ZnTe:O phosphor development for x-ray imaging applications

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An efficient ZnTe:O x-ray powder phosphor was prepared by a dry synthesis process using gaseous doping and etching medias. The x-ray luminescent properties were evaluated and compared to standard commercial phosphors exhibited an x-ray luminescent efficiency equivalent to 76% of Gd_2O_2S:Tb and an equal resolution of 2.5 lines/mm. In addition, the fast decay time, low afterglow, and superior spectral match to conventional charge-coupled devices-indicate that ZnTe:O is a very promising phosphor candidate for x-ray imaging applications. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2185427]

In recent years, charge-coupled devices (CCD) based synchrotron x-ray imaging detectors have been developed for structural biology applications.[1–3] High-resolution macromolecular crystallography, such as the structure of the ribosomal subunit with a resolution of 2.4 Å, can be obtained using this detector system.[3] However, currently available detectors are not as fast, sensitive-and efficient as desired. Because the powder-phosphor screen is a key component to improving the performance of these detectors, higher quality x-ray phosphors are required. Recently, Bruker Advanced X-ray Systems (AXS) Inc. developed ZnSe:Cu phosphors that exhibited energy conversion efficiencies higher than any other known x-ray phosphor and incorporated them into commercial CCD detectors.[4] It was reported that the ZnSe:Cu phosphor screens were ~1.7 times brighter than the equivalent conventional Gd_2O_2S:Tb screens used for chemical crystallography detectors. However, ZnSe cannot be used for multiwavelength anomalous dispersion (MAD) studies because the atomic absorption edge of the Se atom interferes with the x-ray scattering lines for some biological cells.

As a semiconductor with a relatively low band gap (E_g) equal to 2.3 eV, ZnTe theoretically has superior properties as a high efficiency x-ray phosphor compared to other candidates. From Einstein's photoelectric effect, x-ray photoluminescence (PL) is initiated with the absorption of an x-ray photon by the host atom, producing an energetic photoelectron that travels through the material and generates a large number of secondary electron-hole pairs. If the energy of the incident x-ray photon is $E_{\text{x ray}}$, and the mean creation energy required to form an electron-hole pair is $\langle E_{eh} \rangle$, then the mean creation energy can be estimated as

$$\langle E_{eh} \rangle = \beta E_g, \tag{1}$$

where β is an inefficiency parameter that is much larger than unity due to energy loss from phonon scattering, and E_g is the host band gap. As the electrons and holes diffuse through the host lattice, a fraction, η_{eh}, recombine at active luminescent centers. These excited centers then produce a visible photon with quantum efficiency QE_l. Thus, the combined quantum gain g_{ph} of the phosphor is given by[5]

$$g_{\text{ph}} = \frac{E_{\text{x ray}} \eta_{eh} QE_l}{\langle E_{eh} \rangle} = \frac{E_{\text{x ray}} \eta_{eh} \text{QE}_l}{\beta E_g}. \tag{2}$$

The maximum possible gain is realized when the electron-hole transport and luminescent center conversion efficiency are perfect, i.e., $\eta_{eh}=QE_l=1$. Also, the smaller the $\langle E_{eh} \rangle$ the higher the gain of the phosphor. Table I summarizes these parameters for various host materials (using $E_{\text{x ray}}=17$ KeV). Among these materials, Gd_2O_2S, CsI and ZnS are widely used conventional x-ray phosphor hosts.[6] However, Table I implies that there are better host candidates than these materials, such as low-band-gap ZnSe and ZnTe. ZnSe:Cu phosphors were recently developed and to date have exhibited the highest known x-ray conversion efficiency, proving that these theoretical estimates are reasonable and implying that ZnTe could be a better candidate for x-ray phosphors.

However, little work has been reported on the synthesis of ZnTe for powder phosphor applications. Although the photoluminescence of doped ZnTe has been widely reported,[7–13] with effective dopants including oxygen,[7–10] copper,[11] ytterbium,[12] arsenic,[13] etc., luminescence with suitable intensity and spectral properties for powder phosphor applications has not been achieved in ZnTe. This is attributed to its high moisture sensitivity and chemical instability dur-

TABLE I. X-ray photoluminescence related parameters for various host materials.

Host material	E_g (eV)	β	E_{eh} (eV)	g_{eh}
ZnTe	2.3	2.2	5.0	3400
ZnSe	2.7	2.2	5.9	2880
ZnS	3.8	2.9	11.0	1545
Gd_2O_2S	4.4	3.9	17.2	990
CsI	6.4	2.5	16.0	1060

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TABLE II. Summary of luminescence properties of ZnTe:O and comparison with standard ZnSe:Cu and Gd_2O_2S:Tb conventional x-ray phosphors.

Phosphor material	Screen density (mg/cm^2)	Particle size (μm)	Peak emission (nm)	Decay time ($1/e$) (μs)	Afterglow (10 ms later)	Gain% (Mo, 17 MeV)	Gain% (Cu, 8 KeV)	Resolution (line/mm)
ZnTe:O	46	51	680	1.1	1×10^{-4}	56.1	111.3	2.5
ZnSe:Cu	45	20	650	8.9	1×10^{-4}	100	100	2.5
Gd_2O_2S:Tb	12	9	545	470	7×10^{-4}	73.4	163.6	2.5

ing synthesis. In the presence of water or moisture, ZnTe easily decomposes to form precipitates of ZnO, Te, and TeO_2,[14] which produce deep level electronic defect states in the energy gap that can quench luminescence. Therefore, in order to prepare efficient ZnTe powder phosphors, the key is to develop a dry synthesis process.

In this letter, ZnTe:O x-ray phosphors were prepared by a dry synthesis process using gaseous doping and etching medias. ZnTe:O powders were dry doped by ball milling the bulk ZnTe (99.999% in purity) crystals for 48 h in an ultrahigh purity O_2 (99.994%) atmosphere. After milling the powders were annealed and slightly etched in a forming gas ($95\%N_2/5\%H_2$) atmosphere at 1000 °C for 1 h. 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. Experimental details are reported elsewhere.[15]

Table II summarizes the x-ray luminescence properties of ZnTe:O phosphor screens compared to standard commercial ZnSe:Cu and Gd_2O_2S:Tb x-ray phosphor screens. A 6×6 cm^2 screen showed x-ray luminescence efficiencies equivalent to 56% of ZnSe:Cu and 76% of Gd_2O_2S:Tb when Mo 17 KeV x-ray excitation was used, and 111% of ZnSe:Cu for Cu 8 KeV excitation. The success in preparing efficient powder phosphors from ZnTe is attributed to the moisture-free doping process and removal of surface oxides by a dry etching process. By ball milling in an O_2 atmosphere, mechanically stimulated ion implantation of active oxygen into the lattice occurs due to the large local electric fields generated in the microcracks formed during crystal destruction.[16] This results in high phase purity and oxygen doping with a high degree of crystal stoichiometry. Additionally, the formation of a tellurium oxide layer on the crystal surface is an important mechanism that significantly reduces the photoluminescence intensity of ZnTe.[14] However, by annealing ZnTein a $95\%N_2/5\%H_2$ forming gas atmosphere the surface tellurium oxides can be removed-resulting in a five times improvement in the luminescence efficiency.[15] The morphology of the prepared ZnTe:O powder phosphors is shown in Fig. 1(a) as investigated by scanning electron microscopy. The particle size of the phosphor powders has a Gaussian distribution with a mean size of 51 μm. Particles exhibited irregular shapes with a smooth rounded surface taht decreases surface area and defects. Fig. 1(b) shows the surface morphology of a ZnTe:O powder phosphor screen. It can be observed that the phosphor particles are buried in an epoxy matrix. For a screen density of 46 mg/cm^2, the film thickness was ~150 μm.

Under 470 nm excitation at room temperature, a broad red emission centered at ~680 nm was observed from oxygen doped ZnTe, as shown in Fig. 2(a). The luminescence band is attributed to emission from an exciton bound to an isoelectronic oxygen which forms a deep electron trap in ZnTe.[7–10] For comparison, the PL spectra of standard ZnSe:Cu and Gd_2O_2S:Tb x-ray phosphors are also shown, and normalized to the peak intensity of ZnSe:Cu according to their relative gain in x-ray luminescence efficiency measurements using 17 KeV Mo irradiation. The ZnSe:Cu phosphors exhibited a broad red emission centered at ~650 nm. In contrast, the PL spectrum of Gd_2O_2S:Tb has several discrete emission peaks in the green with the maximum located at 545 nm. The sensitivity spectrum of a conventional CCD detector, also displayed in Fig. 2(a), exhibits the highest quantum efficiency (40–42%) between 660 and 790 nm.Therefore, the PL spectrum of ZnTe:O provides a better match to the spectral sensitivity of the CCD, compared with the ZnSe:Cu and Gd_2O_2S:Tb x-ray phosphors.

Figure 2(b) compares the cathodoluminescence (CL) decay curves of ZnTe:O phosphors with ZnSe:Cu. The ZnTe:O phosphors show a very fast exponential decay of 1.1 μs. This is eight times faster than ZnSe:Cu, which exhibits a $1/e$ decay time of 8.9 μs. For the traditional x-ray phosphor Gd_2O_2S:Tb, a significantly slower decay time of 470 μs was measured. The temporal response of the imaging system is affected by the luminescence decay time of the

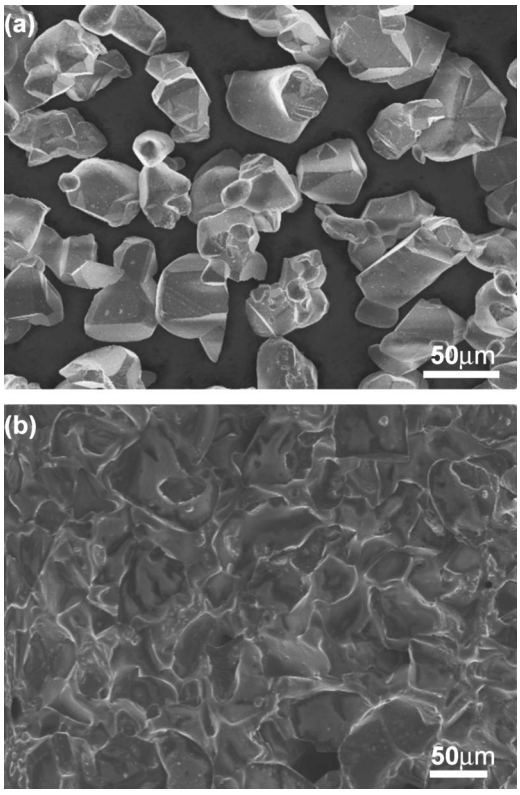

FIG. 1. Images of ZnTe:O phosphor powders (a) and screen (b).

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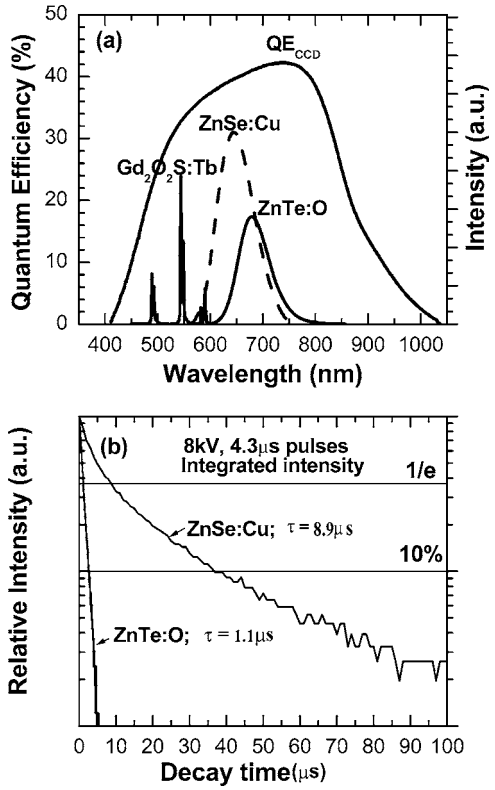

FIG. 2. (a) PL spectrum of ZnTe:O powder phosphors and comparison with standard ZnSe:Cu and Gd_2O_2S:Tb x-ray phosphors. The quantum efficiency curve of the CCD detector is also shown. (b) CL decay curve of ZnTe:O compared with a standard ZnSe:Cu x-ray phosphor.

phosphor. Slow response resulting from long decay time can potentially deteriorate the image quality by causing blurring of the acquired image. Therefore, for high-resolution x-ray imaging applications, a phosphor with the fastest possible decay properties is preferred.

In addition to the decay time, another very important temporal property of x-ray phosphors that affects the image resolution is the afterglow, especially when used in a scanning imaging system. In this study, the afterglow properties of phosphors were studied by x-ray luminescence measurements. X-ray pulses with a width of 0.1 s were used as the excitation source. As shown in Table I, the ZnTe:O phosphors exhibited a very low afterglow. After 10 ms the relative luminescence intensity of ZnTe:O had decreased to $\sim 1 \times 10^{-4}$, comparable to ZnSe:Cu and nearly an order of magnitude better than Gd_2O_2S:Tb.

Figures 3(a) and 3(b) compares the imaging resolution of the ZnTe:O screen with a standard commercial Gd_2O_2S:Tb screen. Little difference was observed between the two images. A resolution of 2.5 lines/mm was resolved from the ZnTe:O screen, which was comparable to that of an optimized commercial Gd_2O_2S:Tb screen. It should be noted that the film thickness and particle size of the ZnTe:O phosphors were not optimized, thus using thinner phosphor screens is expected to result in higher resolution. Further improvements in the performance of this material will therefore be of great benefit in enhancing the sensitivity of x-ray

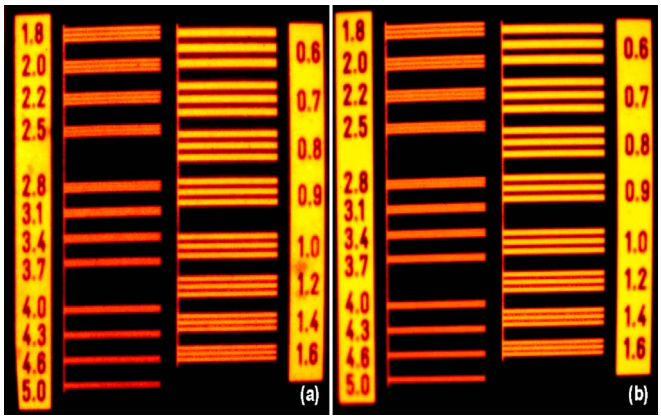

FIG. 3. (Color online) Comparison of x-ray imaging resolution between a ZnTe:O phosphor screen (a) and standard Gd_2O_2S:Tb x-ray phosphor screen (b).

detector, thus allowing high-resolution imaging systems.

In conclusion, an efficient ZnTe:O x-ray powder phosphor was prepared by ball-milling bulk ZnTe crystals in an O_2 atmosphere followed by annealing in a $95\%N_2/5\%H_2$ forming gas atmosphere. It was found that this dry synthesis process was critical for the fabrication of high performance ZnTe based powder phosphors. The excellent x-ray luminescence results, including high efficiency, high-resolution, fast decay, low afterglow, and an improved spectral match to the CCD detector, indicated that ZnTe:O is a promising phosphor candidate for x-ray imaging applications.

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