Oxygen Doped ZnTe Phosphors for Synchrotron X-Ray Imaging Detectors

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September 20, 2005

Outline

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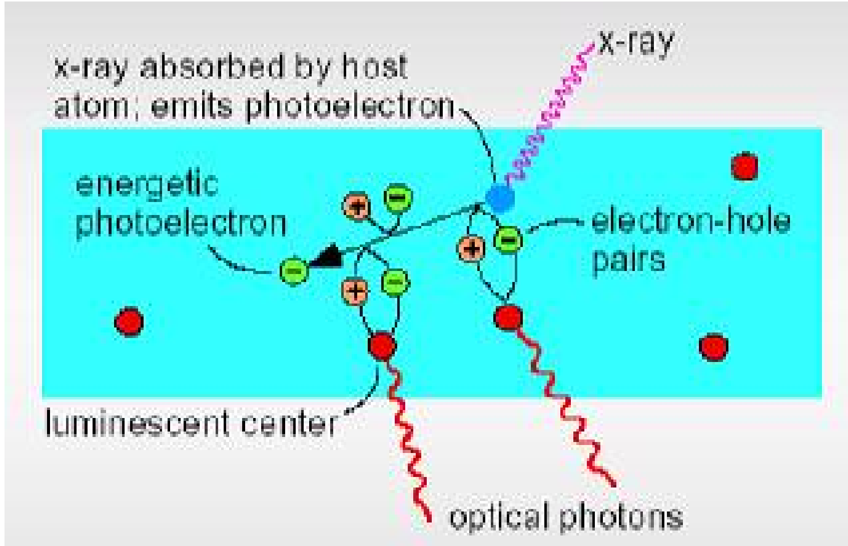
  - X-ray image phosphors
- **Objective**
  - Synthesis of ZnTe:O for biological imaging
- **Experimental**
  - Dry doping by ball-milling in O_2
  - Dry etching in H_2 atmosphere
- **Results and Discussion**
  - Optical and structural analysis
  - Comparison with standard X-ray phosphors
- **Conclusions and Future Work**

X-ray luminescence and phosphors

Principle of x-ray luminescence

- Absorbing of an X-ray photon
- Producing an energetic photoelectron
- Generating secondary e-h pairs
- E-h recombining at luminescent centers
- Emitting visible photons



Characteristics of efficient x-ray phosphors

- High x-ray absorption ($\alpha_{x\text{-}ray}$) and large density;
- Low cost per e-h pair (small $<E_{eh}>$ and E_g)
- Efficient electron-hole transport (η_{eh})
- High luminescent efficiency (QE_l)
- Low optical self absorption (α_{ph})

Quantum gain of X-ray phosphors

Expression of quantum gain $\boldsymbol{g_{eh}}$ (light photons/X-ray photon) of X-ray phosphors:

$$g_{eh} = \frac{E_{xray}\,\eta_{eh} QE_l}{\langle E_{eh} \rangle} = \frac{E_{xray}\,\eta_{eh} QE_l}{\beta E_g}$$

Host material	E_g (eV)	β	$\langle E_{eh} \rangle$ (eV)	g_{eh}
ZnTe	**2.3**	2.2	5.0	**2400**
ZnSe	2.7	2.2	5.9	2040
ZnS	3.8	2.9	11.0	1040
NaI	5.9	2.7	15.9	755
CsI	6.4	2.5	16.0	750
Gd_2O_2S	4.4	3.9	17.2	700
$CaWO_4$	4.6	7.0	32.3	370

g_{eh}

$\langle E_{eh} \rangle$: mean creation energy to form an e-h pair; η_{eh}: e-h transport efficiency; QE_l: luminescent center conversion efficiency.

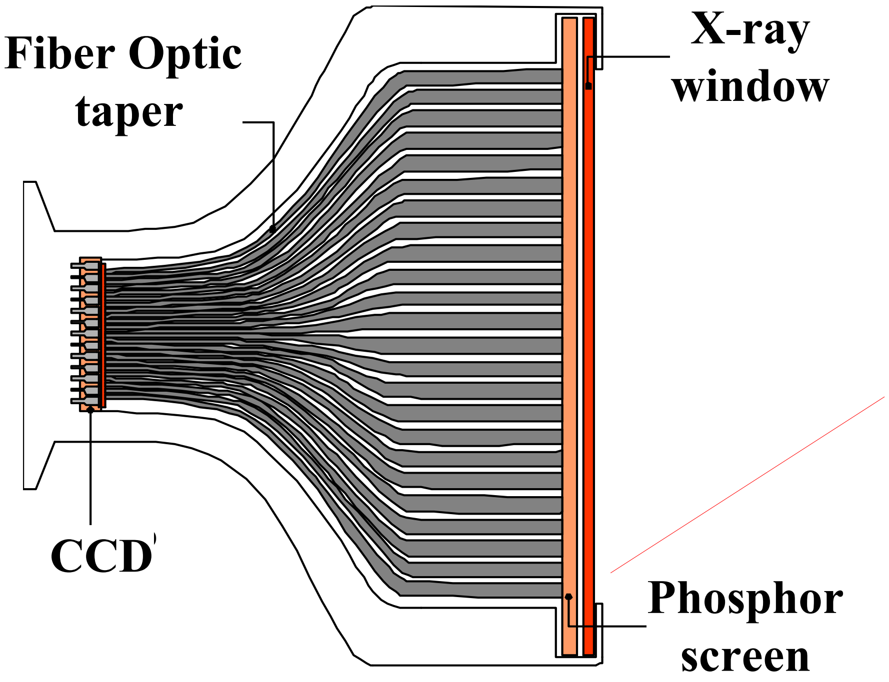
Inoue et al., J. Appl. Phys., 55, 1558 (1984)

X-ray phosphors for biological imaging

Applications:

- **Efficient and fast X-ray phosphors needed for CCD detectors used for synchrotron-based structural biology**
- **Macromolecular imaging such as biologic cells, protein, ribosome**

- **ZnSe:Cu,Ce,Cl has the highest known x-ray conversion efficiency**
  - 1.7 times higher than Gd_2O_2S:Tb
  - However, not suitable for imaging of biologic cells because of Se edge
- **ZnTe under development for macromolecular applications**
  - Efficiency potentially superior to ZnSe
  - No Se edge, suitable for MAD experiments



Synthesis issues for ZnTe:O X-ray phosphors

Issues:

- ZnTe is very sensitive to moisture during synthesis.
- Tellurium oxides are formed on the particle surface.

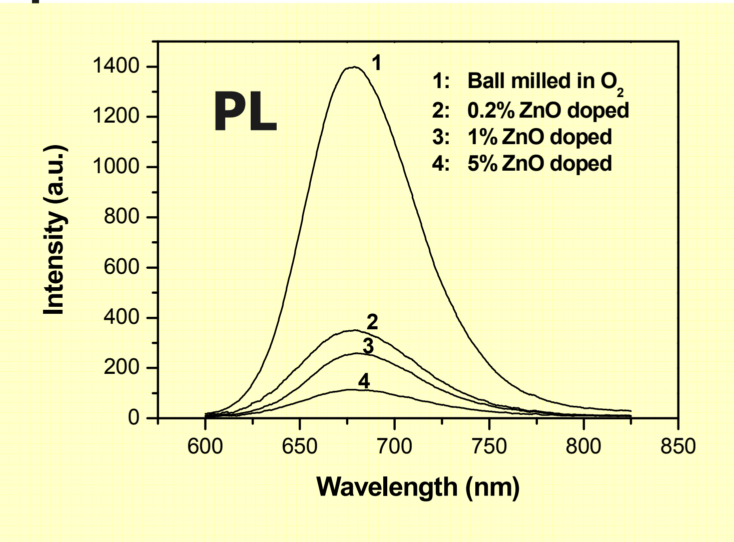
Conventional wet doping process used for ZnS and ZnSe phosphors synthesis is very difficult for ZnTe;
A dry doping process is needed.

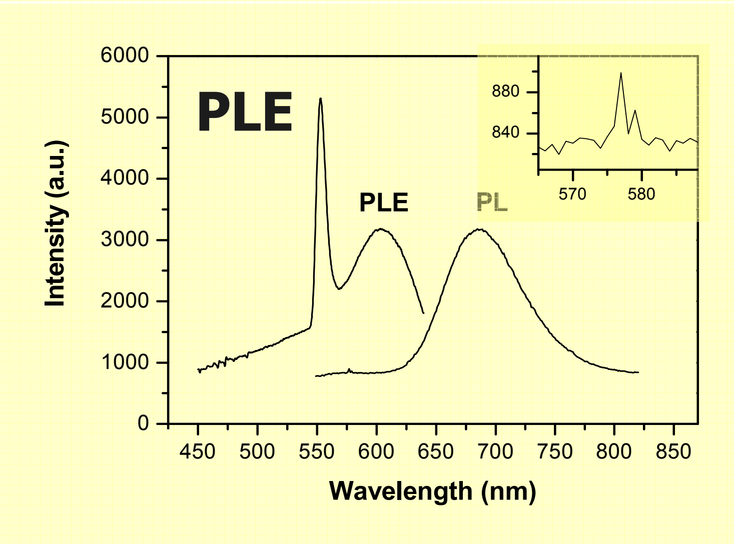
Dry synthesis process:

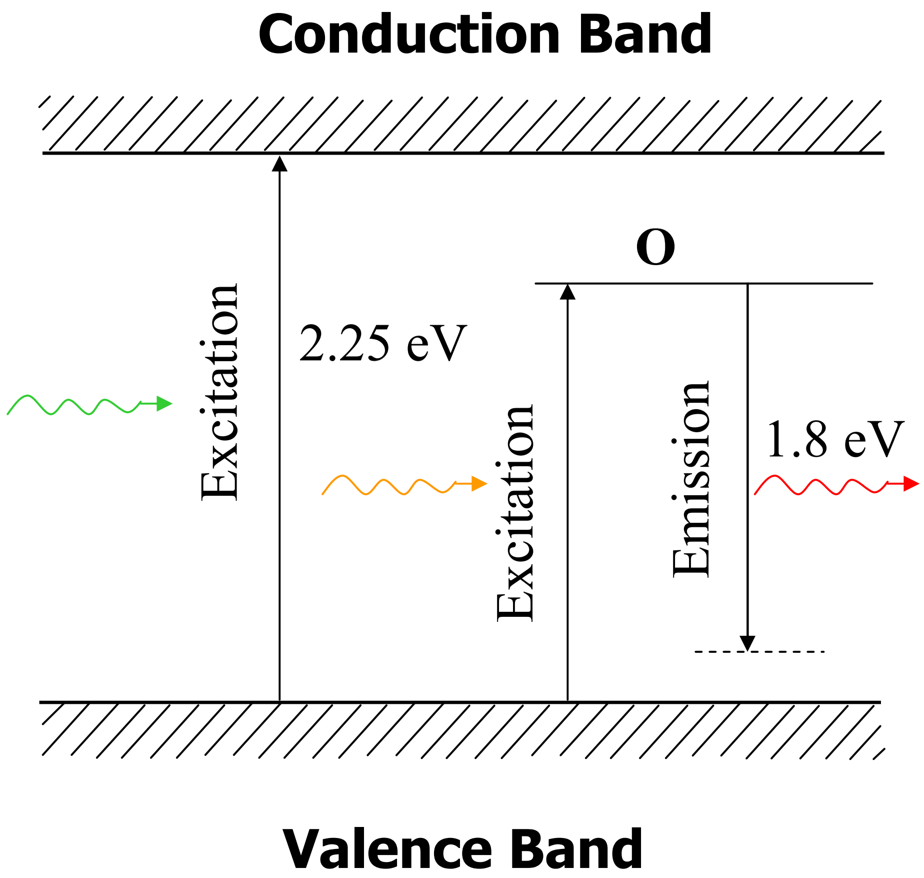
Ball-milling in O_2 or Ar/ O_2 → **Drying** → **Crystallization in N_2-5%H_2** → **Annealing in Zn vapor** → **Coating**

- Ball-milling of ZnTe in O_2 can lead to mechanically stimulated ion implantation of oxygen into the crystal lattice;
- Doping ZnTe with a gas media through ball milling is much more effective than doping by solid or liquid medias.

PL properties of ZnTe:O phosphors

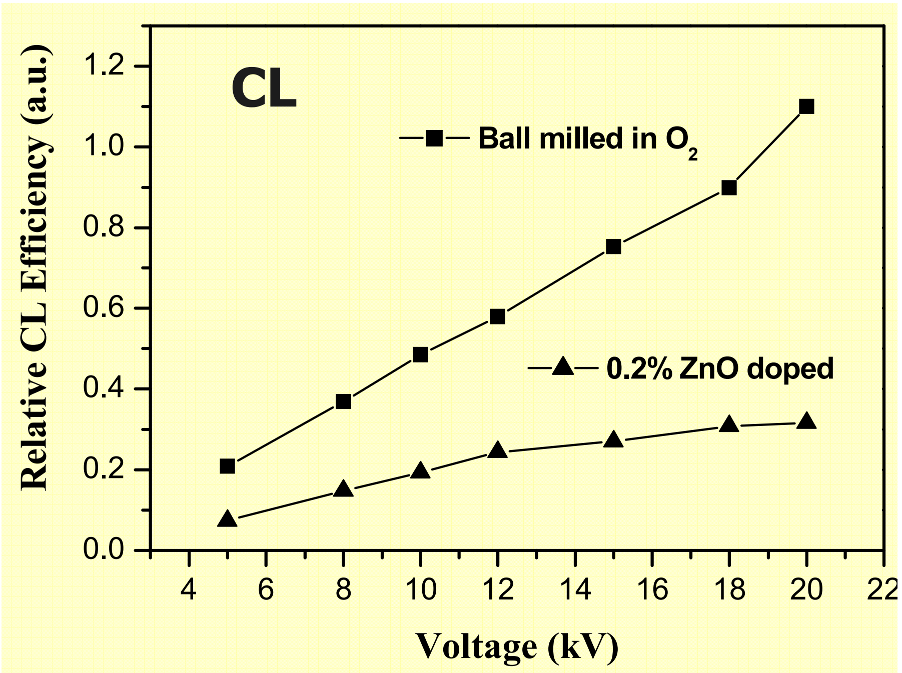


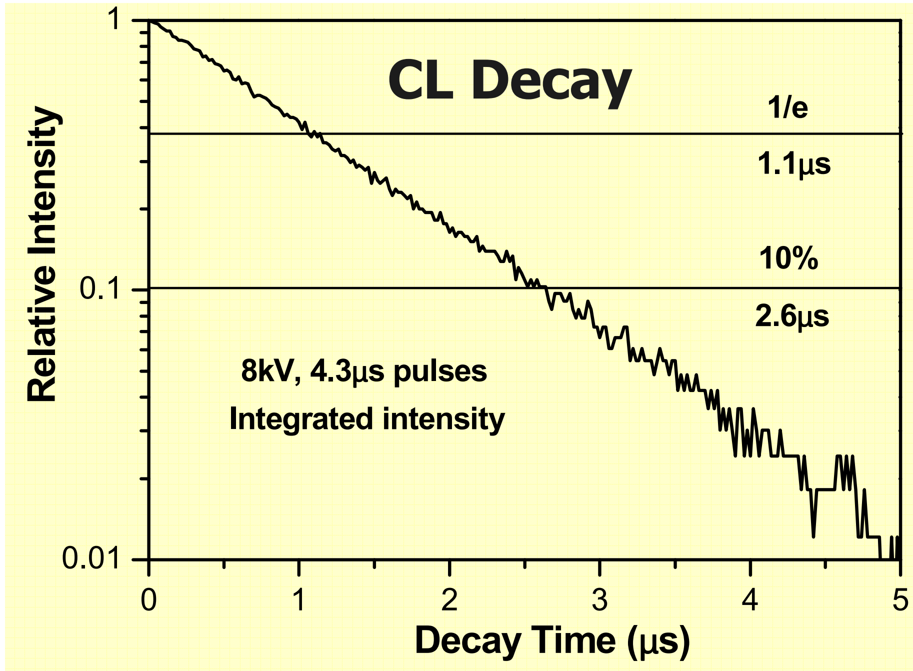




- **680nm emission from oxygen centers**

CL properties of ZnTe:O phosphors

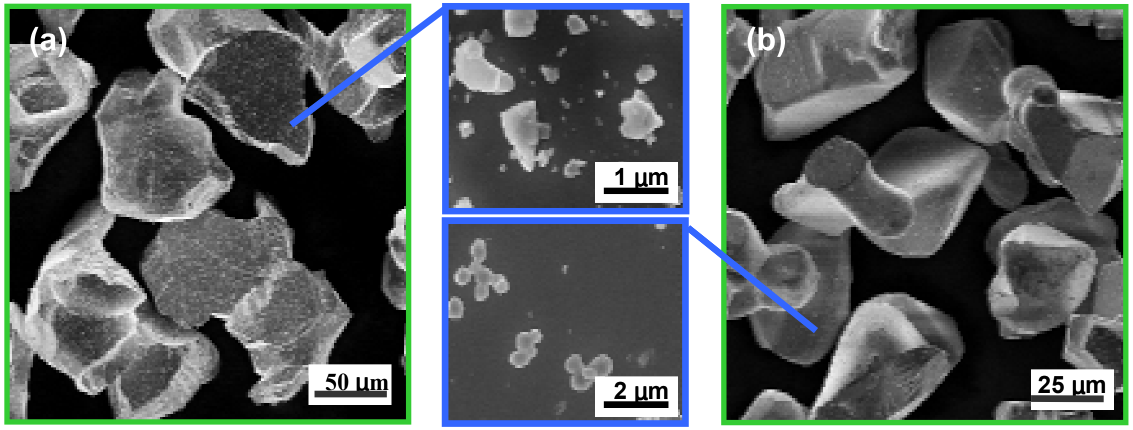




- O_2 doping significantly improved the CL efficiency compare to ZnO doping.
- Fast CL exponential decay time of 1.1µs was observed.

Effect of $N_2/5\%H_2$ annealing on surface property

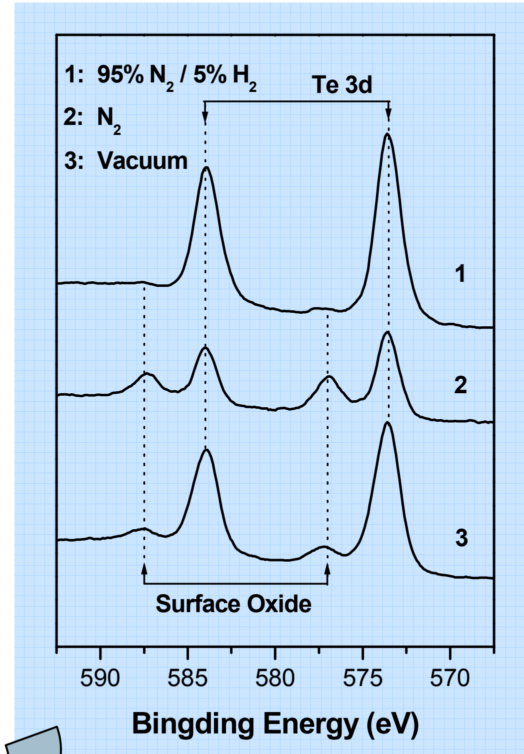
Particle morphology by SEM



(a) ZnTe:O annealed in Vacuum;
(b) ZnTe:O annealed in $N_2/5\%H_2$.

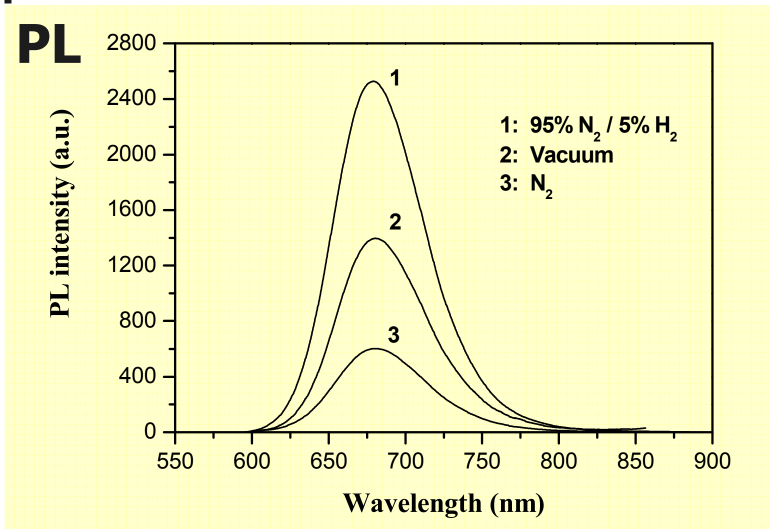
Smoothed surface morphology

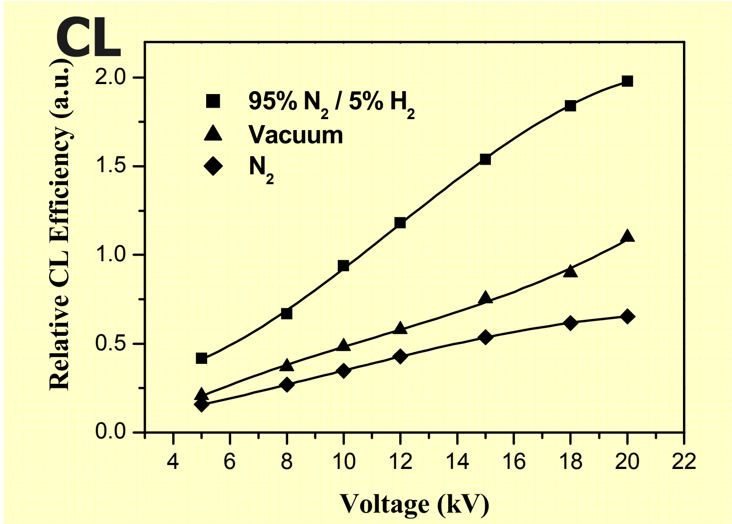
Surface chemistry by XPS



Removal of surface tellurium oxides

Improvement of optical property by H_2 annealing



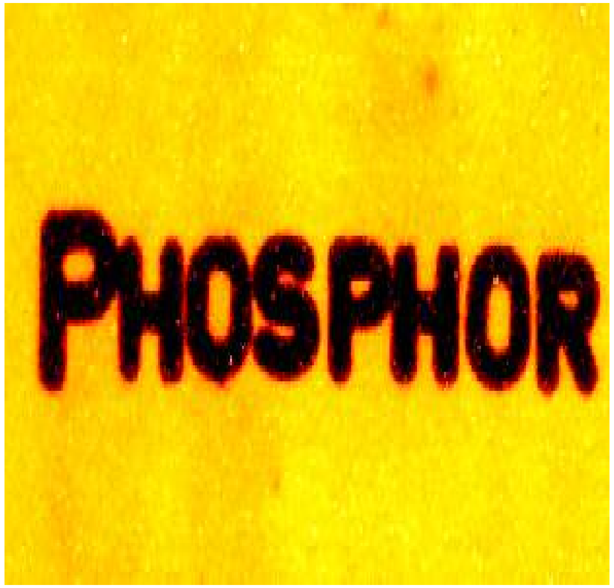


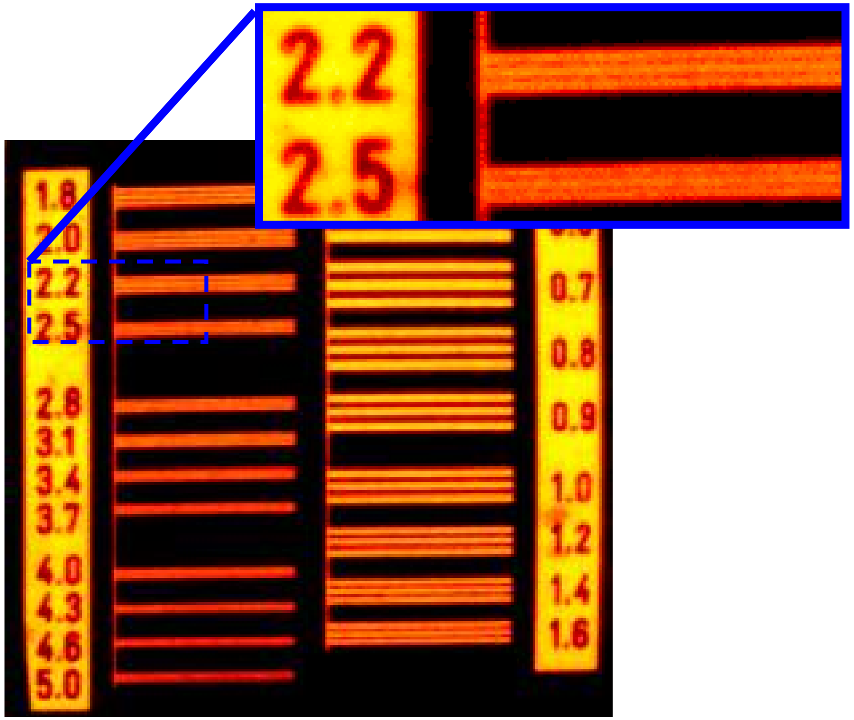
X-ray luminescent efficiency

Sample No.	Annealing atmosphere	% gain (ZnSe: Cu,Cl)	% gain (Gd_2O_2S: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

- Luminescent efficiency of ZnTe:O improved ~5 times after H_2 annealing

Preliminary X-ray imaging results



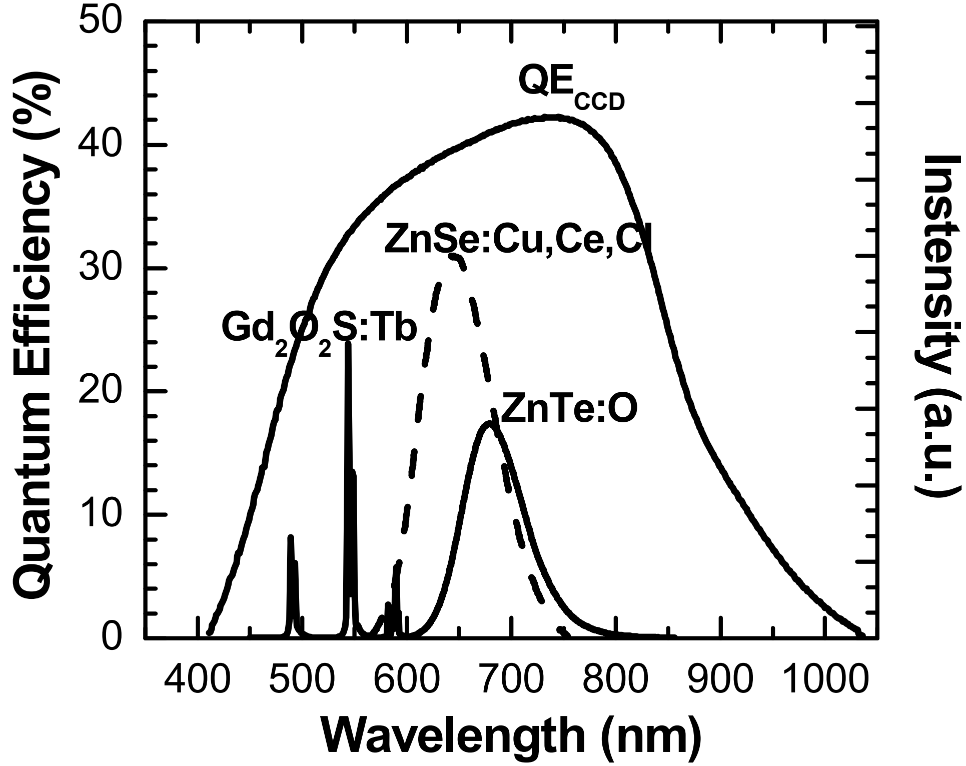


ZnTe:O screen x-ray imaging

Resolution: 2.5 lines/mm

Mo (17 KeV) radiation is used

Comparison with standard phosphors (1)



- **The emission spectrum of ZnTe:O is an very good match to the spectral sensitivity of front-illuminated CCD**

Comparison with standard phosphors (2)

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

- High efficiency, high resolution, fast decay, low afterglow and improved spectral match to the CCD detector, indicate that ZnTe:O is a promising phosphor candidate for X-ray imaging applications.

Conclusions and Future work

- **Conclusions**
  - **ZnTe:O powder phosphors successfully prepared by dry synthesis using gaseous doping and etching**
    - **Red emission centered at 680nm; decay time 1.1μs.**
  - **5 times improvement of X-ray luminescent efficiency was observed after annealing in a forming gas atmosphere, attributed to the removal of surface tellurium oxides.**
  - **The X-ray luminescent properties were evaluated and compared to standard commercial phosphors.**
    - **Efficiency equivalent to 76% of Gd_2O_2S:Tb**
    - **An equal resolution of 2.5 lines/mm**
- **Future Work**
  - **Optimize doping & annealing to further improve QE**
  - **Develop dry coating technique**

Acknowledgement

- Financial support from Molecular Beam Consortium
- Support by Ga Tech Research Institute Shackelford GRA Fellowship