

# Photoluminescence and cathodoluminescence properties of Tb-activated calcium zirconate phosphor

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## Abstract

CaZrO<sub>3</sub>:Tb as a new green-emitting phosphor, has been synthesized by solid state reaction. Photoluminescence and cathodoluminescence properties for the phosphor with a Perovskite structure were investigated. The CaZrO<sub>3</sub>:Tb phosphor, which has several emission peaks due to energy transfer from <sup>5</sup>D<sub>4</sub> to <sup>7</sup>F<sub>J</sub>(J=6,5,4,3) of Tb<sup>3+</sup> ion, exhibited strong green luminescence with the main emission peak centered at 545 nm. Optimum Tb concentration was 0.02mol%.

## 1. Introduction

The improvement of optical performances of green emitting phosphors is needed in order to increase the brightness of flat panel displays and fluorescent lamps.[1] The emission properties about Tb<sup>3+</sup> activator have been investigated extensively in a variety of host lattices. As is well known, the efficient blue-green emissions of Tb<sup>3+</sup> are originated from the <sup>5</sup>D<sub>3</sub> <sup>7</sup>F<sub>J</sub> (J=6,5,4,3) and <sup>5</sup>D<sub>4</sub> <sup>7</sup>F<sub>J</sub> transitions and Tb<sup>3+</sup>-activated phosphors have been used in many applications.[2] In the present work, it was attempted to prepare CaZrO<sub>3</sub>:Tb phosphors by conventional solid state reaction and their luminescent properties under ultraviolet ray and low-voltage electron excitation were compared with commercial green phosphor containing Tb<sup>3+</sup> activator.

The hosts is applied CaZrO<sub>3</sub> which had a orthorhombic phase of perovskite structure (ABO<sub>3</sub>) crystallographically and its cell

parameters are a= 5.587 Å, b= 8.008 Å and c=5.758 Å. In additionally, a unit cell was compositing four molecular.[3] In this study, we prepared the novel green emission phosphor CaZrO<sub>3</sub>:Tb<sup>3+</sup> by the traditional solid state reaction. Tb<sup>3+</sup> is a good activator with high lumen output, good color purity and great radiation stability.[4,5] CaZrO<sub>3</sub> is attracting much attention as host material because of the thermal stability, reasonable dielectrics and similar ionic radius between Tb<sup>3+</sup> ion and Ca<sup>2+</sup> ion, which can be expected that the Tb<sup>3+</sup> ions are incorporated substitutionally at the Ca<sup>2+</sup> sites. The photoluminescence measurements showed that the novel phosphor CaZrO<sub>3</sub>:Tb<sup>3+</sup> has good green emission.

## 2. Experimental

The Tb<sup>3+</sup> - doped CaZrO<sub>3</sub> phosphors were prepared using the solid state techniques. The starting materials used in the preparation of this phosphor were pure powders greater than 99.9% of CaCO<sub>3</sub>, ZrO(OH)<sub>2</sub>, and Tb<sub>4</sub>O<sub>7</sub>. Prewighed powders were mixed thoroughly in ethanol in an agate mortar and heat-treated at 1300 for 3h. The resulting powders were identified using a Rigaku D/MAX-33 X-ray diffraction (XRD) system with Cu K radiation. The photoluminescence spectra of the powders were measured using aPerkin Elmer LS-50 luminescence spectrometer at room temperature. Cathodoluminescence spectra were measured by CL spectrometer using an

electron beam with the excitation voltage of 900 V and the current of 1.5mA.

### 3. Results and Discussion

Fig. 1 exhibits X-ray patterns of  $\text{CaZrO}_3:\text{Tb}^{3+}$  phosphor fired at 1300 for 3h. The powder sample was confirmed to be a  $\text{CaZrO}_3$  single phase with a orthorhombic structure and  $\text{Tb}^{3+}$  ion was not detected. It agrees well with the ICDD-PDF(35-0790) of  $\text{CaZrO}_3$ . The diffraction peaks at  $d=$  4.0091, 2.8752, 2.8343, 2.7967, 2.0051, 1.7928, 1.6213 are corresponding to (101), (200), (121), (002), (202), (222), (123) diffraction faces, respectively.

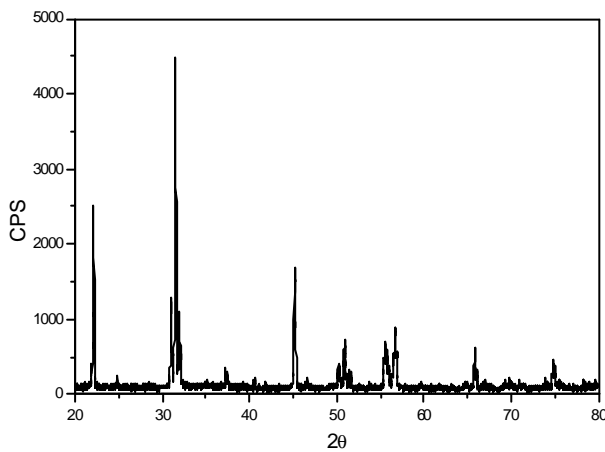


Fig. 1. X-ray diffraction pattern of the  $\text{CaZrO}_3$  powder fired at 1300 .

As shown in Fig. 2 the particles are agglomerated and show a spherical shape with a grain size in the range of 0.5 ~ 5  $\mu\text{m}$ .

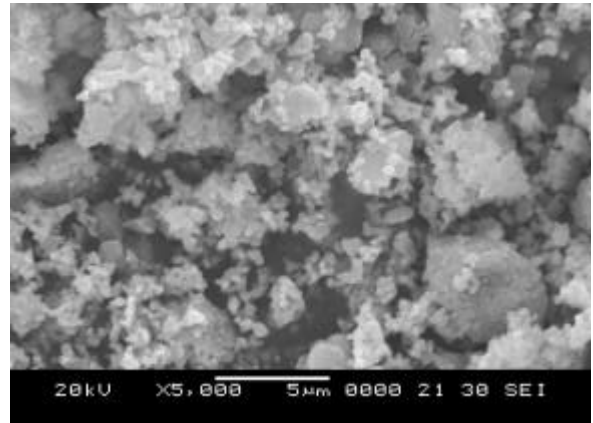


Fig. 2. The SEM image of the  $\text{Ca}_{0.97}\text{Tb}_{0.03}\text{ZrO}_3$  powder.

Fig. 3 presents the excitation and emission spectrum of the  $\text{Ca}_{0.97}\text{ZrO}_3:0.03\text{Tb}$  sample. To investigate the effect of  $\text{Tb}^{3+}$  concentration in  $\text{CaZrO}_3$ , various powder samples were prepared with different  $\text{Tb}^{3+}$  contents. The  $\text{Tb}^{3+}$  concentration has little influence on the position of the excitation and emission spectrum. The optimum emission was obtained at 0.03 mole  $\text{Tb}^{3+}$  ion concentration as shown in Fig. 4. The 490 nm and 545 nm emission band is attributed to the  $^5\text{D}_4 \rightarrow ^7\text{F}_6$  and the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transitions of  $\text{Tb}^{3+}$ , respectively. And the green emission of  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition is obviously predominant in the present case.

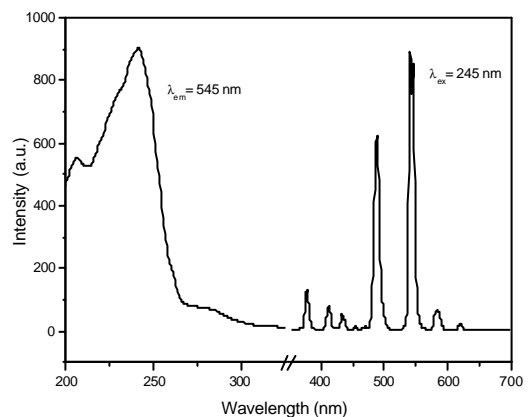


Fig. 3. The excitation and emission spectrum of the  $\text{Ca}_{0.97}\text{ZrO}_3:0.03\text{Tb}$  sample.

Fig. 4 shows concentration dependence of the emission intensity as a function of  $x$ . The emission intensity increases with the concentration of Tb at the lower Tb content region. It reaches maximum at Tb concentration of 0.03mol and then decreases with increasing Tb content, indicating the concentration quenching.

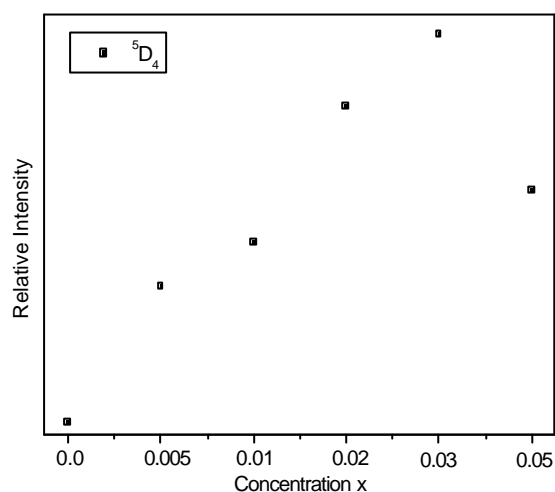


Fig. 4. VUV-PL emission intensity changes on the various Tb concentrations.

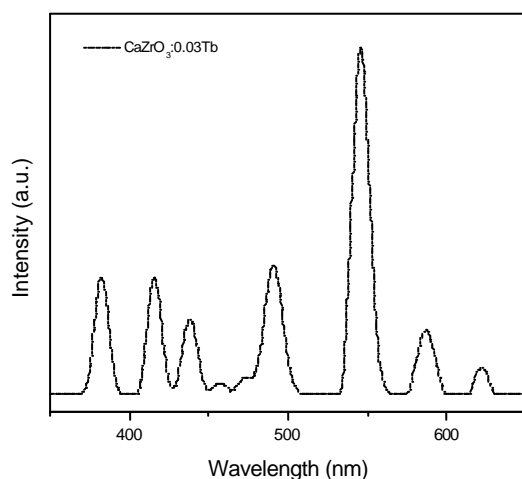


Fig. 5. CL emission spectrum of  $\text{CaZrO}_3:0.03\text{Tb}$ .

The CL emission spectrum of  $\text{CaZrO}_3:\text{Tb}$  phosphors under electron beam with 900 V acceleration voltage is showed in Fig. 5. The CL emission band similar band with PL emission as show in Fig. 3. The  $\text{CaZrO}_3:0.03\text{Tb}$  phosphor exhibits emission band centered at around 545 nm.

#### 4. Conclusions

Novel green phosphor with the chemical formula of  $\text{Ca}_{1-x}\text{ZrO}_3:\text{Tb}_x$  has been synthesized by the conventional method. The single phase of  $\text{CaZrO}_3:\text{Tb}$  phosphor was obtained by firing at 1200 in ambient air atmosphere. The optimum concentration of  $\text{Tb}^{3+}$  showing the maximum emission intensity in PL and CL spectra was 0.03 mole. This phosphor will be investigated for the application of general lighting and FEDs.

#### 5. Acknowledgement

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#### 6. References

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