

Synthesis and characterization of oxygen doped ZnTe for powder phosphor application

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The synthesis of efficient ZnTe powder phosphors is very difficult due to its high moisture sensitivity and chemical instability during processing. In this study, an efficient ZnTe:O powder phosphor for x-ray imaging application was successfully synthesized by vacuum firing ZnTe powder prepared from ZnTe bulk crystals ball-milled in an O₂ atmosphere. The phosphors were characterized by x-ray diffraction, x-ray photoelectron spectroscopy, photoluminescence, and cathodoluminescence (CL) measurements and found to exhibit a luminescent efficiency three times that of ZnTe:O prepared by ZnO doping. The ZnTe:O samples exhibited a deep red emission centered at 680 nm and a CL decay time of 1.1 μs.

I. INTRODUCTION

As one of the most efficient and versatile phosphors, with application in cathode ray tubes and electroluminescent devices, doped ZnS has been widely used for many years to produce blue to red light. Intense green and red luminescence has also been achieved in doped ZnSe.¹ ZnSe:Cu,Cl is a red emitting (650 nm) scintillator with the highest known x-ray conversion efficiency. However, ZnSe is not suitable for multi-wavelength anomalous dispersion (MAD) studies because the atomic absorption edge of the Se atom interferes with some biological cells. As the counterpart of ZnS and ZnSe, ZnTe can avoid this problem and can potentially achieve efficiencies comparable to ZnSe.² The objective of this research is to synthesize ZnTe powder phosphor materials that can be screened for large-area (20 × 20 cm) x-ray imaging screens and match the spectral sensitivity of conventional red sensitive charge coupled device (CCD) detectors, which has a quantum efficiency that peaks near ~700 nm.

However, unlike ZnS and ZnSe, high-efficiency ZnTe phosphors are very difficult to synthesize in powder form, probably due to their high moisture sensitivity and chemical instability during synthesis. Thus, most of the recent research on ZnTe has been focused on the synthesis of pure or doped ZnTe films for electro-optic appli-

cations. Bulk ZnTe crystals can be synthesized by melt- or vapor-phase techniques.^{3–6} Also, ZnTe thin films have been fabricated by epitaxial growth techniques.^{7–10} However, little work has been reported on the synthesis of efficient luminescent ZnTe for powder phosphor applications. The photoluminescence of doped ZnTe has been widely reported,^{3,4,8–18} with effective dopants including oxygen,^{3,11–17} copper,^{4,18} ytterbium,⁹ arsenic,¹⁰ etc. However, no emission of suitable intensity and spectral properties for phosphor applications was reported. In 1962, Dietz et al. reported a broad red emission centered at ~660 nm from vapor-grown ZnTe bulk crystals measured at 20 K.¹¹ 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.¹² The origins and properties of this emission have been investigated further and attributed to the recombination of excitons bound to isoelectronic oxygen centers.^{3,12–17}

In this paper, we report on the preparation of efficient ZnTe powder phosphors doped with oxygen and characterized by structural and optical measurements. To avoid reaction with water and moisture and to achieve pure substitution of oxygen at tellurium sites, oxygen was incorporated by using two different forms of a dry doping process: (i) an admixture of ZnTe and ZnO and (ii) the ball-milling of bulk ZnTe crystals into small particles in an O₂ atmosphere. For comparison, Cu was also used to activate ZnTe by a regular wet doping process, since Cu is a very effective dopant for ZnS and ZnSe.

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II. EXPERIMENTAL

A. Synthesis

For the synthesis, bulk ZnTe crystals of 99.999% purity were used as the raw host material and ZnO particles of 99.99% purity were used for oxygen doping. Ultra-high-purity O₂ (99.994%) and/or N₂ (99.999%) gas was used as the ball-milling atmosphere. CuCl₂ and ZnCl₂ of 99.999% purity were dissolved into de-ionized water for wet doping.

The samples under study were classified into four groups: an undoped ZnTe reference sample, two oxygen-doped samples, and another Cu-doped sample. The methods of preparation were thus: (i) ZnTe powders with particle size of 10–50 μm , which were produced by ball-milling bulk crystals in N₂ atmosphere for 48 h (S1); (ii) ZnTe powder ball-milled from bulk crystals in O₂ atmosphere for 48 h (S2); (iii) dry mixtures of ZnTe–ZnO (S3) prepared at concentrations of [ZnO] = 0.2, 1, and 5 wt% (ZnTe powder is from S1); and (iv) ZnTe:Cu,Cl (S4) formed by wet doping with CuCl₂ and a 2 wt% ZnCl₂ solution into ZnTe powder obtained from S1, at concentrations of [Cu⁺] = 0.01 to 0.1 at%. Thus, as shown in Table I, samples S2 and S3 were dry-doped ZnTe:O, sample S4 was wet doped ZnTe:Cu,Cl, and sample S1 was undoped.

After being dried and evacuated to 10^{−2} to 10^{−3} Torr in a quartz tube, all the samples were fired in the quartz tubes at 1000 °C in vacuum for 1 h, and then the tube was quenched in air. The S4 samples were synthesized according to the regular procedures used for ZnS and ZnSe phosphor synthesis.¹⁹ Efficient ZnSe powder phosphors have been previously synthesized in our laboratory using the same procedures.

B. Characterization

Physical characterization was performed to analyze the bulk phase purity and the surface chemical properties. For the phase purity studies, the samples were analyzed by x-ray diffraction (XRD) on a Phillips PW-1800 x-ray diffractometer with Cu K α (λ = 0.15405 nm) radiation (40 kV, 30mA). Surface chemical analysis was performed by 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). The photoluminescence (PL) intensities of the samples were compared using an OceanOptics USB2000 (Dunedin, FL)

TABLE I. Sample conditions and doping methods.

No.	Crystal	Dopants	Doping method
S1	ZnTe
S2	ZnTe:O	O ₂	dry
S3	ZnTe:O	ZnO	dry
S4	ZnTe:Cu,Cl	CuCl ₂ ,ZnCl ₂	wet

spectrometer connected to an integrating sphere equipped with a 470 nm blue LED as the exciting source. The photoluminescent excitation spectra (PLE) and also some of the PL spectra were obtained with a Spex1000M spectrometer (Edison, NJ) using a 150 W xenon lamp/monochromator combination as the excitation source. The cathodoluminescent (CL) emission spectra were direct-current (dc) excited at various 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 (Wilton, NH) as the excitation source. All the CL measurements were performed at room temperature and recorded with a SpectraScan PR705 spectrophotometer (Kempston, UK). Pulsed CL measurements were also performed to investigate the time-resolved luminescence properties.

III. RESULTS AND DISCUSSION

A. Effect of doping method on phase purity

The experimental results showed that the doping method had a strong effect on the phase purity and luminescence properties of the ZnTe phosphor. Both ZnO and Te impurity phases were detected from almost all of the wet doped ZnTe:Cu,Cl samples (S4) after they had been fired at 1000 °C. The XRD spectrum of a typical S4 sample is shown in Fig. 1(a); the intense diffraction peaks at 36.8° and 28.1°, respectively, indicate a large proportion of a hexagonal ZnO phase and a hexagonal Te phase are present in the sample. These phases are believed to be the reaction products of ZnTe with H₂O during the long term mixing, drying, and firing procedures and are attributed to the moisture sensitivity and chemical instability of ZnTe. Absorbed water in ZnTe is very difficult to fully remove from the wet-doped samples and is very reactive during the following high-temperature firing process. In contrast, a pure ZnTe phase was obtained from the dry-doped ZnTe:O samples (S2) synthesized by ball-milling in O₂. As shown in

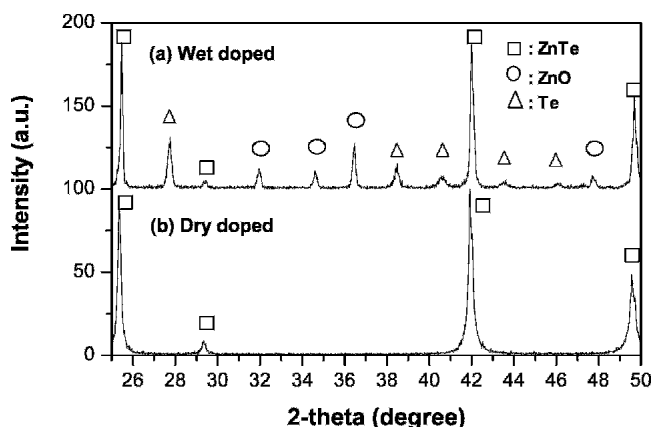


FIG. 1. XRD patterns of ZnTe samples fired at 1000 °C: (a) wet-doped ZnTe:Cu,Cl (S4) and (b) dry-doped ZnTe:O (S2) prepared by ball-milling in O₂.

Fig. 1(b), only diffraction peaks at 25.5° , 42.0° , 49.8° , and 29.2° were observed, which are respectively from the (111), (220), (311), and (200) planes of a cubic ZnTe phase, confirming that a pure ZnTe phase was achieved. The XRD spectra of the dry-doped S3 samples (which are not shown in Fig. 1) also indicated that only a pure ZnTe phase was detected after firing at 1000°C . This was directly attributed to the fact that no water was introduced into the raw materials during the dry synthesis process. Thus, any reaction with H_2O was avoided or greatly reduced.

A reaction between the wet-doped samples and quartz was also observed by the formation of a white dendritic layer on the wall of the quartz tube. A similar deposit was also observed by Valdna et al.¹⁹ when they fired wet-doped ZnTe or $\text{ZnSe}_{1-x}\text{Te}_x$ solid solution powders in quartz ampoules. From x-ray microanalysis measurements, they identified this layer to be $\text{SiO}_x\text{-ZnO}_x$. In contrast, for the undoped ZnTe, no reaction was observed between the sample and the quartz tube during the firing process. Also, for the dry doped S2 and S3 samples, the reaction between ZnTe and the quartz ampoule was greatly reduced, thus giving further confirmation that this reaction was related to the presence of absorbed water on the raw starting materials.

B. Surface chemical state

After synthesis, the samples exhibited different body colors. The undoped S1 samples exhibited a deep red color, whereas the dry oxygen doped S2 and S3 samples were brown in appearance. For the S3 samples, the color became deeper with increased ZnO additions. To understand this change in body color, the chemical state of surface 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.²⁰ These peaks are accompanied by two peaks at 577 and 587.5 eV, which are identified as being due to the emission from the 3d core levels of Te in an oxide environment. Thus, Fig. 2(a) indicates that tellurium oxide was formed on the surface of O_2 -doped ZnTe, while undoped ZnTe showed no oxidation because the tellurium oxide peaks were not detected. As shown in Fig. 2(b), for ZnO-doped ZnTe, the tellurium oxide surface layer was much thicker than that on the S2 samples, as estimated from the relative intensities of the tellurium and tellurium oxides peaks. Additionally, with increasing ZnO concentration, the surface oxide layer thickness increases. Morris et al.²¹ also reported that the thin brown layer formed on the crystal surfaces is a tellurium oxide.

For the wet-doped S4 samples, the body color was much darker than that of the dry-doped ones, with some samples even looking black. The heavily oxidized surface revealed by XPS measurements and the presence of

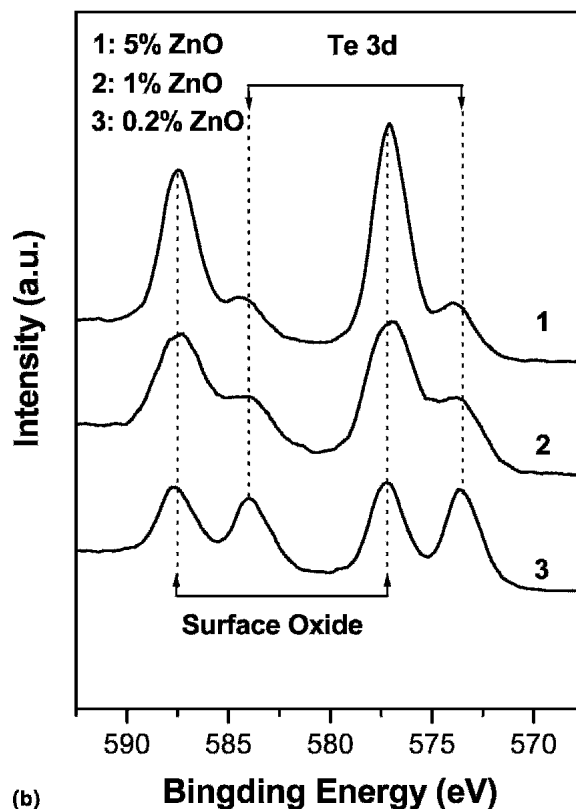
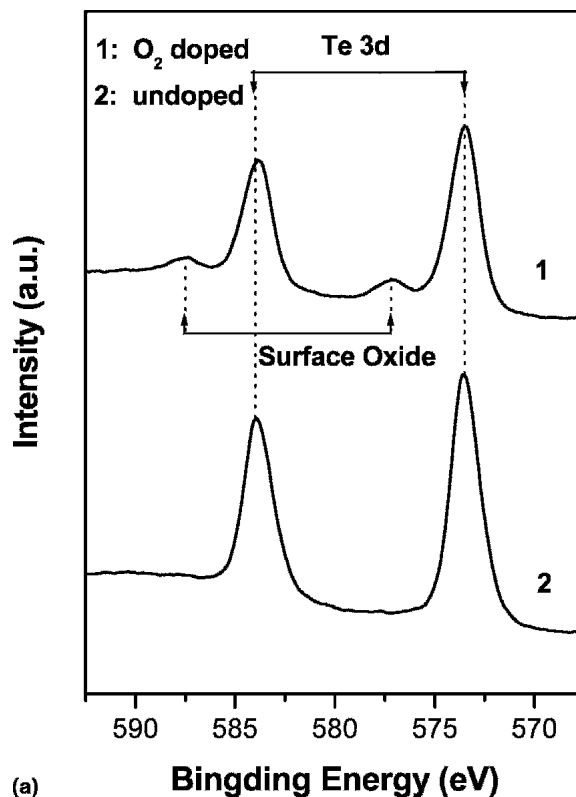


FIG. 2. XPS spectra of (a) ZnTe:O (S2) doped by ball-milling in O_2 (curve 1) and undoped ZnTe (S1) prepared by ball-milling in N_2 (curve 2), and (b) ZnTe:O (S3) samples doped with ZnO concentrations between 0.2% and 5%.

a pure tellurium phase in the samples may also be responsible for the dark color.

C. Photoluminescence properties

Under 470 nm excitation, both the undoped ZnTe (S1) and the wet-doped ZnTe:Cu,Cl samples exhibited no PL at room temperature, while a broad red emission centered at ~ 680 nm was observed from the oxygen doped S2 and S3, as shown in Fig. 3. This luminescence band is attributed to the emission from an exciton bound to an isoelectronic oxygen, which forms a deep electron trap in ZnTe.^{3,11–17} It was also observed that the S2 samples doped by ball-milling in O_2 exhibited a much higher PL intensity than the S3 samples doped by ZnO addition. And with increasing ZnO doping concentration, from 0.2% to 5%, the PL intensity decreased. The PL emission intensities from the 0.2%, 1%, and 5% ZnO-doped samples were about 27%, 20%, and 9% that of the typical O_2 doped sample, respectively.

From previous studies Valdina et al. have identified two possible mechanisms that can reduce the PL intensity in tellurides, which do not exist or which are negligible in the sulfides and selenides:¹⁹ (i) a tellurium oxide layer is formed on the crystal surface and (ii) an interstitial tellurium or a complex defect formed with Te_i . Interstitial Te is probably the PL killer in the tellurides and is precipitated when an excess of tellurium is formed during the thermal treatment. Therefore, the absence of luminescence from the wet-doped S4 samples could be attributed to both the heavily oxidized surface structure and the presence of an excess tellurium impurity phase after firing. For the ZnO-doped S3 samples, the luminescence intensity decreased with increasing ZnO concentration, which could also be attributed to the increase in the surface tellurium oxide layer thickness, as indicated by XPS results.

As was reported for ZnSe:O and $ZnSe_{1-x}Te_x$:O formed

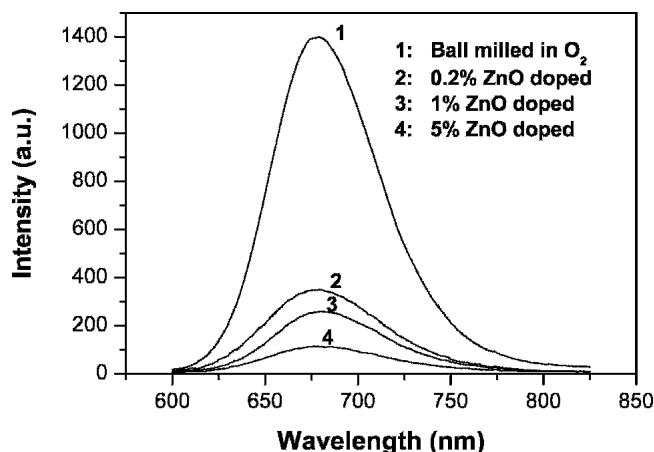


FIG. 3. PL spectra of ZnTe:O doped by O_2 or ZnO (470 nm excitation at room temperature).

by grinding bulk crystals in an O_2 atmosphere, the ball-milling of ZnTe crystals in an O_2 atmosphere mechanically stimulates ion implantation of active forms of oxygen (O' , O_2' , O^x , etc.) into the lattice due to large local electric fields in the region of microcracks formed during crystal destruction.²² Thus, a high concentration of oxygen related centers can be incorporated and uniformly distributed in the crystals, leading to the efficient luminescence of S2 samples. It is also interesting to note that the O_2 atmosphere ball-milling of ZnTe powders, which had already been thoroughly ground into small particles, did not lead to oxygen induced luminescence. This is because ion implantation emulation cannot be achieved without the creation of microcracks in the powder. In contrast, in a ZnTe–ZnO admixture the ZnO particles are likely bonded onto the ZnTe surface and have a lower solubility and diffusion rate in the ZnTe crystal during the firing process. Thus, a uniform distribution of oxygen is difficult to achieve by firing dry mixed ZnTe and ZnO particles, and the addition of ZnO is not an efficient way to dope ZnTe. In addition, a thicker tellurium oxide surface layer was observed in the S3 samples, which would also result in a lower luminescent efficiency.

Figure 4 shows the typical PL and PLE spectra of ZnTe:O samples prepared by ball-milling in O_2 . The PL spectrum was measured at room temperature using 470 nm excitation. The main emission peak is centered at 685 nm with a half maximum width of ~ 73 nm, as reported for isoelectronic oxygen centers in ZnTe.^{3,12–17} Two very weak peaks located at 577 and 579 nm were also observed, as shown in the inset of Fig. 4. For the PLE spectra, the investigated excitation wavelength was from 450 to 640 nm. The excitation spectrum consists of two strong excitation bands, a broad band centered at 606 nm on which is imposed a sharp peak centered at 553 nm. The broad band is due to the absorption of

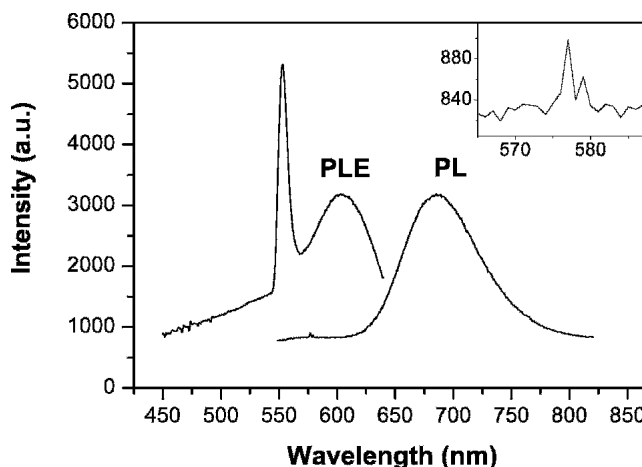


FIG. 4. PL and PLE spectra of a typical ZnTe:O sample doped by ball-milling in O_2 (inset shows the near band edge PL emission; the PL was measured at room temperature with 470 nm excitation.).

oxygen centers, which is very symmetrical to the emission band.¹¹ The sharp band extends between 545 and 570 nm. Iida has reported similar PLE results for ZnTe:O at 77 K,¹⁵ but no interpretation of the origin of this sharp excitation band was given.

The band gap of pure ZnTe at 300 K is 2.25 eV (552 nm). Doping of oxygen in ZnTe could cause a small shift of the band gap. The 553 nm excitation band is possibly attributed to the band edge absorption, although it seems too sharp to be a band edge absorption. The 577 and 579 nm emission might be caused by shallow donor–acceptor pairs or free to bound transitions. Further experiments are needed to identify the origin of this excitation band.

D. Cathodoluminescence properties

Figure 5(a) shows the CL spectra of ZnTe samples when excited by 20 keV electrons. A broad emission centered at ~684 nm was also observed both from the O₂ doped and 0.2% ZnO doped samples. The CL efficiency of the O₂-doped sample was more than 3 times higher

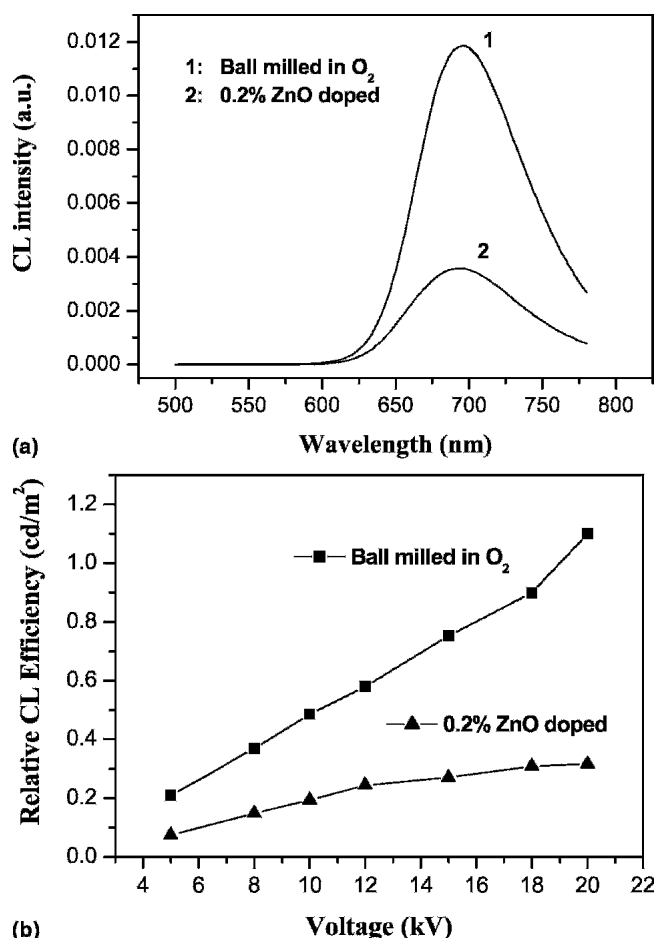


FIG. 5. (a) CL spectra of ZnTe:O doped by O₂ or ZnO and (b) CL efficiency of ZnTe:O in (a).

than the 0.2% ZnO-doped sample. The relative CL efficiencies of O₂-doped and 0.2% ZnO-doped ZnTe samples as a function of electron energy are shown in Fig. 5(b). Both samples showed no saturation at high voltages, which may indicate a long diffusion length of electron-hole pairs. The CL efficiency for ZnO-doped samples increases at a relatively slower rate with increasing voltage compared to the O₂-doped sample, and the slope decreases at higher voltages. This may be due to the decreasing oxygen concentration with depth because of the slower diffusion rate of ZnO in ZnTe.

Compared to the CL efficiency of commercial ZnS:Cu,Cl phosphor, the CL efficiency of synthesized ZnTe:O is low, ~1% of ZnS:Cu,Cl. However, for x-ray phosphor applications, due to the lower bandgap, and higher x-ray absorption efficiency of ZnTe, the x-ray conversion efficiency of ZnTe phosphors can potentially be comparable to ZnSe and ZnS phosphors.² Recent x-ray luminescence results of the ZnTe:O phosphors, which will be reported elsewhere,²³ exhibited an efficiency of up to 56% of the most efficient ZnSe:Cu,Cl phosphors.

Figure 6 shows the CL decay curve of ZnTe:O doped by ball milling in O₂. It is seen that the luminescence exhibits an exponential decay, and no afterglow was observed from the sample. The phosphor shows a very fast decay with 1/e decay time of about 1.1 μs. This result is close to the value measured by Cuthbert et al.¹⁷ on bulk ZnTe:O crystals at the wavelength of peak emission intensity.

IV. CONCLUSIONS

ZnTe:O powder phosphors were successfully prepared by vacuum firing ZnTe powder ball-milled in O₂ atmosphere from bulk crystals. It is very difficult to synthesize ZnTe powder phosphor by a wet-doping process because

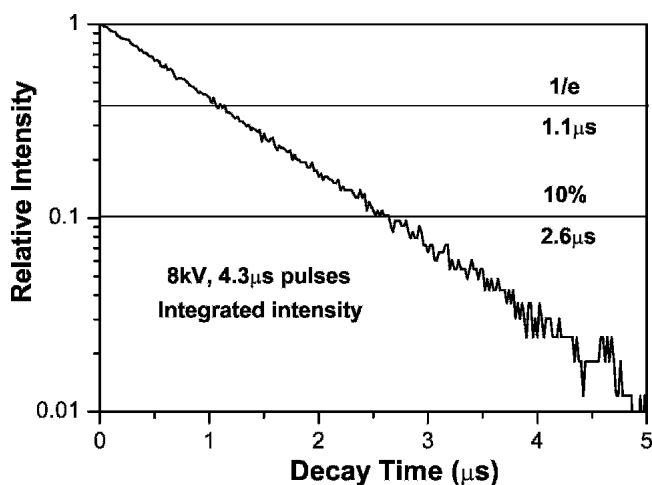


FIG. 6. 8 kV CL decay curve of ZnTe:O doped by ball milling in O₂.

a pure phase usually cannot be obtained due to the reaction of ZnTe with H₂O. Dry doping by O₂ through ball-milling is an effective way to synthesize ZnTe:O powder phosphors with a strong red emission centered at 680 nm and a decay time of 1.1 μ s. Two excitation bands centered at 553 and 606 nm, respectively, were observed to be responsible for this red emission. The emission intensity of O₂-doped samples was found to be more than three times as efficient as for the ZnO-doped samples due to a more uniform distribution of oxygen substitutional doping on tellurium sites.

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