Synthesis of Nano-Grained $ZnWO_4$ Thin Film Scintillator by Thermal Evaporating Deposition Method

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1. Introduction

High-resolution X-ray imaging system is composed of a scintillator and an optical detector coupled with lens. Spatial resolution is the one of most important parameters of high-resolution X-ray imaging. When this optical detector has an effective pixel size from nano to micro meter, X-ray images are developed with micron spatial resolution. However, spatial resolution of this system is affected by the structure of a scintillator because the optical detector coupled with lens is highly sensitive to the optical diffusion phenomenon caused by the scintillator structure.

In this study, nano-grained zinc tungstate ($ZnWO_4$) was used for the thin-layer transparent film scintillator on quartz glass using the thermal evaporating deposition method. $ZnWO_4$ has been used for a long time as an X-ray scintillator. [1] For this reason, $ZnWO_4$ has 2.3 times more luminescence characteristics under X-ray irradiation than commonly used Bi4Ge3O12 (BGO). [2] In addition, the material is high density (ρ = 7.87 g/cm3), high effective atomic number (Zeff = 61), short decay time, high stability and economical price. [3] Since $ZnWO_4$ has high X-ray absorption capability relative to ρZ^4_{eff}, it has the potential to be utilized in thin film scintillators used for high-resolution X-ray imaging. $ZnWO_4$ can be easily utilized in the thermal evaporating deposition method because it has a relatively low melting point (~1166 °C). [1] For the above reasons, we demonstrated that thermal evaporating deposition method can easily fabricate thin-layer transparent nano-grained ZnWO4 film.

2. Methods and Results

2.1 Fabrication of $ZnWO_4$ Thin Film

Zinc oxide and tungsten oxide nanoparticles were purchased from Sigma-Aldrich (St. Louis, MO, USA). These nanoparticles were added to ethanol with a 1:1 atomic ratio between zinc and tungsten. The solutions were mixed through the vibrating ball milling, and then dried in air at 60 °C. The resulting powders were heated in an electric furnace at 1000 °C for 5 h to induce the solid-state reaction.

$ZnWO_4$ powders fabricated by the solid-state reaction were used as the source material in thermal evaporating deposition method. Tungsten boats were used as evaporating crucible. The deposition of film on quartz glass (B&C Tech, Daejeon, South Korea) was carried out at 10^{-6} Torr. The holder of quartz glass is rotated 25 cm away from a evaporating crucible. After thermal evaporating deposition, the bare $ZnWO_4$ thin films were sintered in air furnace at 700, 800 and 900 °C for 1 hour.

2.1 Characterization

The cross-sectional structures of bare $ZnWO_4$ thin film were analyzed using a Focused Ion Beam (FIB, (Helios 450 F1, FEI, Hillsboro, OR, USA) equipped with a scanning electron microscope (SEM) and an energy dispersive X-ray spectroscopy (EDX) detector system. The crystallinity of the bare $ZnWO_4$ thin film was analyzed using a X-ray diffraction spectrometer (XRD, D/MAX-2500, Rigaku, Tokyo, Japan) with an analysis 2θ angle range of 10–90°. The surface structure was determined using an atomic force microscope (AFM, XE70, Park systems, Suwon, Korea).

The structures of the sintered $ZnWO_4$ thin film were analyzed using a field emission scanning electron microscope (FE-SEM, FEI MAGELLAN 400, FEI, Hillsboro, OR, USA). The crystallization and transparency of the sintered $ZnWO_4$ thin film was analyzed using a XRD.

3. Result

3.1 $ZnWO_4$Powder

The $ZnWO_4$ powders were fabricated by solid-state reaction at 1000°C for 5 hours. When the $ZnWO_4$ powder were irradiated by 254 nm ultra-violet (UV), these powders glowed blue. (Figure 1a) Figure 1b shows the XRD patterns of the $ZnWO_4$ powders with an analysis 2θ range 10–70 °C. Comparing the peak value of the XRD pattern with the standard card (PDF ICDD card #01-078-0251), these powders crystallized into monoclinic $ZnWO_4$.

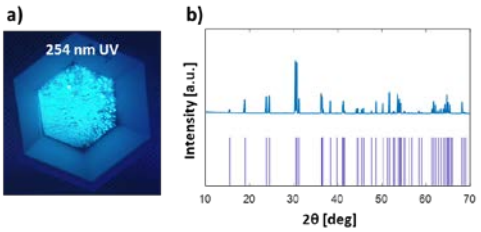

Fig. 1. a) $ZnWO_4$ powders irradiated by 254 nm UV, b) XRD spectrum of ZnWO4 powders

3.2 Theraml Evaporating Deposited $ZnWO_4$ Film

Cross-sectional SEM images show the structure of the evaporating deposited $ZnWO_4$ film. (Figure 2a) The deposition rate is 200 nm/min. As can be seen from the cross-sectional SEM image, no grain was formed in dense structure. Also, no cracks and pores were found.

Figure 1b show EDX spectrum obtained from the bare $ZnWO_4$ film. EDX spectrum have an zinc, tungsten and oxygen peak, confirming that this film were oxidized; the observed silicon peaks are from quartz glass. Figure 1c shows the XRD spectrum of bare $ZnWO_4$ film. Since no peak in the spectrum were observed, this film had an amorphous structure. Figure 1d shows the surface roughness of the films analyzed by AFM. The maximum roughness is about 5 nm. This result shows that the surface of bare $ZnWO_4$ film is highly uniform.

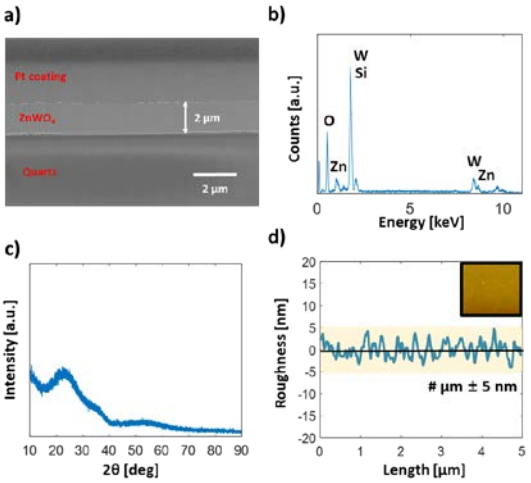

Fig. 2. a) Cross-sectional SEM images of the bare $ZnWO_4$ obtained by FIB , b) EDX spectrum of the bare $ZnWO_4$ film, c) XRD spectrum of the bare $ZnWO_4$ film, d) the surface morphology and roughness of the bare $ZnWO_4$ film by AFM analysis

3.3 Sintered $ZnWO_4$ Film

The structure morphology of sintered $ZnWO_4$ film are showed in Figure 4 by FE-SEM. In the case of $ZnWO_4$ film sintered at 900 °C, many pores and cracks were formed. (Figure 4c) These pores and cracks in the wavelength scale of optical light reduce transparency. In other words, when used as a scintillator, light scattering occurs, resulting in a problem of reducing spatial resolution. The $ZnWO_4$ film sintered at 700 °C and 800 °C consists of grained structure free from pores and cracks. The grains were sized through FE-SEM. As a result, the average sizes of grains sintered at 700 °C and 800 °C were 176.4 nm and 626.7 nm. The difference of transmission rate resulting from grain size can be explained by mie scattering mechanism. When the grain size is comparable to the wavelength of light, mie scattering becomes relevant at grain boundaries. However, when the grain size is sufciently small compared to the wavelength of optical light, Mie scattering at grain boundaries is suppressed to permit light passing through the film. Therefore, $ZnWO_4$ sintered at 700 °C with a grain structure smaller than the wavelength of optical light was the most transparent. Based on this fact, $ZnWO_4$ sintered at 700 °C has the highest utilization value in high-resolution X-ray imaging.

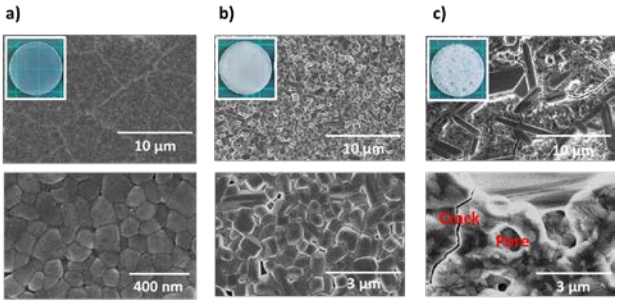

Fig. 3. a) Photographs of $ZnWO_4$ thin film sintered at A)700 °C, B)800 °C and C)900 °C, b) XRD spectrum of $ZnWO_4$ thin film sintered at 700 °C, 800 °C and 900 °C, c) transmission spectra of $ZnWO_4$ thin film sintered at 700 °C, 800 °C and 900 °C

3. Conclusions

We have demonstrated nano-grained thin-layer transparent film can be fabricated by thermal evaporating deposition method. Since it has a nano-grained structure, mie-scattering for optical light is minimized. Therefore, the optimized $ZnWO_4$ scintillator film has high optical property. These results indicated that nano-grained $ZnWO_4$ thin flm scintllator fabricated by thermal evaporating deposition method is expected to be used effectively in the field of high-resolution X-ray imaging.

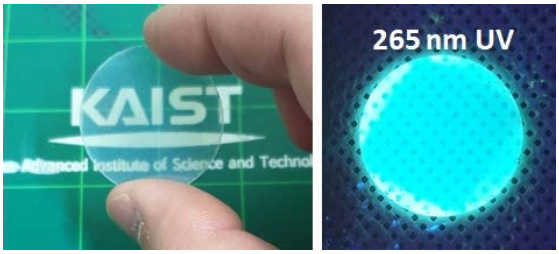

Fig. 4. Nano-grained thin-layer transparent ZnWO4 scintillator film

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of $ZnWO_4$ and Eutectics ZnO/$ZnWO_4$