



Effects of annealing atmosphere on the luminescent efficiency of ZnTe:O phosphors

Z.T. Kang^a, H. Menkara^a, B.K. Wagner^a, C.J. Summers^{a,*}, R. Durst^b,
Y. Diawara^b, G. Mednikova^b, T. Thorson^b

^aPhosphor Technology Center of Excellence, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

^bBruker AXS 5465 East Cheryl Parkway, Madison, WI 53711, USA

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Abstract

The effect of the annealing atmosphere on the luminescent efficiency of ZnTe:O phosphors for X-ray imaging applications was studied. The phosphors were doped by ball-milling bulk ZnTe crystals in an O₂ atmosphere and annealed in various atmospheres: vacuum, N₂ or forming gas (95%N₂/5%H₂). All samples exhibited a deep red emission centered at 680 nm. The samples annealed in forming gas atmosphere exhibited an X-ray luminescent efficiency five times higher than the samples annealed in vacuum or N₂ atmospheres, which was attributed to the removal of surface tellurium oxides.

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1. Introduction

ZnSe:Cu,Cl is a new red emitting (650 nm) scintillator with the highest known X-ray conversion efficiency. Its light output is ~1.3 times higher, and its radiation hardness is 3–4 orders of magnitude higher than CsI:Tl, which is

widely used in detectors for low energy X-ray introspection and tomography [1]. Also, ZnSe:Cu,Cl phosphor screens are ~1.7 times brighter than equivalent Gd₂O₂S:Tb screens, which is the conventional X-ray phosphor used for chemical crystallography detectors [2]. However, ZnSe cannot be used in macromolecular crystallography detectors for multi-wavelength anomalous dispersion (MAD) studies because the atomic absorption edge of the Se atom interferes with some biological cells.

*Corresponding author. Tel.: +1 404 385 0697.

E-mail address: chris.summers@mse.gatech.edu
(C.J. Summers).

As a counterpart of ZnSe, ZnTe can avoid this problem and can potentially achieve an X-ray conversion efficiency comparable to or higher than ZnSe. It is a good host material for X-ray imaging applications because of its relatively small band gap and subsequently small average energy required to create an electron–hole pair. Additionally, the relatively high density and X-ray absorption efficiency of ZnTe is also potentially beneficial for achieving higher X-ray luminescence efficiencies. The other issue is to find appropriate dopants to activate ZnTe. Oxygen has been shown to be an effective activator in ZnTe [3–12]. In 1962, Dietz et al. [3] reported a broad red emission centered at ~ 660 nm from vapor-grown ZnTe bulk crystals measured at 20 K. From additional investigations on melt-grown 5 mol% ZnO doped ZnTe bulk crystals, this emission was attributed to an isoelectronic oxygen trap by Hopfield et al. [4]. Further investigations have attributed this emission to the recombination of excitons bound to isoelectronic oxygen centers [5–12].

The objective of this research was to synthesize efficient ZnTe:O powder phosphors that match the spectral sensitivity of conventional red sensitive CCD detectors, which peaks at ~ 680 nm. However, high efficiency ZnTe phosphors are very difficult to synthesize in powder form due to their high moisture sensitivity and chemical instability during synthesis. In the presence of water or moisture, ZnTe quickly decomposes to form precipitates of ZnO, Te, and TeO₂, etc., which generate non-radiative defects in the crystal lattice and quench the luminescence. Recently, we reported that efficient ZnTe:O phosphors could be synthesized by vacuum annealing ZnTe powder prepared from ZnTe bulk crystals ball-milled in an O₂ atmosphere [13]. In this process ball-milling mechanically emulates the ion implantation of active forms of oxygen (O', O₂', O^x, etc.) into the crystal lattice [14]. Secondly, the luminescent efficiency of ZnTe can be degraded by the formation of tellurium oxides on the surface. These can be removed by a dry etching process so as to improve the luminescent efficiency. For example, Foad et al. [15] reported the use of a CH₄/H₂ gas to dry etch ZnTe bulk crystals. In this study, forming gas (95% N₂/5% H₂) was used

as the annealing atmosphere to both crystallize and etch the ZnTe:O powder phosphors. The effects of the annealing atmosphere on the luminescent efficiency of ZnTe:O were studied by comparing forming gas, vacuum and N₂ annealed samples.

2. Experimental

For the synthesis processes, bulk ZnTe crystals of 99.999% purity were used as the raw host material and forming gas or ultrahigh purity N₂ as the annealing atmosphere. Oxygen doped ZnTe powders were prepared by ball-milling the bulk ZnTe crystals for 48 h in an ultrahigh purity O₂ (99.994%) atmosphere. After milling the powders were loaded into quartz ampoules and annealed under various atmospheres: vacuum (10^{-2} – 10^{-3} torr), N₂ (99.999% high purity) and forming gas (a commercial certified mixed gas). For the vacuum annealed samples, the powder was placed in a quartz ampoule which was then evacuated; dried at room temperature for 4 h and then at 145 °C for 20 h. The charge was then sealed in vacuum by necking off the evacuated ampoule. For N₂ and forming gas annealed samples, the powders were placed in quartz tubes and purged in the atmosphere gas for half an hour at room temperature and then the temperature was raised to 145 °C for 2 h before being raised to the annealing point to crystallize the sample. The quartz tubes were kept rotating during annealing. All the samples were annealed at 1000 °C for 1 h followed by rapid quenching to room temperature by removing the ampoules from the furnace. In order to perform the X-ray luminescence measurements, ZnTe:O phosphor films were prepared on Mylar substrates by screen printing using an epoxy as the liquid binder material. After sieving the prepared phosphor in a N₂ purged glove box and removing particles larger than 75 μm, the phosphor powders were mixed with epoxy to form a paste. The paste was then screened to form a uniform film with density of 45–65 mg/cm² over an area of 2–6 cm². The ratio of the weight of binder to phosphor was 1:2 and the screen was cured with UV light for 10 min.

The particle morphology and surface properties were studied by scanning electron microscopy (SEM) in a LEO 1530 microscope with an energy dispersive spectroscopy (EDS) attachment, and X-ray photoelectron spectroscopy (XPS) with a Surface Science model SSX-100 Small Spot ESCA system using the Al K_{α} line (1486.6 eV), respectively. The optical properties were evaluated by photoluminescence (PL), cathodoluminescence (CL), and X-ray excitation. The PL spectra and intensities were compared using an Ocean Optics USB2000 spectrometer connected to an integrating sphere equipped with a 470 nm blue LED as the excitation source. For the CL measurements the samples were DC excited at energies up to 20 keV at a low current density of $\sim 5 \mu\text{A}/\text{cm}^2$, using a custom Kimball Physics EFG-11 electron gun. All the CL measurements were performed at room temperature and recorded with a Spectra-Scan PR705 spectrophotometer. The X-ray lumi-

nescence intensities of the screened samples were measured by Bruker AXS, Inc. using 17 keV X-ray source and also compared to standard commercial ZnSe:Cu,Cl and $\text{Gd}_2\text{O}_3\text{:Tb}$ X-ray phosphors.

3. Results

The morphology of the ZnTe:O powder phosphors annealed in vacuum and a forming gas atmosphere are shown in Figs. 1(a, b) and (c, d), respectively. Figs. 1(b) and (d) are higher magnification images that clearly show the surface microstructure of a particle. It was observed that annealing in forming gas produced a much smoother and “cleaner” surface than annealing in vacuum. The sharp edges of the particles become rounded and the small nano-sized particles bonded onto the surface were completely removed by etching, leaving only much smooth surface

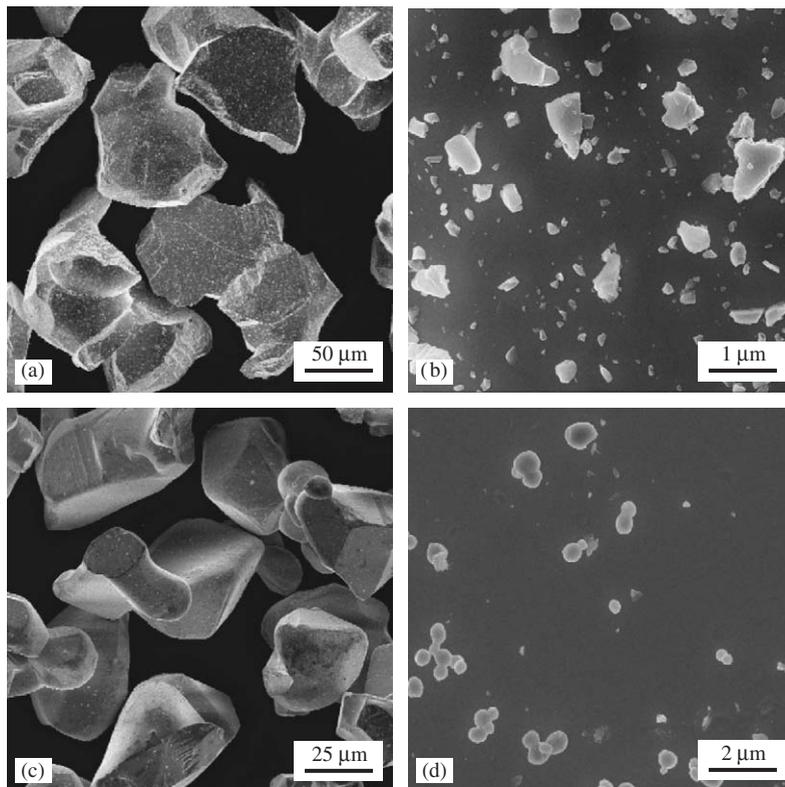


Fig. 1. Morphology of ZnTe:O powder phosphors: (a,b) annealed in vacuum and (c,d) a forming gas atmosphere.

particles ($\sim 1 \mu\text{m}$ in diameter) with a well rounded shape. This was attributed to the H_2 etching effect. The morphology of the N_2 annealed particles was similar to the vacuum annealed materials.

The surface chemical state of ZnTe:O annealed in various atmospheres was analyzed by XPS, as shown in Fig. 2. For ZnTe, the XPS spectra of the Te 3d core levels show two Te peaks, Te $3d_{5/2}$, and Te $3d_{3/2}$, at energies of 573.5 and 584 eV, respectively [15]. However, it was observed that these peaks were accompanied by two peaks, at 577 and 587.5 eV, respectively, which were identified as emissions from the 3d core levels of Te in an oxide environment. Thus, Fig. 2 indicates that tellurium oxide was formed on the vacuum and N_2 annealed samples, but that for the samples annealed in forming gas, oxidation was significantly suppressed because the intensity of the tellurium oxide XPS peaks were reduced by $\sim 85\%$ compared to the vacuum annealed samples. The N_2 annealed samples were more severely oxidized than those annealed in vacuum, as estimated from the relative intensities of the tellurium and tellurium oxides peaks. The body color was also observed to be related to the surface chemical

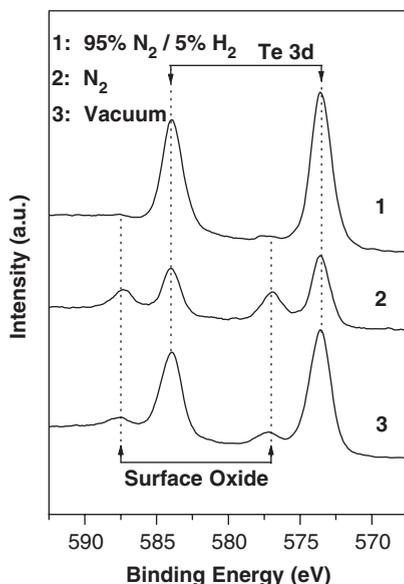


Fig. 2. XPS spectra of ZnTe:O phosphors annealed in various atmospheres.

state. The forming gas annealed samples exhibited a deep red color, whereas the vacuum and N_2 annealed samples were brown in appearance. Also the body color of the N_2 annealed powders was darker, which was attributed to the formation of a thicker surface oxide layer.

Under 470 nm excitation, a broad red emission centered at $\sim 680 \text{ nm}$, with a half maximum width of $\sim 69 \text{ nm}$, was observed from all of the samples annealed in various atmospheres, as shown in Fig. 3. This luminescence band is attributed to emission from an exciton bound to isoelectronic oxygen which forms a deep electron trap in ZnTe [4–12]. The samples annealed in a forming gas atmosphere exhibited much higher luminescent efficiency than samples annealed in vacuum or a N_2 atmosphere. The spectral shape of the emission spectra from typical N_2 and vacuum annealed samples were identical. However, their intensities were $\sim 24\%$ and 56% , respectively, of the typical intensity observed from the forming gas annealed samples.

Similar spectra were observed when the samples were excited by electrons with energies between 5 and 20 keV. The relative CL efficiency as a function of electron energy is shown in Fig. 4. For samples annealed in a forming gas atmosphere the luminescent efficiency was significantly higher than those samples annealed in vacuum or a N_2 atmosphere. At 20 keV the CL efficiencies of the vacuum and N_2 annealed samples were $\sim 20\%$ and

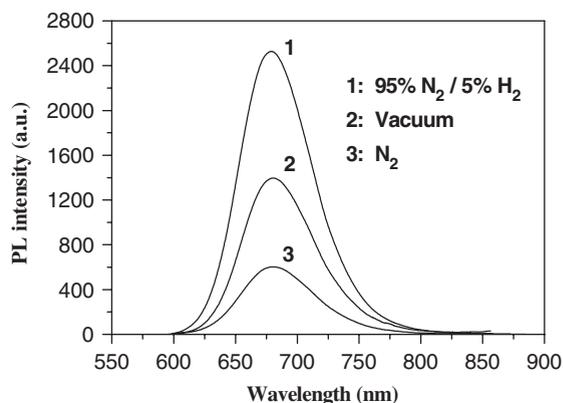


Fig. 3. PL spectra of ZnTe:O phosphors annealed in various atmospheres.

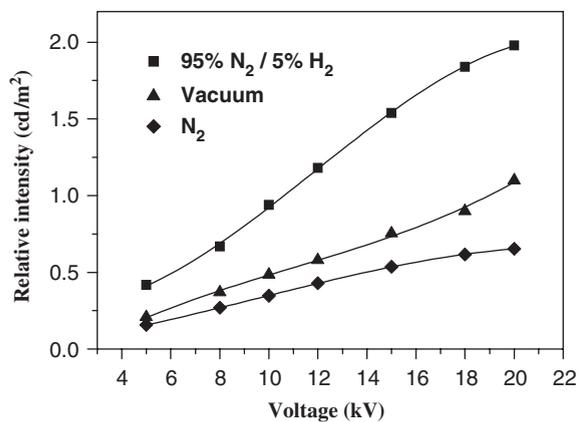


Fig. 4. Relative CL efficiency of ZnTe:O phosphors as a function of electron voltage.

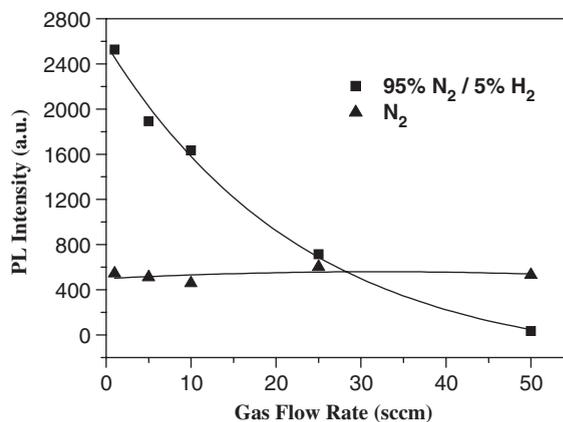


Fig. 5. Effect of the gas flow rate on the PL intensity of ZnTe:O.

Table 1

X-ray luminescence at 17 keV of ZnTe:O phosphor screens annealed in various atmospheres

Sample No.	Annealing atmosphere	% gain (ZnSe:Cu,Cl)	% gain (Gd ₂ O ₃ :Tb)
ZT05	Vacuum	11.6	21.9
ZT11	N ₂	9.2	12.4
ZT120	95%N ₂ /5%H ₂	56.1	76.4

50%, respectively, of the efficiency measured from a typical forming gas annealed sample. These samples showed no saturation at higher electron energies, which may indicate a long diffusion length for electron–hole pairs in these samples.

Table 1 shows the X-ray luminescence results obtained on screens prepared from typical ZnTe:O samples annealed in various atmospheres. Sample ZT120 which was annealed in a forming gas atmosphere exhibited the highest luminescent intensity, and was five times more intense than either the vacuum or the N₂ annealed samples. However, compared to the standard X-ray phosphor materials the luminescence from forming gas annealed samples was 56% of that of ZnSe:Cu,Cl and 76% of the gain of Gd₂O₃:Tb. Although in general, the vacuum annealed ZT05 samples were a little brighter than the N₂ annealed ZT11 samples.

The effects of the gas flow rate on the PL intensity of ZnTe:O were also investigated, as shown in Fig. 5. It was observed that for N₂, the gas flow rate had little effect on the PL intensity. However, for forming gas annealed samples, the PL intensity decreased quickly with increasing gas flow rate. The highest luminescence efficiency was observed at small flow rates of ~2 sccm, whereas when the flow rates exceeded 50 sccm, no luminescence was detected from the sample. This was attributed to the removal of effective oxygen doping centers from the ZnTe:O sample. Therefore, although H₂ can successfully etch and remove the surface tellurium oxide from ZnTe:O, it appears that the oxygen doping centers can also be removed. Thus, careful control of the H₂ flow rate is needed to synthesize an efficient ZnTe:O phosphor.

4. Discussion

In summary, all of the PL, CL and X-ray luminescence results showed that oxygen doped ZnTe powder annealed in forming gas exhibited significantly higher luminescent intensities than either the vacuum or N₂ annealed samples. Additionally, the XPS studies indicated that tellurium oxide was formed only on the surfaces of vacuum and N₂ annealed samples, but not on the

forming gas annealed samples, and, therefore, is most probably responsible for the lower luminescent intensity.

The surface tellurium oxide could be formed during the ball-milling process in oxygen atmosphere. In addition, in the presence of absorbed moisture from air, tellurium oxide is easily formed during the annealing process. By evacuating and drying the ball-milled powder from room temperature to a relatively low temperature (145 °C) one can remove part of the absorbed water; however, it is quite difficult to completely remove it in a gas atmosphere and so a low vacuum (10^{-2} – 10^{-3} torr) was used in this experiment. During annealing water vapor cannot escape from the sealed tube and reacts with ZnTe. Therefore, a tellurium oxide layer is formed on the surface of vacuum annealed ZnTe:O with a consequent decrease in the luminescent intensity. For the N₂ annealed samples, because the absorbed water was not removed at all, during the heating and annealing process a thicker tellurium oxide film was formed compared to the vacuum annealed samples; as indicated by the XPS results. As a result, the luminescent efficiency is lower than the vacuum annealed samples as shown by the PL, CL and X-ray luminescence data.

When ZnTe:O was annealed in a forming gas atmosphere, H₂ reacted with the surface tellurium oxide to form water vapor and H₂Te, which was removed by the gas flow. However, ZnTe could also react with H₂ and generate H₂Te, which escapes from the tube, forming an excess atmosphere of Zn in the tube. In fact, a Zn film was observed to condense on the cold side of the tube after annealing. Therefore, annealing ZnTe in forming gas atmosphere has many advantages in improving the luminescence efficiency. First, the etching effect of the H₂ annealing removes the surface tellurium oxide, which is believed to deteriorate the luminescent efficiency. Secondly, it prevents the formation of excess tellurium in the tube which results in the precipitation of interstitial tellurium. Valdna et al. have reported that interstitial tellurium is the most likely PL killer center in the tellurides and is precipitated when an excess of tellurium is formed during the thermal treatment [16]. On the contrary, a Zn atmosphere

was formed and interestingly Norris has reported that Zn-vapor heat treatments greatly enhance the red emission band of ZnTe:O bulk crystals [17]. Third, the smoother surface after H₂ etching results in fewer defects and a higher luminescent efficiency. The smoother surface also has a greatly reduced surface area which may also be responsible for the improved efficiency. Fourth, H₂ could probably passivate the surface and increase the efficiency. Last but not least, H₂ atmosphere annealing is simple and more cost effective compared to vacuum annealing, especially for large volume synthesis.

5. Conclusions

ZnTe:O powder phosphors for X-ray imaging applications were prepared by ball-milling bulk ZnTe crystals in an O₂ atmosphere followed by annealing in various atmospheres. The phosphors annealed in a forming gas atmosphere exhibited a five times higher X-ray luminescent efficiency than the powders annealed in vacuum or a N₂ atmosphere. PL and CL efficiency of the forming gas annealed ZnTe:O phosphors were also significantly increased. This improvement was attributed to H₂ etching, which removes surface tellurium oxides and defects present on ZnTe:O powder phosphors.

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