

V-doped MgAl₆O₁₀: novel luminescence substrate for phosphor-free UV-white LEDs

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V-doped MgAl₆O₁₀ is grown by the conventional Czochralski method. The crystal structure and the cell parameters are analyzed through X-ray diffraction experiments. The absorption and emission spectra are investigated. Under pumping at 324 nm, the emission spectra of V-doped MgAl₆O₁₀ obtain two emission peaks at the wavelengths of 471 and 570 nm. Two emission bands of the spectra combine to produce a spectrum that is perceived as white by the naked eye. Therefore, V-doped MgAl₆O₁₀ single crystal can be applied as substrate for phosphor-free ultraviolet (UV)-white light-emitting diodes (LEDs).

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Light-emitting diodes (LEDs) have been intensively investigated because of their superior features such as high efficiency, compactness, long operational lifetime, and environmental friendliness^[1,2]. The search for proper substrates for GaN epitaxy is a critical issue which has limited the development of LEDs^[3]. Sapphire (Al₂O₃) has been the most widely used substrate material for GaN heteroepitaxy in the absence of commercially available and cost-effective GaN substrates. According to Ref. [4], sapphire offers excellent crystal quality, surface finish, and stability under the severe metal-organic chemical vapor deposition (MOCVD) growth conditions used for GaN. However, its high thermal and lattice mismatches with GaN ($3 \times 10^{-6} \text{ K}^{-1}$ and 13.9%, respectively) induce deformation of the wafer during growth and subsequent cooling, resulting in high density defects in the epitaxial layers. Stoichiometric spinel (MgAl₂O₄) has been investigated as a promising alternative substrate. MgAl₂O₄ offers both better thermal and lattice matches with GaN ($2 \times 10^{-6} \text{ K}^{-1}$ and 10.4%, respectively)^[4-7]. However, stoichiometric spinel has not been accepted as mainstream substrate for GaN epitaxy because of its inherent brittleness. Instead, an Al-rich spinel (MgO·3Al₂O₃) has been proposed as substrate for GaN epitaxy. Al-rich spinel is less brittle and chemically close to sapphire, thus it can easily be sliced and polished into large diameter wafers^[8]. Reports have shown that MgAl₆O₁₀ demonstrate better performance in terms of brightness and spectral purity under direct current (DC) operation below 0.3 kA/cm²^[4].

The conventional white LEDs, produced by combining blue or ultraviolet (UV) LED chips with phosphor, emit white light. ZnSe has been initially reported as phosphor-free substrate for white LEDs. ZnSe can convert the bluish light emission by the active layer of a P-N junction diode into an intense broadband yellow emission centered at 585 nm. This means that two emission bands combine to produce a spectrum which is perceived

as white by the naked eye. However, ZnSe has not been commercially used because of its short lifetime induced by generation and migration of microscopic point defects during device operation^[9]. At present, because of significant worldwide efforts on GaN, ternary InGaN, Al-GaN, and quaternary AlInGaN alloys, the emission range of LEDs ranges from 210 to 550 nm^[10-13]. It has been reported that V-doped MgAl₂O₄ produces white emission spectra^[14]. This leads to the topic of optical property of V-doped MgAl₆O₁₀. Thus, in this letter, the V-doped MgAl₆O₁₀ is grown by the Czochralski method. The crystal structure and the optical property of as-grown V-doped MgAl₆O₁₀ are analyzed.

The doping concentration of V₂O₅ in MgAl₆O₁₀ was 0.5 wt.-%, the reagents V₂O₅ (99.99%), Al₂O₃ (99.999%), and MgO (99.99%), were properly mixed together with alcohol in a mortar. After thorough mixing and drying at room temperature, the powder sample was calcined at 1200 °C for 24 h in open air, and subsequently cooled down in the furnace to room temperature. The polycrystalline V-doped MgAl₆O₁₀ formed by solid-state reaction was charged in an iridium crucible in an intermediate-frequency furnace. A rectangular <111> oriented spinel as seed crystal, was introduced at an appropriate temperature higher than the melting point (1995 °C) of MgAl₆O₁₀. The pulling rate is 1 mm/h and the rotation rate is 4 rpm. The temperature was controlled by Eurotherm 818 controller/programmer with a precision of ± 0.1 °C under an atmosphere of pure N₂. The growth period was allowed to continue for 160 h followed by a cooling down period of 20 h.

Sample wafers for investigation were cut from the as-grown bulk crystal and polished to spectral quality. The X-ray diffraction (XRD) pattern of polished wafer was obtained by an X-ray diffractometer (Ultima IV diffractometer, Rigaku, Japan), using Cu K α radiation (40 kV and 100 mA) at a scanning width of 0.02° within $2\theta = 10^\circ - 90^\circ$. The absorption spectra of the V-

doped $\text{MgAl}_6\text{O}_{10}$ were recorded by a spectrophotometer (Lambda 900, Perkin-Elmer, USA) at room temperature. The fluorescence spectrum of samples was obtained by a spectrofluorometer (FP-6500/6600, JASCO, Japan).

Figure 1 shows the polished slices cut from the as-grown bulk crystal which is free from cracks, inclusions, and scattering centers. The wafers are transparent and light brown in color. Figure 2 presents the X-ray diffraction pattern of the polished wafers, which illustrates that the polished plane is perpendicular $\langle 111 \rangle$ and without any parasitic phase. Except for (111), (222), (333), and (444), the other diffraction peaks are silent, because only one face of the wafer sample was scanned in the XRD experiment. Only the planes which are perpendicular $\langle 111 \rangle$ can diffract. The space group of $\text{MgAl}_6\text{O}_{10}$ is $Fd\bar{3}m$ and the XRD pattern reveals that the cell parameter is $a = 0.7991$ nm.

The room temperature absorption spectrum of V-doped $\text{MgAl}_6\text{O}_{10}$ and pure $\text{MgAl}_6\text{O}_{10}$ between 200 to 800 nm is presented in Fig. 3. The absorption coefficient of the pure $\text{MgAl}_6\text{O}_{10}$ is at a relatively low level after a sharp decrease at the wavelength around 200 nm. The strongest absorption peak of $\text{MgAl}_6\text{O}_{10}:\text{V}$ is around 274 nm (4.52 eV), which is attributed to charge transfer excitation from O^{2-} (2p)-orbital to the hybridized (3d)-orbital near the conduction band edge. The hybridized (3d)-orbital is composed of 3d-orbital of V^{4+} , $\text{Mg}^{2+}(3s)$ and $\text{Al}^{3+}(3s)-(3p)$ orbital^[8]. A weak absorption shoulder around 400 nm and an absorption peak around 580 nm exist, the reason of which is unclear. It is possible that these have been caused by Mg deficiency and the Mg-Al antisite defect. The absorption edge of $\text{MgAl}_6\text{O}_{10}:\text{V}$ shows a red shift to 324 nm induced by V doping which is not observed in pure

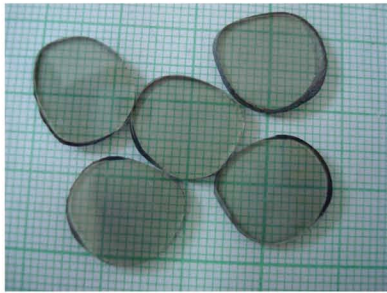


Fig. 1. Polished V-doped $\text{MgAl}_6\text{O}_{10}$ crystal wafers.

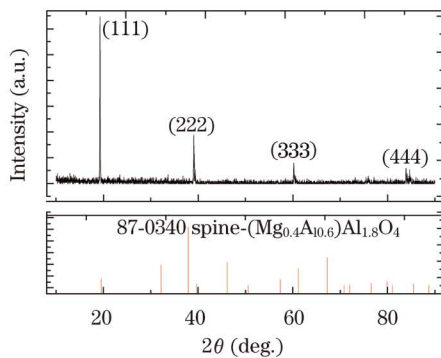


Fig. 2. X-ray diffraction pattern of polished $\text{MgAl}_6\text{O}_{10}$ crystal perpendicular $\langle 111 \rangle$.

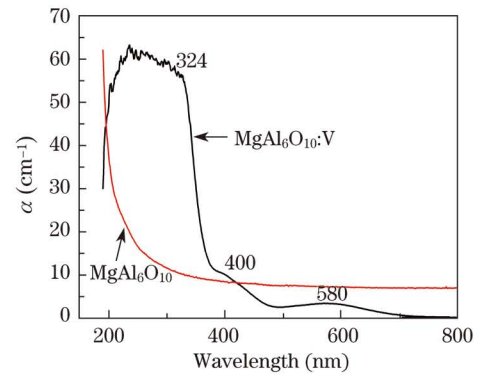


Fig. 3. Room temperature absorption spectra in the 200–800 nm spectral range of polished V-doped $\text{MgAl}_6\text{O}_{10}$ wafer and pure $\text{MgAl}_6\text{O}_{10}$ crystal.

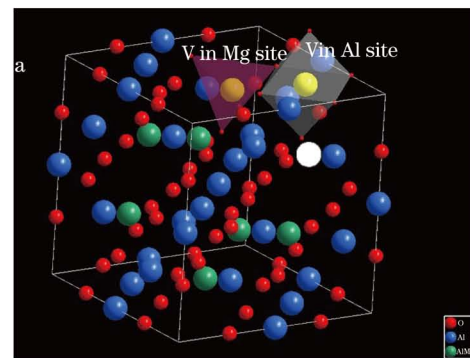


Fig. 4. (Color online) Structure of the $\text{MgAl}_6\text{O}_{10}$ with the V ions in Mg and Al sites.

$\text{MgAl}_6\text{O}_{10}$.

Figure 4 shows the crystal structure of $\text{MgAl}_6\text{O}_{10}$. Mg^{2+} and several Al^{3+} ions at the center with a tetrahedral coordination of O^{2-} ions with T_d symmetry (A site). The other Al^{3+} ion is located at the position of D_{3d} symmetry (B site). Several antisite deficiencies of Mg^{2+} ions and Al^{3+} ions are likewise observed. Severe Mg deficiency occurred in the crystal because MgO can easily evaporate at high temperature. The V ions in the form of V^{5+} occupy the B site dominantly and provide the 3d electron to the Mg deficiency as charge compensation^[15]. In Fig. 4, the yellow atom surrounded by the gray octahedron is the effect of stimulation of V^{5+} ions in B site. The other yellow atom with the purple tetrahedron is the V^{4+} ion which substitutes the Mg in the A site. The white hole is the Mg vacancy. Figure 5 reveals that the emission spectra of V-doped $\text{MgAl}_6\text{O}_{10}$ and pure $\text{MgAl}_6\text{O}_{10}$ excite at the absorption edge of 324 nm. Two broadband blue and yellow emission peaks are observed respectively at 471 and 570 nm. These two emission bands combine to obtain a spectrum which appears white to the naked eye. This property of $\text{MgAl}_6\text{O}_{10}:\text{V}$ facilitates its application as a promising substrate of phosphor-free UV-white LEDs. According to Ref. [15], the bluish violet emission peak at 471 nm can be attributed to the radioactive decay of V^{4+} at B-site (D_{3d}) 3d electron into the hole state in valence band where the Stock shift is from 324 to 471 nm. A bluish violet emission peak with the wavelength at 420 nm was observed in pure $\text{MgAl}_6\text{O}_{10}$, which may

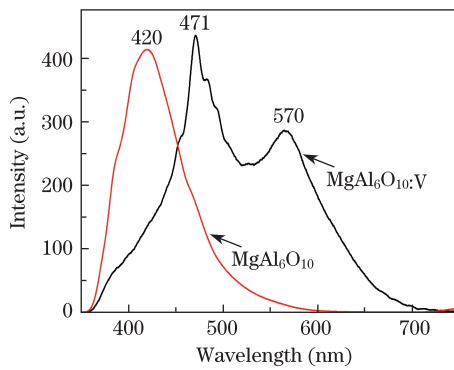


Fig. 5. Emission spectra under pumping at 324 nm of V-doped $\text{MgAl}_6\text{O}_{10}$ and pure $\text{MgAl}_6\text{O}_{10}$ crystal at room temperature.

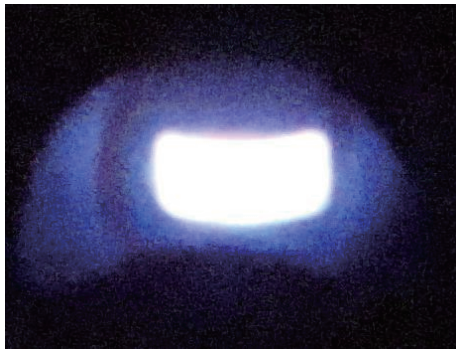


Fig. 6. White emission of the polished V-doped $\text{MgAl}_6\text{O}_{10}$ excited at 324 nm.

be due to the defect of Mg^{2+} created by the evaporation of Mg ions. The yellow peak at 570 nm of V-doped $\text{MgAl}_6\text{O}_{10}$, is lower in intensity but broader in spectral range compared with the peak at 471 nm. This can be ascribed to the transition from the (3d)-orbital of V^{5+} ion at B site.

The white emission of the polished V-doped $\text{MgAl}_6\text{O}_{10}$ wafer excited at 324 nm is shown in Fig. 6. V ions in the substrate produce the white central rectangular area. The CIE chromaticity coordinate (0.29, 0.34) is close to the standard white CIE chromaticity coordinate (0.33, 0.33). Compared with typical CIE chromaticity coordinates of YAG:Ce (0.31, 0.38), the color temperature of V-doped $\text{MgAl}_6\text{O}_{10}$ is lower. Therefore, the V-doped $\text{MgAl}_6\text{O}_{10}$ is a promising luminescent substrate for phosphor-free UV-white LEDs.

In conclusion, V-doped $\text{MgAl}_6\text{O}_{10}$ is grown using the conventional Czochralski method. The V-doped $\text{MgAl}_6\text{O}_{10}$ crystal is light brown in color and free from cracks, inclusions, and scattering centers. The XRD pattern of the wafer shows that the crystal is monocrystalline with a cell parameter of $a = 0.7991$ nm. The

strong absorption band of V-doped $\text{MgAl}_6\text{O}_{10}$ is located around the 250- to 320-nm wavelength, and the absorption coefficient is approximately 60 cm^{-1} at 250 nm. The absorption edge is approximately 324 nm. Under pumping at 324 nm, the emission spectra of V-doped $\text{MgAl}_6\text{O}_{10}$ obtained two strong peaks at the blue band of 471 nm and yellow band of 570 nm. The CIE chromaticity coordinate of V-doped $\text{MgAl}_6\text{O}_{10}$ (0.29, 0.34) closely adheres to the standard CIE white chromaticity coordinate (0.33, 0.33). Therefore, V-doped $\text{MgAl}_6\text{O}_{10}$ is a promising phosphor-free substrate for UV-white LEDs.

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