of the relationship between sintering conditions, microstructure, crystallinity, and optical and x-ray scintillation properties of the sol-gel-derived CWO films is presented and discussed.

II. EXPERIMENTAL

Cadmium tungstate films were made by a new sol-gel processing with tungstic acid (H_2WO_4, 99%, Aldrich, St. Louis, MO) and cadmium nitrate as [$Cd(NO_3)_2 \cdot 4H_2O$, 99%, Aldrich] precursors and hydrogen peroxide (H_2O_2, 30%, Aldrich) as solvent. First, 2.62 g tungstic acid was dissolved in 35 ml hydrogen peroxide aqueous solution. The mixture was stirred for 2 h at 60 °C to obtain a clear solution of tungstic acid. Then a stochiometrically equivalent amount of cadmium nitrate was added into above solution. This mixture was stirred at room temperature for 30 min and then divided equivalently into two beakers. In the first beaker, ethylene glycol (EG, CH_2OHCH_2OH, Aldrich) and glycerin [Gly, $CH_2OHCH(OH)CH_2OH$, Aldrich] were added with a volume ratio of H_2O_2: EG = 1:3. In the other beaker, ethylene glycol and glycerin were added with a volume ratio of H_2O_2:EG:Gly = 1:0.9:0.1. The two sols were stirred continuously for another 1 h and aged at room temperature for 20 days prior to making films.

CWO films were made by the dip-casting method on glass substrates. Forty microliters CWO sol from the first beaker were dropped on a 1 × 1 in. glass substrate, which was heated on a 60 °C hot plate. The film was dried at room temperature for 30 min. Then, 40 μl CWO sol from the second beaker was dropped on top of it when it was heated at 60 °C. Five films were made by exactly the same procedure and were dried at 100 °C for 1 h. Those films were then put directly into 500 °C furnace and kept for different periods of time to investigate the sintering effects on the microstructure, crystallinity, and optical and scintillation properties of the resultant CWO films.

Those CWO films after sintering were ready for structure and property characterizations. XRD patterns were obtained by using x-ray diffractometry (XRD; PW 1820, Phillips, Kassel, Germany). Morphologies and film thickness were characterized by scanning electron microscopy (SEM; JSM 7000, JEOL, Tokyo, Japan). The optical transmittance was measured by ultraviolet-visible (UV-VIS) spectrometry (PC 2000, Ocean Optics, Inc., Winter Park, FL). The photoluminescence (PL) spectra were obtained with an Oriel Instaspec IV CCD camera using a mercury lamp for excitation, at a PL excitation wavelength of 298 nm. Finally, x-ray excitation optical luminescence (XEOL) experiments were carried out at beamline 20-BM at the Advanced Photon Source (APS) at Argonne National Laboratory (Chicago, IL), at an x-ray excitation energy of 10.21 keV. All the films used for PL and XEOL tests have the same lateral dimension of 1 × 1 in.

III. RESULTS AND DISCUSSION

CWO sols prepared using the procedure described in Sec. II were clear, homogeneous, and optically transparent. The sols were stable at room temperature for 60 days without change of optical transparency, appearance, or precipitation. The sols can be readily diluted by adding alcohol or water-based solvents. Further study, discussed later in Sec. III, suggested that minimal or no homogeneous condensation existed because no crystalline phase other than CWO was detected when the sol-gel derived films were subjected to heat treatment at elevated temperatures.

The exact reaction mechanism during the sol-gel processing is not known to us at this time and is under further study by our group. However, some general discussion is offered below. Tungstic acid is relatively moisture insensitive and reacts with hydrogen peroxide to form a complex through the following reaction:

$$WO_3H_2O + H_2O_2 \rightarrow WO_3{\cdot}H_2O_2{\cdot}H_2O \quad . \qquad (2)$$

A more complicated tungstic acid–water complex, $[WO_2(O_2)H_2O]{\cdot}nH_2O$ may form.[20] Such complexation reactions will effectively reduce the chemical reactivity of the tungstic acid and thus render it less moisture sensitive. Tungstic acid occurs in the form of a number of tungsten oxide hydrates with one to two associated water molecules in an aqueous system and readily forms colloidal dispersion or colloidal sol.[21] It is well known that the transition metal precursors often exhibit cross catalytic effects and thus affect the hydrolysis and condensation reactions when precursors of transition metal are introduced to a system consisting of more than one metal element.[22,23] Such cross catalytic effects often lead to homogeneous condensation between the same element and cause undesired precipitation and phase segregation. Such cross catalytic effects also alter the microstructure of sol-gel derived xerogels and films and often result in highly porous structures. The mixing condition was chosen at 60 °C for 60 min, to allow the reaction to proceed sufficiently. It was particularly hoped that sufficient hydrolysis of the tungstic acid precursor would occur to ensure the preferred heterogeneous condensation reaction with cadmium upon the addition of the cadmium precursor.

When cadmium nitrate was added into the tungstic acid–hydrogen peroxide solution, little change was observed, suggesting that only relatively slow and mild chemical reactions might take place. Room temperature and 30 min were chosen for the stage of the sols preparation, considering the possible cross catalytic effects of cadmium and tungsten precursors. Various organic solvents were added to dilute and stabilize the sols to prevent premature gelation and possible precipitation. The addition of ethylene glycol and glycerin also adjust the viscosity of the CWO sols.

For the fabrication of sol-gel-derived CWO films, a modified coating process was applied in the present study. Instead of using spin or dip-coating at ambient temperature as most commonly practiced in laboratories and industrial settings, we used a drop-casting of sol on a preheated substrate for the first layer of CWO films because the prepared sols were hydrogen peroxide based and did not wet the substrate surface as most of the alcohol based sols did. The second layer of CWO film could be more easily deposited than the first layer because the surface chemistry was changed to amorphous CWO after the deposition of the first layer. The typical contact angle of this CWO sol on glass substrate was 60°. Conventional dip or spin coating methods with various withdrawal and spin speeds failed to produce continuous coating on substrates. Preheated substrates also failed to retain a uniform coating because the substrate temperature drops quickly before sol-gel transition takes place. Preheating substrates to 60 °C ensures the excellent wetting of sol on the surface and promotes the evaporation of solvent, resulting in a more extensive collapse of gel network. As a result, uniform crack-free sol-gel derived CWO films with initial thickness of ~1.8 μm per coating were routinely achieved with this approach. Such prepared CWO films, like most sol-gel-derived films, are amorphous and highly porous, and thus require sintering at elevated temperatures to achieve full densification and crystallization.

Densification of CWO films imposes another great challenge because CdO is relatively volatile at high temperatures, and the evaporation of CdO would effectively prevent the densification. The loss of CdO would also seriously compromise the luminescent and scintillation properties of the film.[24] A rapid sintering at 500 °C was investigated to achieve the full densification of CWO films. Such a rapid sintering process has been widely used for sol-gel-derived or chemical-solution-derived oxide films containing volatile components such as PbO in lead zirconate titanate films.[25] It is obvious that the loss of volatile constituent through evaporation during sintering is directly related to the sintering temperature and time, as well as the open surface area. Sol-gel-derived films are typically porous and possess a relatively large surface area (up 1000 m^2/g).[23] Effective densification thus can be achieved only at a relatively low temperature with a relatively short dwelling time. In addition, the initial sol-gel films should consist of minimal open surface area.

Figure 1 compares the SEM cross-section morphologies of CWO films sintered at 500 °C in air with different periods of time: (a) no sintering, (b) 20 min, (c) 40 min, (d) 60 min, and (e) 80 min; Fig. 1(f) is the top view of CWO film sintered at 500 °C for 20 min. The first change is the decrease of the film thickness from ~1.8 μm without sintering to ~0.4 μm with 80 min sintering at 500 °C, which is presented in Fig. 2. Another noticeable change is from the amorphous appearance in film without sintering to the typical polycrystalline cross section with prolonged sintering, which

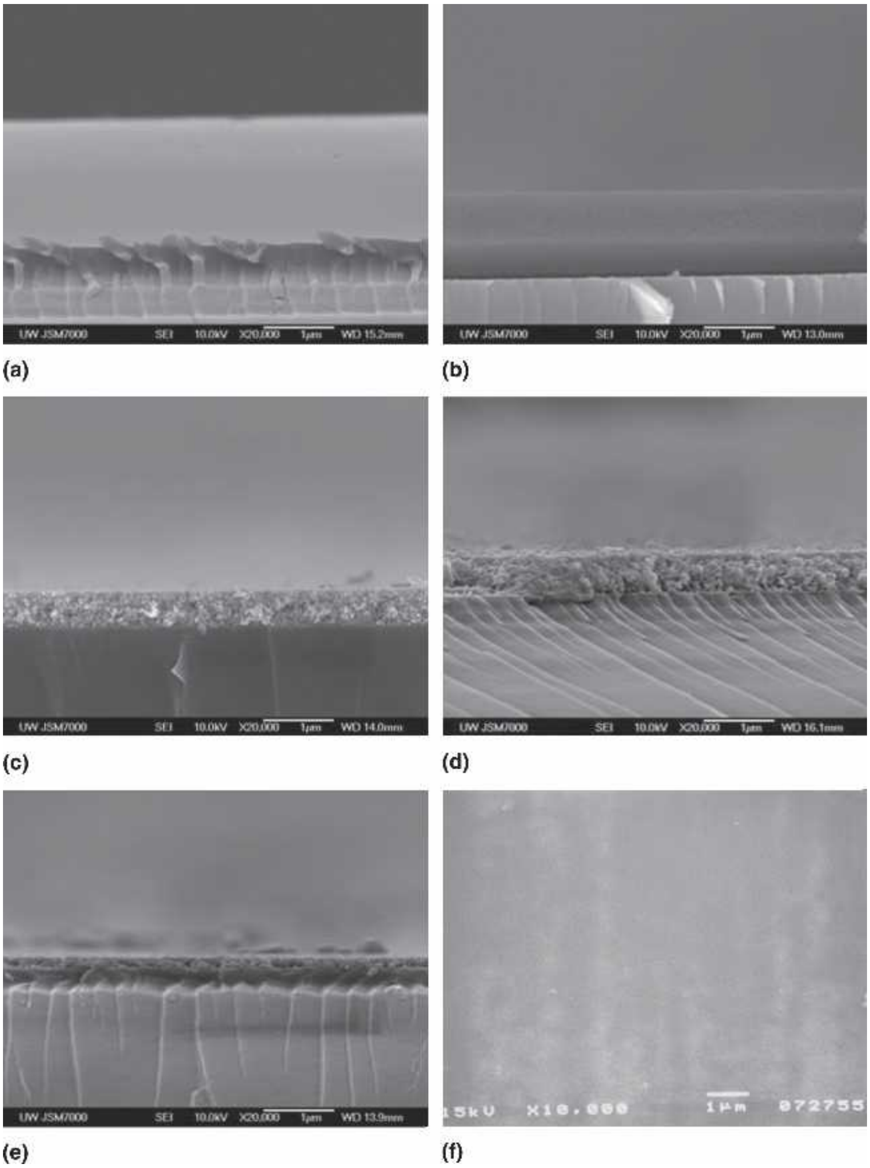

FIG. 1. SEM images showing the morphologies and thickness of CWO films derived from a fast sintering method for different sintering times: (a) side-view of unsintered CWO film, (b) CWO film sintered for 20 min, (c) 40 min, (d) 60 min, (e) 80 min, and (f) top-view of CWO film sintered for 20 min.

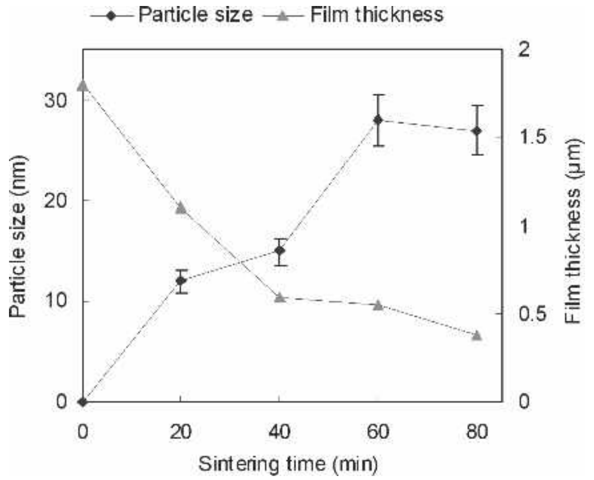

FIG. 2. Comparisons of film's thickness measured from SEM side-view images as shown in Fig. 1 and particle size estimated from XRD data shown in Fig. 2.

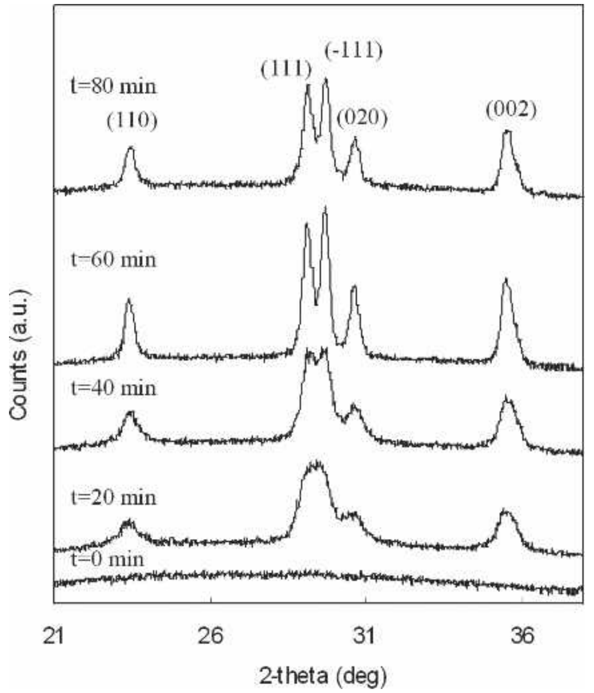

FIG. 3. XRD spectra comparison of CWO films sintered for different times from 0 to 80 min.

corroborates the XRD results summarized in Fig. 3. The significant shrinkage of thickness (over 70%) can be attributed to both the pyrolysis of organic residues and the densification. Because high boiling point (bp) organic solvents are added (EG bp = 196 °C, Glycerin bp = 182 °C), it is probable that significant organic matter remains after the film drying process at 100 °C is complete. Heating at elevated temperatures is a combination of both removal of organics and removal of pores from the films. Separate thermal gravimetric analysis on sol-gel derived CWO powder revealed negligible weight loss during the short and rapid heating process. The ability to achieve full densification of sol-gel-derived CWO films in the present study can be attributed to the combination of the new sol-gel processing and the rapid sintering processing, as discussed below. First, the new sol-gel processing eliminated the formation of parasitic crystalline particles during sol preparation and during sintering. Such homogeneous sol permits the formation of uniform amorphous films upon coating with better packing of colloids upon the removal of solvent. The resultant film is hypothesized to possess fewer open voids, eliminate any large voids, and thus have much less open surface area. As a result, the evaporation of volatile components during sintering would be much suppressed. Relatively fewer and smaller voids would be more kinetically favorable to densification than large voids, as seen in previously reported sol-gel CWO films.[7,14] The amorphous nature of the initial CWO films is thermodynamically more favorable for sintering at relatively low temperatures; the in situ crystallization would further promote densification. That is in sharp contrast to the previously reported sol-gel-derived CWO films where crystalline particles exist prior to sintering. Such crystalline particles constitute inclusions that hinder sintering by inhibiting contraction of the gel network. Secondly, the rapid sintering process is hypothesized to effectively seal the surface voids and minimize further loss of constituents through evaporation during the remaining sintering process; as a result, significant densification is achieved. The density of the CWO films with rapid sintering is substantially higher than the previously reported sol-gel-derived CWO films.[14]

The comparison of XRD patterns of CWO films sintered for various times is shown in Fig. 3. The CWO film without sintering was amorphous, whereas all the films rapidly sintered from 20 to 80 min consisted of CWO as the only crystalline phase. The absence of an intermediate crystalline phase is also indicative that possible molecular level homogeneity was obtained during the sol-gel process through desired hetero-condensation. The diffraction peaks generally became sharper with increasing sintering time, suggesting improved crystallinity of CWO phase; the film sintered for 80 min showed reduced XRD peak intensity relative to the film sintered for 60 min.

Figure 2 compares the thickness of CWO films measured from SEM cross-section images shown in Fig. 1 and the particle size of CWO estimated from the XRD data in Fig. 3. The thickness of CWO films was 1.8, 1.1, 0.6, 0.55, and 0.38 μm with sintering time increased from 0 to 80 min. The particle size was estimated by choosing the main diffraction peaks of CWO films using the following Scherer equation[26]:

$$L = \lambda K/\beta\cos\theta \quad , \tag{3}$$

where L is the mean crystallite dimension (Å), λ is the peak position 2θ, K is a constant (0.9), and β is full width at half-maximum (FWHM) of the peak in radii of 2θ. The average particle sizes of the CWO films were found to be 0, 12, 15, 28, and 27 nm with sintering time increased from 0 to 80 min, respectively. The particle size in all the films increased with an increasing sintering time except the film sintered for 80 min, which showed a small reduction.

Figure 4 compares the optical transmittance of CWO films sintered for times from 0 to 80 min and shows that the original film had a much higher optical transmittance throughout the entire visible light spectrum than all other films. The transmittance of films sintered for 20 and 40 min was approximately 80%, and films sintered for 60 and 80 min were translucent with transmittance below 50%. The different transmittance is possibly attributable to the differences in particle size, density, or porosity. Although the initial film without sintering exhibited much higher porosity, many organic components filling in the pores, the pores are likely to be very small, and the film is amorphous. As a result, there might be very little scattering leading to high optical transmittance. Films with 20 or 40 min rapid sintering with significantly higher density possessed far fewer pores; however, in viscous sintering, small pores typically combine to form large ones prior to collapse. Short sintering also resulted in significant crystallization. Consequently, there was more photon scattering in these films than there was in the initial film without sintering. The CWO films sintered for 60 and 80 min show little decrease in thickness, suggesting little further densification; however, long sintering time led to appreciable increase in particle size with the particle size almost doubled (Fig. 3). Such increase in particle size may be attributable to the decrease in optical transmittance, particularly in the short wavelength range; however, the loss of oxygen during sintering may cause absorption at short wavelength. Further experiments are underway to verify the impact of oxygen vacancies on the optical absorption and will be reported separately.

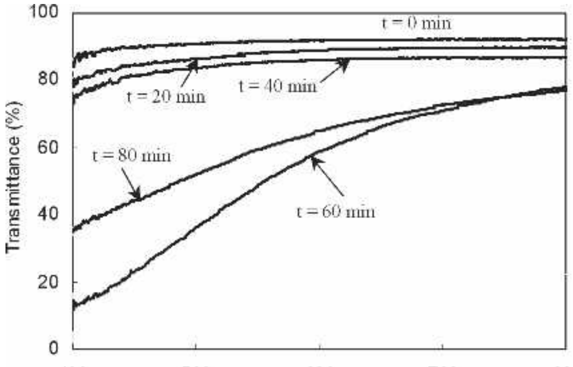

FIG. 4. Comparison of optical transmittance spectra of CWO films sintered for different times from 0 to 80 min in the wavelength region from 400 to 800 nm.

Figure 5 is a comparison of PL spectra of CWO films. All sintered CWO films emitted intrinsic luminescence at ~480 nm when excited by UV at $\lambda = 298$ nm. The amorphous CWO film did not emit intrinsic photoluminescence as expected because the intrinsic luminescence is crystal structure dependent. PL intensity increased with increasing sintering time, except that for the CWO film sintered for 80 min, which had a slightly lower PL emission.

Figure 6 is the x-ray absorption spectrum of the CWO films and clearly shows the absorption peak at ~10.21 keV, corresponding to the characteristic absorption of the tungsten L_3 edge. This excitation energy was chosen in the subsequent measurements of XEOL spectra shown in Fig. 7. XEOL is a relatively simple photon-in photon-out technique but a promising method to study optical decay channels and their relation to the absorption process. Some good papers have been published recently describing XEOL in details.[27,28] All the films sintered for 20–80 min at 500 °C emitted the intrinsic luminescence peaked at ~480 nm, which was the same as PL excited with photons of $\lambda = 298$ nm. However, the luminescence intensity increased with the increasing sintering time, except for the 80 min sintered film; this result is similar to the PL results discussed earlier. Some noticeable differences existed between the PL spectra and XEOL spectra of the same CWO films. XEOL

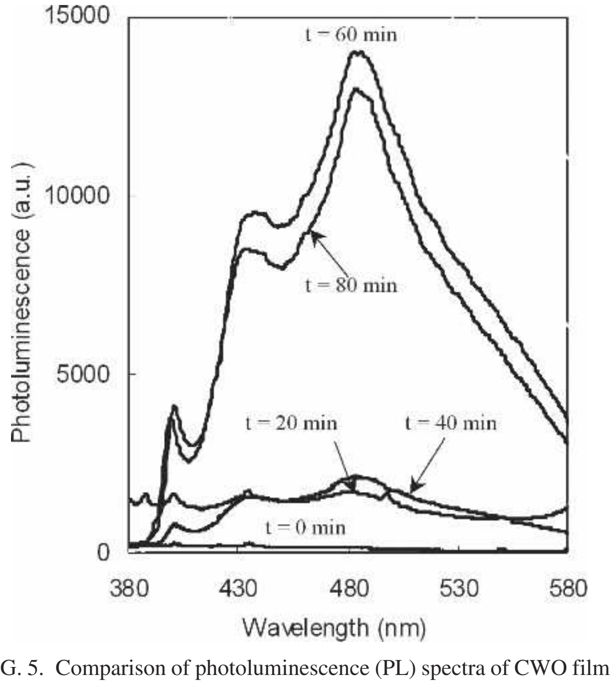

FIG. 5. Comparison of photoluminescence (PL) spectra of CWO films sintered for different times from 0 to 80 min.

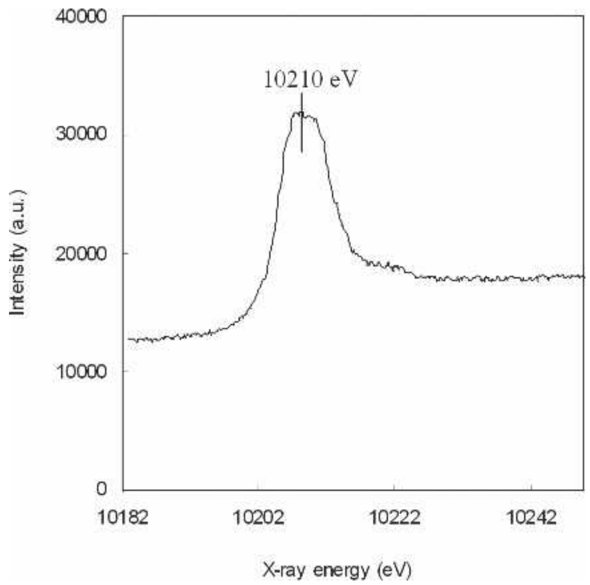

FIG. 6. X-ray absorption near edge structure (XANES) tungsten in CWO film fast sintered at 500 °C for 60 min.

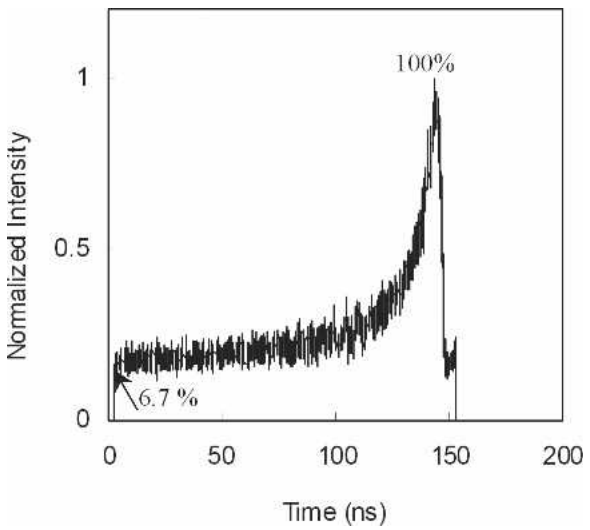

FIG. 8. X-ray excited optical luminescence decay spectrum of CWO film fast sintered at 500 °C for 60 min. Due to the experimental setup the time scale is inverted.

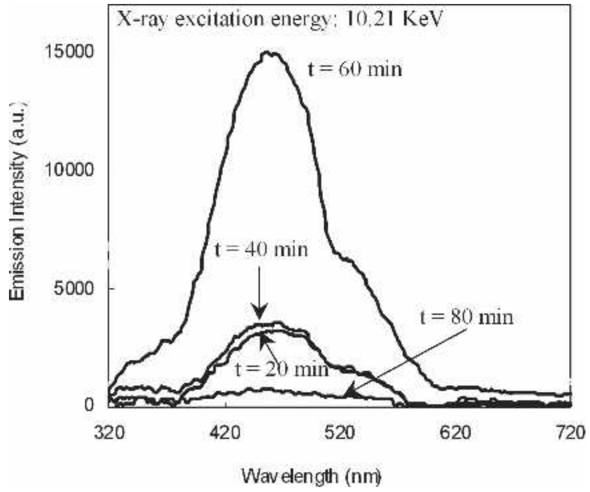

FIG. 7. X-ray excited optical luminescence (XEOL) spectra of CWO films sintered for different times from 20 to 80 min.

spectra showed an extra peak at ~530 nm that was far less visible in the PL spectra. On the other hand, two extra peaks in the PL spectra at ~400 nm and ~440 nm became weak or invisible in the XEOL spectra. These two PL peaks are known and attributed to the glass substrates. In the XEOL measurements, these two peaks were indeed observed when using the excitation x-ray at high energy other than the tungsten absorption peak, for instance, 11 keV. Figure 8 is the XEOL decay spectrum of CWO films. It showed that the intensity decayed from 100% to 6.7% by ~20 ns. This decay time was much shorter than the bulk counterpart, which had a decay time around 20,000 ns. However, the possible mechanism is not known to the authors and should be studied further.

All the experimental data discussed reveal a clear trend: the CWO film sintered at 500 °C for 60 min reached a peak performance whereas there was a noticeable decrease in all the properties of the CWO film sintered for 80 min. To reiterate, the most noticeable experimental observations are: (i) a sharp increase in crystal size and/or quality until 60 min, (ii) the lowest optical transmittance measured on CWO film sintered for 60 min, (iii) PL reached maximal intensity for 60 min sintered CWO film, and (iv) 60 min sintered CWO film demonstrated significant XEOL whereas almost no XEOL was observed in 80 min sintered CWO film. The exact mechanism that caused such a drastic change is not fully known to us; however, a possible explanation is discussed below. It is known that the intrinsic luminescence emission at ~480 nm originated from the WO_4^{2-} tetrahedral complex[29]; therefore, a simple mixture of CdO and WO_3 or amorphous CWO does not possess luminescence emission. Therefore, distortion or imperfection in the WO_4^{2-} complex will result in a reduction or even loss of its intrinsic luminescence. This explains well the fact that the sol-gel-derived CWO film without sintering did not emit a luminescence. It also explains very well the fact that both PL and XEOL intensities increase significantly with an increased sintering time till 60 min because of the increased crystal size and/or crystallinity. The increase is far more pronounced than the nominal increase in the luminescence intensity, considering the significant loss of optical transmittance in 60 min sintered CWO film, which may be attributable to the increased grain boundary scattering with large crystal particles.

However, the above explanation is obviously not applicable to the 80 min sintered CWO films that had noticeable reduction in almost all the properties studied in the present study. During sintering at 500 °C, several processes occur simultaneously: crystallization, grain growth, densification, and loss of volatile components. Although a new sol-gel process was developed in the current study and a rapid sintering was applied to minimize the loss of relative volatile CdO, a certain loss of CdO can not be prevented entirely. With longer sintering time, the loss of CdO via evaporation can become significant. This may well explain the reduction of crystal particle size and crystallinity. The loss of CdO will result in destruction of some WO_4^{2-} tetrahedra in the CWO crystal lattice. As a result, both PL and XEOL would be significantly reduced. Some extra experiments were designed and carried out to verify the above hypothesis.

Figure 9 is the comparison of SEM cross-section images and XRD patterns of CWO films sintered for 5 and 24 h. Thicker CWO films were prepared in this study to ensure any change in morphology, crystallinity, and size is significantly large enough to draw unambiguous conclusion. Both films had a thickness comparable to the film sintered for 80 min (not shown); however, they became much more porous. Although it is difficult to tell from the SEM images, both films collapsed when a force was applied onto the film surface. CWO film sintered for 24 h had much less mechanical integrity than that sintered for 5 h, and both were far less than CWO sintered in less than 1 h. Figure 9(c) reveals that in addition to the peaks of CWO, there exists an extra peak corresponding to crystalline tungsten oxide (JCPDS Card No. 32-1394) [inset in Fig. 9(c)]. It should be noted that the formation of crystal WO_3 at a temperature as low as 500 °C may not be easy and the XRD pattern of WO_3 is always weak. The presence of the tungsten oxide suggested that a long sintering time may indeed result in loss of volatile elements, CdO, which in turn would explain the reduction of PL and XEOL intensity. More experiments are underway to confirm the hypothesis presented here and find solutions to improve the CWO properties.

The light output in a scintillation film was controlled collectively by three sequential steps or processes. The first was the capture of incident high-energy photons, which was determined by the cross section of scintillation materials (dependent on its density and effective atomic number). However, for a given scintillation material, the nominal cross section or the capture ability of the scintillation film is directly related to its porosity and film thickness. The second was the amount of luminescence photons that can be generated, which was related to the efficiency energy conversion and transfer as well as undesired luminescence quench. For intrinsic scintillation materials such as CWO, crystallinity plays a determining role. Both impurity and vacancy in the crystal lattice should be minimized or eliminated. The last step was the luminescent photons coming out through the films to be detected, which was directly determined by

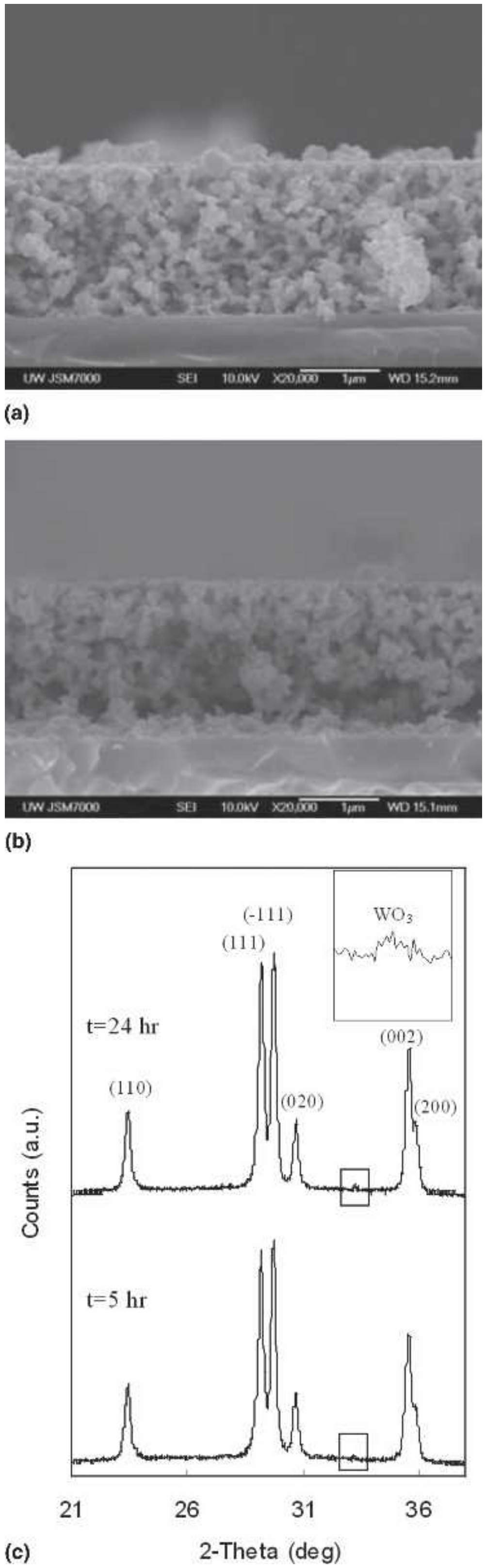

FIG. 9. Comparison of SEM and XRD of CWO films sintered for 5 and 24 h, respectively, (a) side-view of CWO film sintered for 5 h, (b) side-view of CWO film sintered for 24 h, (c) XRD of CWO films sintered for 5 and 24 h. The inset in (c) is an enlarged part of the XRD spectrum to show the extra phase of WO_3.

the optical transparency of films at the luminescent wavelength. Taking all three factors into account, it is obvious that thick and dense films with perfect crystallinity and complete optical transparency are desired for scintillation applications for detecting high energy photons and particles including x-rays, γ-rays, and neutrons. The experimental results and discussion presented in this paper present significant progress toward such ideal scintillation films.

IV. CONCLUSIONS

Dense and optically transparent CWO films have been made by a new sol-gel process followed with rapid sintering. The new sol-gel process resulted in the formation of homogenous and stable CWO sol. Different sintering times were investigated to make dense and optically transparent films with high light output. XRD and SEM analyses revealed a polycrystalline CWO phase was formed with an average grain size from 0 to 28 nm, depending on the sintering time. The fast sintering method effectively promoted densification at a relatively low temperature by suppressing loss of volatile CdO, leading to enhanced optical transmittance higher than 80% for short time sintered film. All of the films sintered at 500 °C showed intrinsic PL and XEOL around 480 nm when excited by UV light at 298 nm and x-ray at 10210 eV, respectively. Further analyses indicated that light output was influenced significantly by the sintering time. Film sintered for 60 min had the highest PL and XEOL emission intensity.

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