Photo- and low-voltage cathodoluminescence in lithium zinc gallate blue and green thin-film phosphors

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The photo- and cathodoluminescence properties of epitaxial lithium-doped zinc gallate thin-film phosphors grown on (100) MgO single crystal substrates using pulsed laser ablation were investigated. The addition of lithium to both undoped and Mn-doped $ZnGa_2O_4$ films significantly enhanced the photo- and low-voltage cathodoluminescent intensity. Cathodoluminescent efficiencies for as-deposited undoped and Mn-doped lithium zinc gallate films as high as 0.21 lm/W and 0.29 lm/W, respectively, were achieved for 1 kV and 2.26 $\mu A/cm^2$. Based on these results, lithium-doped zinc gallate thin-film phosphors appear to be attractive for applications in low-voltage field emission display devices. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1448863]

I. INTRODUCTION

The development of highly efficient phosphor materials is one of the more challenging areas in the application of field emission displays (FEDs). Within these activities, considerable effort has focused on enhancing the low-voltage cathodoluminescence (CL) efficiency in thin-film phosphors, both for oxide and sulfide luminescent materials. For FED devices, thin-film phosphors offer several advantages as compared to powder-based structures, including higher pixel resolution, enhanced lifetime at high current density, excellent mechanical and thermal stability, and available thin-film processing methods. Unfortunately, the inferior luminous efficiency and brightness presently realized in films as compared to powders limit their applicability for display applications. Efforts to alleviate these limitations and to understand the factors that determine efficiency for thin-film phosphors have focused on increasing light scattering centers using surface modification, reducing defect density by post-annealing and/or epitaxy at high temperatures, and searching for superior phosphor materials.[1–3] Since CL is a complex photonic process involving the creation, relaxation, and recombination of excited electrons, modification of phosphor electronic properties via cation doping also provides an opportunity for improved performance.

One thin-film oxide system of interest is the gallates. Gallate-related phosphor materials having a spinel crystal structure include $ZnGa_2O_4$, $MgGa_2O_4$, $LiGa_5O_8$ and their mixed solid solutions. These compounds exhibit promising photoluminescence (PL) and CL properties, and have been suggested as possible alternatives to sulfur-based CL phosphors, whose properties degrade under high-energy electron bombardment due to sulfur loss, thus shortening device lifetime. Progress in understanding and exploiting the low-voltage CL characteristics for $ZnGa_2O_4$ and mixtures of $Li_2O/LiGa_5O_8$ and $ZnGa_2O_4$ powders has been reported by several researchers. Itoh *et al.*[4] reported CL efficiencies of 0.15 lm/W for the CIE color coordinates $x=0.175$ and $y=0.186$ measured at an anode voltage of 400 V and an anode current density of 75 mA/cm^2 for $ZnGa_2O_4$ powders. An efficiency of 0.198 lm/W ($x=0.175$ and $y=0.1608$) at 5 kV and 2.54 μA has been reported for $ZnGa_2O_4$ by Yang *et al.*[5] Suh *et al.*[6] has observed promising low-voltage CL characteristics for the mixture of $LiGa_5O_8$ and $ZnGa_2O_4$ powders. Dmitrienko *et al.*[7] also obtained an efficiency of 0.2 lm/W ($x=0.20$ and $y=0.21$) at an anode voltage of 500 V in $(Li_{0.25}Ga_{0.25})Zn_{0.5}Ga_2O_4$ powder.

II. RESULTS AND DISCUSSION

In this article, we report on the luminescence properties of epitaxial lithium zinc gallate thin-film phosphors. CL efficiencies, comparable to that observed in powders, are observed for Li-doped blue ($ZnGa_2O_4$) and green ($Mn–ZnGa_2O_4$) epitaxial films grown using pulsed laser ablation. For blue emission, we investigated the compositions $ZnGa_2O_4$(ZGO), $Li_{0.05}Zn_{0.95}Ga_2O_4$(5LZGO), and $Li_{0.25}Zn_{0.5}Ga_{2.25}O_4$(25LZGO). For green phosphors, Mn-doped $ZnGa_2O_4$(ZGO:Mn), $Li_{0.05}Zn_{0.95}Ga_2O_4$(5LZGO:Mn), and $Li_{0.25}Zn_{0.5}Ga_{2.25}O_4$(25LZGO:Mn) films were deposited. These Li/Zn ratios represent the compositions in the ablation

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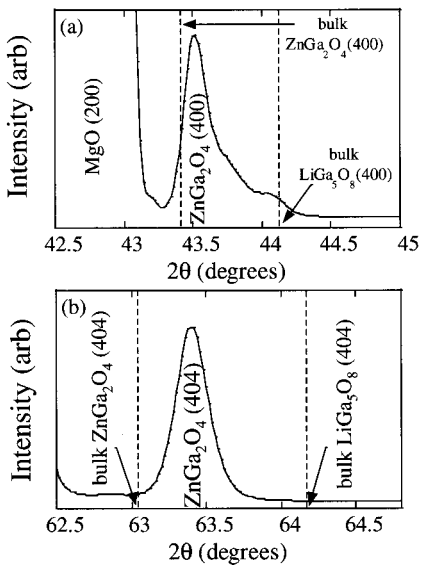

FIG. 1. High-resolution x-ray θ–2θ scans showing the (a) (400) $ZnGa_2O_4$ and (b) (404) $ZnGa_2O_4$ peaks for a 25LZGO film.

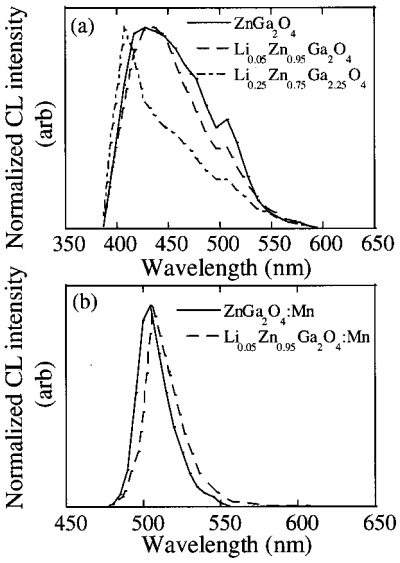

FIG. 2. CL emission spectra of (a) blue lithium zinc gallate without Mn and (b) green lithium zinc gallate with Mn.

target material. Polycrystalline 1 in. diameter ablation targets were prepared by mixing Li_2O [Alfa, 99.99%], ZnO[Alfa, 99.999%], Ga_2O_3[Alfa, 99.9995%], and MnO_2 [Alfa, 99.999%] powders, followed by sintering in air at 1250 °C for 24 h. The targets were encapsulated in excess powder during sintering to prevent Zn and Li loss. To compensate Zn loss in the films during film growth, all films were deposited using mosaic targets, which are composed of a phosphor target ZnO mosaic with an area ratio of 50/50.[8] Previous work on $ZnGa_2O_4$ film growth has shown that this composite target configuration is effective at yielding near-stoichiometric films under conditions used. No attempt was made to compensate for Li loss; thus we anticipate that the Li content in the films may be somewhat less than that in the target. Quantitative determination of Zn/Ga and Zn/Li ratios is complicated by the near-identical atomic mass of Zn and Ga, and by the fact that Li is a light element. Efforts are currently underway to circumvent this challenge to provide accurate determination of cation stoichiometry. Epitaxial films that were approximately 2 μm-thick were grown using an excimer KrF laser with a wavelength of 248 nm. The laser fluence was approximately 3.5 J/cm^2. Blue light emitting lithium zinc gallate films were grown at 730 °C under oxygen partial pressure $[P(O_2)]$ of 100 mTorr, while Mn-doped green phosphor films were deposited at 750 °C under $P(O_2)$ of 40 mTorr. These pressures were optimized for the respective compositions. Crystallinity was investigated using four-circle x-ray diffraction (XRD) with Cu$K\alpha$ radiation (0.15406 nm wavelength). The PL spectra were measured at room temperature using a broad band incoherent UV light excitation source with a dominant excitation wavelength of 254 nm. Low-voltage CL was measured with a Plasma Scan PSS-2 spectrometer; CL intensity measurements were taken with an International Light 1700 photometer equipped with a photonic filter.

Figure 1 shows the x-ray diffraction data for a 25LZGO:Mn film. In this study, all of the films exhibited a $ZnGa_2O_4$ (400) diffraction peak in the θ–2θ scan. Occasionally a low intensity Ga_2O_3 peak was also evident. In the case of films deposited from a Li_2O-doped $ZnGa_2O_4$ target, one should also consider the possible formation of $LiGa_5O_8$ as a secondary phase. Unfortunately, it is somewhat difficult to observe the separation of diffraction peaks between $ZnGa_2O_4$ and $LiGa_5O_8$ because of their similar lattice constants $[d_{400} = 0.2083$ nm (Ref. 9) for $ZnGa_2O_4$ and $d_{400} = 0.20509$ nm (Ref. 10) for $LiGa_5O_8]$. This is further complicated by the fact that the in-plane lattice spacing for films will be different from that observed in bulk due to epitaxial strain in the film. The high-resolution θ–2θ scan shown in Fig. 1(a), taken along the surface normal with a Ge analyzer, shows a small peak at the position for bulk $LiGa_5O_8$ (400). However, a corresponding peak did not appear in the high-resolution scan in the (404) region shown in Fig. 1(b), which was obtained by four-circle XRD. This suggests that the peak is not associated with $LiGa_5O_8$ (400). Moreover, this side peak was sometimes observed in films that contained no lithium. In-plane ϕ-scans confirm that the films were epitaxial with a single in-plane orientation.

Since luminescence efficiency is dependent on surface roughness via internal reflection of light, we also investigated the surface microstructure in the films using atomic force microscopy. Undoped $ZnGa_2O_4$ films show a smooth surface with root-mean-square (rms) roughness of about 2.3 nm, while irregular-shaped surface features were observed for the lithium-doped films. The rms roughness values for the 5LZGO and 25LZGO films were approximately 2.9 nm and 4.9 nm, respectively. Mn-doped films exhibited higher values in rms roughness as compared to films grown without Mn. The values were 5.6 nm, 3.8 nm, and 8.0 nm for ZGO:Mn, 5LZGO:Mn, and 25LZGO:Mn films, respectively. Despite these variations, a systematic relationship between the specific surface microstructural features and lithium content could not be observed.

Figure 2 shows the normalized CL emission spectra for

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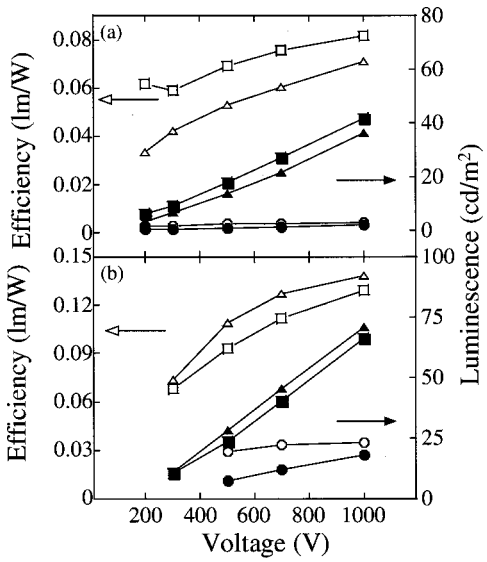

FIG. 3. CL efficiency (open symbols) and brightness (filled symbols) of (a) ZGO (circle), 5LZGO (triangle), and 25LZGO (square) blue lithium gallate without Mn, as well as (b) ZGO:Mn (circle), 5LZGO:Mn (square), and 25LZGO:Mn (triangle) green lithium zinc gallate with Mn. Anode current density was fixed at 22 μA/cm^2.

films deposited from ZGO, 5LZGO, and 25LZGO targets. These blue phosphor films exhibit significant differences in intensity and maximum peaking wavelength of the CL spectra, with a shift to lower wavelengths as Li content is increased. Peak wavelengths in the spectra for ZGO, 5LZGO, and 25 LZGO films were measured at 427 nm, 430 nm, and 406 nm, respectively. With the blue luminescence due to a self-activated center in the gallate lattice,[5,11] the Li dopant appears to modify the electronic environment at the defect, resulting in a spectral shift. Note that the weak shoulder at about 506 nm may originate from contamination of Mn, as the Mn-doped films were deposited in the same chamber. In contrast, the PL and CL emission spectra for Mn-doped films show no discernable shift with Li doping, with peak wavelengths located from 507 to 509 nm. This corresponds to the $^4T^1 \rightarrow {}^6A_1$ transition of the 3*d* electrons in the Mn^{2+} ion which occupies the four-fold coordinated Zn position in the host lattice.[12]

Low-voltage CL efficiency (η) and luminance (L) as a function of anode voltage for undoped and Mn-doped lithium zinc gallate films are shown in Fig. 3. Measurements were made at a fixed anode current density of 22 μA/cm^2. Without lithium, CL efficiency in $ZnGa_2O_4$ films is relatively low, measured to be approximately 0.01 and 0.03 lm/W for the undoped and Mn-doped $ZnGa_2O_4$ films, respectively. Appreciable enhancement in the efficiency and brightness is not observed upon increasing anode voltage up to 1 kV. In contrast, both blue (no Mn) and green (Mn-doped) zinc gallate films show remarkable improvement in CL efficiency and brightness with the addition of lithium. The efficiencies of undoped and Mn-doped lithium zinc gallate films at 1 kV and 22 μA/cm^2 were measured to be 0.08 lm/W and 0.138 lm/W, respectively. These values are about five-to-eight times higher than the values measured for films without lithium. The highest efficiencies measured at 1 kV and 2.26 μA/cm^2 for the blue and green lithium zinc gallate films were 0.21 lm/W and 0.29 lm/W, respectively, as shown in Table I. In addition to CL, lithium zinc gallate films also show a significant enhancement in PL emission spectra under UV excitations as summarized in Table I. These results clearly show that the addition of lithium ions in zinc gallate phosphor films enhances CL characteristics as well as PL intensities.

As described, a small increase in film surface roughness is observed with the addition of lithium. However, this increase in surface scattering due to roughness appears to be insufficient to explain the enhanced luminescence. If lithium is incorporated in the film via cation substitution or as an

TABLE I. Selected PL and CL data of zinc gallate and lithium zinc gallate films. CL efficiency and luminance was measured at fixed anode voltage of 1 kV.

	PL emission		CL emission			
Films	Wavelength (nm)	Intensity (arb.)	Wavelength (nm)	Current (μA/cm^2)	Efficiency (lm/W)	Luminance (cd/m^2)
				2.26	0.014	0.7
$ZnGa_2O_4$	481	1129	427	11.32	0.009	2.3
				56.61	0.005	6.6
				2.26	0.213	10.9
	455	12510		4.53	0.284	29.1
$L_{0.05}Zn_{0.95}Ga_2O_4$	484	11287	430	11.32	0.147	37.7
				56.61	0.069	89.0
				2.26	0.150	7.7
	458	34468		11.32	0.065	16.7
$Li_{0.25}Zn_{0.50}Ga_{2.25}O_4$	483	34893	406	56.61	0.050	63.5
				2.26	0.077	3.9
$ZnGa_2O_4$:Mn	507	9095	507	11.32	0.050	12.7
				56.61	0.022	27.8
				2.26	0.251	12.9
$Li_{0.05}Zn_{0.95}Ga_2O_4$:Mn	509	27606	507	11.32	0.172	44.1
				56.61	0.082	105.9
				2.26	0.290	14.9
$Li_{0.25}Zn_{0.50}Ga_{2.25}O_4$:Mn	508	29361	507	11.32	0.196	50.3
				56.61	0.089	114.1

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interstitial in the spinel crystal structure, it should modify the electrical properties of the zinc gallate films. From a crystallographic point of view, lithium ions, having small ionization potential and suitable ionic size, could occupy tetrahedral vacancy sites as only 1/8 of the tetrahedral sites are filled by cations.[13] Ionization of Li would provide electrons for transport, and consequently decrease the resistivity of the films. Increased conductivity should enhance the CL efficiency and brightness, as this diminishes charge accumulation on or near the phosphor film surface. Charging effects hinder the incident primary electron beam from penetration into the phosphor surface, resulting in a reduced electron–phosphor interaction volume. It is also possible that the lithium ions substitute for zinc on tetrahedral sites due to their similar ionic radii ($R_{Li^+}=0.059$ nm, and $R_{Zn^{2+}}=0.060$ nm). In this case, lithium may serve as an acceptor in zinc gallate. The electrical properties in the films are currently under investigation.

While these arguments can explain the enhancement in CL, they do not address the observed enhancement in PL intensity. However, previous work has suggested that the transfer of excitation energy from host material to activators can be made more efficient by the addition of Li^+ ions to phosphor host materials. Hatayama *et al.*[14] observed that doping Li^+ in ZnS:Tm significantly enhanced PL intensity. This was attributed to the Li contributing to efficient energy transfer from the host to Tm^{3+} ions, as well as acting as a charge compensator. Lopez *et al.*[15] also observed enhanced intensity of blue emission in $Y_3Al_5O_{12}$:Tm^{3+} doped with Li. Lithium appears to act in a similar manner in Mn-doped lithium zinc gallate.

III. CONCLUSION

In summary, blue and green light emitting lithium zinc gallate thin-film phosphors were grown on MgO (100) substrates using pulsed laser deposition. The addition of lithium considerably improved the PL and low-voltage CL characteristics. The peaking wavelengths in the PL and CL emission bands exhibited a blueshift for lithium zinc gallate, whereas Mn-doped film showed peak locations independent of Li content. The highest efficiencies obtained for blue and green lithium zinc gallate without postannealing were 0.21 lm/W and 0.29 lm/W, respectively, at 1 kV and 2.26 μA/cm^2. Based on these results, lithium zinc gallate films appear to be an attractive phosphor material for low-voltage CL display devices.

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