



Photoluminescence of titanium-doped zinc spinel blue-emitting nanophosphors



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ABSTRACT

A blue-emitting phosphor of titanium-doped zinc spinel (ZnAl₂O₄:Ti; Ti=0–6.0 mol% in relation to Al) nanopowders was prepared by a simple sol–gel method. On annealing at 1000 °C, single-phase ZnAl₂O₄:Ti powders had primary particles of 25–30 nm in size and most Ti ions in the form of Ti⁴⁺. Under UV excitation at 280 nm, a strong and broad blue emission centered at 435 nm was observed. The sources of the excitation and emission were assigned to the charge-transfer excitation and recombination between O²⁻–Ti⁴⁺ and Ti³⁺–O⁻ ion pairs. Optimum brightness occurred at a doping of 2.0 mol% Ti. The decay lifetime of ZnAl₂O₄:2%Ti was calculated to be 3.0 ms for the blue emission with CIE coordinates of $x=0.168$ and $y=0.153$. The results suggest that ZnAl₂O₄:Ti is a promising candidate for application as a blue component phosphor for UV-converting white light-emitting diodes.

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1. Introduction

White-light-emitting diodes (W-LEDs) based on phosphor-conversion are considered as promising candidates for solid-state lighting. Most commercially available W-LEDs are generated by the combination of a blue LED chip and a yellow phosphor (YAG:Ce) [1]. However, such a W-LED has a low color rendering index due to the lack of red and green components. In order to improve the color rendering, the use of ultraviolet-light emitting diodes (UV-LEDs) with red–blue–green (R/G/B) phosphors has attracted significant attention in recent years [2–6]. The development of new phosphors with high quantum efficiencies for UV-LEDs applications is therefore highly desirable, and these should be designed to have a high absorption in the range of 250–410 nm [3,7–10].

Zinc spinel (also called zinc aluminate spinel, ZnAl₂O₄) has been widely used as a catalyst and catalyst support due to its various advantageous properties, such as high thermal and chemical stability, high mechanical resistance, low acidity and hydrophobicity [11]. ZnAl₂O₄ has a cubic, normal spinel crystal structure with the space group of Fd3m. Of the contributing cations, Zn²⁺ is tetrahedrally coordinated and Al³⁺ occupies octahedral sites. ZnAl₂O₄ is a wide bandgap semiconductor ($E_g \approx 3.8$ eV), and is transparent to light of wavelengths above 320 nm, which makes it suitable for optoelectronic devices operating in the UV region

[12,13]. The luminescent properties of ZnAl₂O₄ doped with activators, such as Eu, Tm, Tb, Mn, or Co, have also been reported [14–18].

Titanium-doped sapphire (Al₂O₃:Ti) is a well-known laser material that shows near-infrared and blue emission bands. The former is due to *d*–*d* transitions of trivalent Ti³⁺ ions, the latter to a charge-transfer transition of tetravalent Ti⁴⁺ ions or transitions associated with F⁺ centers [19,20]. UV-excited blue emission has also been observed in titanium-doped MgAl₂O₄ spinel [21]. MgAl₂O₄:Ti shows a broad emission band peaking at around 490 nm under excitation at 280 nm. The blue emission is assigned to the charge-transfer transition of Ti⁴⁺ ions in octahedral sites substituting for Al³⁺ [21,22]. As a result, the luminescence of Ti-doped phosphor is strongly affected by the charge valence of the dopants. The spectroscopic properties of Ti-doped MgAl₂O₄ have been extensively investigated [21–23]. It is also confirmed by electron spin resonance measurement that Ti⁴⁺ ions dominantly occupy the octahedral cation site in spinel-type solid solution [21]. Thus far, there is only one publication on the luminescence of Ti-doped ZnAl₂O₄ powder prepared by the sol–gel process [24], with the samples heated at 800 °C consisting of ZnAl₂O₄ and ZnO phases, and exhibiting emission in the range of 350–800 nm with a peak around 400 nm under excitation at 308 nm. We recently prepared ZnAl₂O₄:Mn²⁺ phosphors by a simple sol–gel method developed in our lab. Under excitation by a 458 nm blue-light, ZnAl₂O₄:Mn²⁺ powders exhibit a strong green emission band peaking at 512 nm corresponding to ⁴T₁(⁴G)–⁶A₁(⁶S) transition of tetrahedral Mn²⁺ ions [25,26].

In the present work, we report blue emission from single-phase ZnAl₂O₄:Ti powder phosphors prepared by a simple sol–gel method. Their phase structure, microstructure, optical absorption

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and photoluminescence are investigated. The valence state of Ti ions is analyzed using X-ray photoelectron spectroscopy (XPS). The powder phosphors exhibit a strong blue emission with a peak at 435 nm under 280 nm irradiation, showing characteristics similar to those of $\text{MgAl}_2\text{O}_4:\text{Ti}$ [21,23]. The sources of the excitation and emission are explained, and the effects of dopant content and annealing temperature are also investigated.

2. Experimental

2.1. Synthesis

$\text{ZnAl}_2\text{O}_4:\text{Ti}$ powders were prepared by a sol-gel method using zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$], aluminum isopropoxide [$\text{Al}(\text{O}-i\text{C}_3\text{H}_7)_3$], and titanium isopropoxide [$\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$] as the starting materials. Stoichiometric amounts of zinc nitrate and aluminum isopropoxide were first dissolved in methanol. The mixed solution was stirred and refluxed at room temperature for 2 h, and then the desired amount of titanium isopropoxide and a small amount of deionized water (1.0 M ratio to Zn) were added for doping and hydrolysis. The transparent sols thus obtained were then kept at ambient temperature until gelation. The powder samples were prepared by drying the transparent gels at 150 °C in an oven and then grinding them, with the resulting xerogel powders then being annealed at various temperatures from 250 to 1000 °C for 2 h in air with a heating rate of 10 °C min^{-1} . The doping levels (x) of Ti were varied with $x=0$ –6.0 mol % of the Al concentration to investigate the effects of doping on the structure and luminescence.

2.2. Characterization

The crystalline phase of the processed samples was examined by powder X-ray diffraction (XRD; Rigaku D/MAX-III) with Ni-filtered $\text{CuK}\alpha$ radiation. The morphology of the powder was observed by field-emission scanning electron microscopy (FE-SEM; Hitachi S4800-I). Optical absorption spectra were recorded from 200 nm to 800 nm at room temperature using a Hitachi U-3010 UV-vis spectrophotometer. The oxidation states of Ti ions were analyzed using X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI 5000 Versa Probe) equipped with an Al $\text{K}\alpha$ X-ray source. The C 1s line at 285.0 eV was used as a reference for binding energy calibration. Photoluminescence excitation (PLE) and emission (PL) spectra were recorded at room temperature using a fluorescence spectrophotometer (F-7000, Hitachi), with a 150 W xenon lamp as the excitation source. Decay time measurements were performed via time-resolved spectroscopy with the same equipment. All samples were measured in powder form.

3. Results and discussion

3.1. Crystalline phase and microstructure observation

Typical XRD patterns of $\text{ZnAl}_2\text{O}_4:\text{Ti}$ xerogel powders annealed at different temperatures are shown in Fig. 1. The dried powders remained amorphous up to annealing at 250 °C, and some weak diffraction peaks appeared after heating at 300 °C. The peaks and intensity increased as the annealing temperature rose from 300 °C to 1000 °C. All the reflections can be well indexed to a cubic ZnAl_2O_4 structure (JCPDS: 82-1043), with no other phase being detected, revealing that the doped Ti ions are incorporated into the host lattice and a single-phase solid solution is expected. Considering that the ionic radius of an octahedral Ti^{4+} ($r=0.605$ Å) is closer to the six-coordinated Al^{3+} ($r=0.535$ Å) than those of octahedral Ti^{3+} ($r=0.67$ Å) and Ti^{2+} ($r=0.86$ Å),

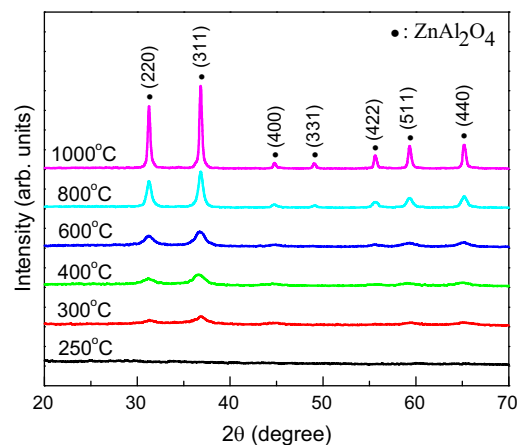


Fig. 1. XRD patterns of $\text{ZnAl}_2\text{O}_4:2\% \text{Ti}$ xerogel powders annealed at various temperatures.

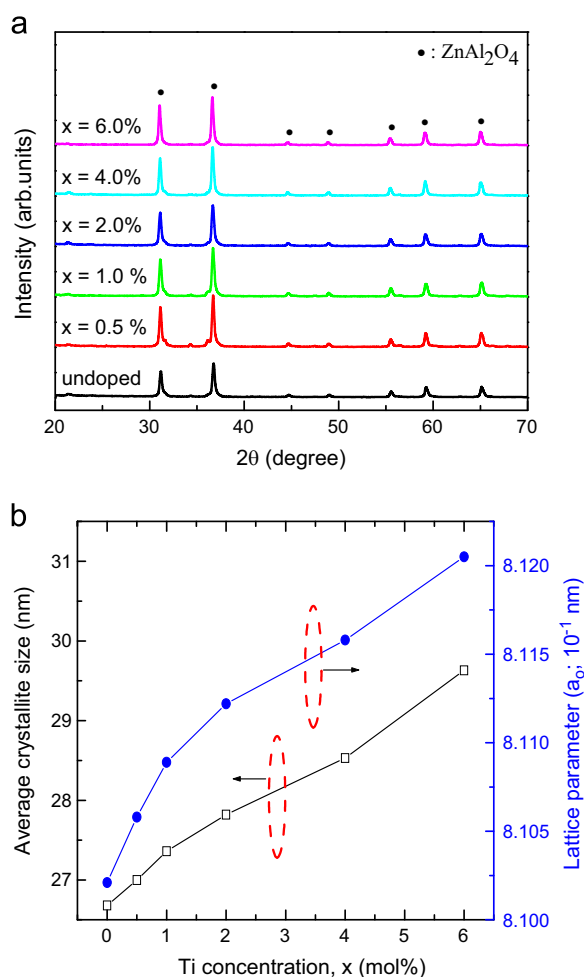


Fig. 2. (a) XRD patterns of $\text{ZnAl}_2\text{O}_4:\text{Ti}$ powders with different Ti contents (x). (b) Variations in crystallite size and lattice parameter with Ti concentration for $\text{ZnAl}_2\text{O}_4:\text{Ti}$ phosphor powders. All samples were annealed at 1000 °C.

we therefore speculate that Ti^{4+} ions are located on the octahedral sites, replacing Al^{3+} ion in the ZnAl_2O_4 host lattice.

Fig. 2(a) illustrates the XRD patterns of $\text{ZnAl}_2\text{O}_4:\text{Ti}$ phosphors with various dopant concentrations after annealing at 1000 °C. The Ti doping level did not cause any significant changes in the structure or crystallinity of the samples. It is noted that the

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