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Novel photoluminescent properties of $LiGaO_2$ nanoflakes

Yu-Jen Hsiao[a], Te-Hua Fang[b,*], Liang-Wen Ji[c], Zhe-Wei Chiu[c]

[a] National Nano Device Laboratories, Tainan 741, Taiwan
[b] Department of Mechanical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan
[c] Institute of Electro-Optical and Materials Science, National Formosa University, Yunlin 632, Taiwan

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ABSTRACT

The luminescence properties of $LiGaO_2$ microflakes synthesized using the sol–gel process are investigated. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and photoluminescence (PL) and absorption spectra. The PL spectra excited at 325 nm have a broad and strong emission band with a peak at 383 nm, which corresponds to the self-activated luminescence of the tetrahedral gallium group. The optical absorption spectra of the sample annealed at 600 °C exhibited a band-gap energy of 3.38 eV.

1. Introduction

The elastic, piezoelectric, dielectric, and optical properties of $LiGaO_2$ have been investigated [1–3]. Recently, there has been renewed interest in tetrahedrally bonded oxides of $LiGaO_2$, which are considered promising nearly lattice-matched substrates for the heteroepitaxial growth of GaN [4,5] and materials in combination with ZnO as wide-gap semiconductor [6,7].

The orthorhombic structure [8] of the compound makes it well suited as a host material for the investigation of the electronic properties of transition metal ions, which have been used as activator ions for generating tunable lasers in a wide spectral domain [9]. $LiGaO_2$ can potentially serve as a nonlinear optical material for the up-conversion of the blue light emitted by devices into UV frequencies for developing compact laser sources [10].

In the present study, a sol–gel synthetic route for the preparation of single-phase $LiGaO_2$ oxides with an orthorhombic structure is investigated. The major advantage of sol–gel processing is its low operation temperature. Chemically synthesized ceramic powders often have better chemical homogeneity, finer particles, and a better controlled particle morphology than those of powders produced using the mixed-oxide route [11]. The luminescence and optical absorption properties of $LiGaO_2$ nanocrystals are investigated.

2. Experimental details

$LiGaO_2$ oxides were prepared using the sol–gel method with lithium nitrate $Li(NO_3)$, gallium nitrate $Ga(NO_3)_3$, ethylene glycol (EG), and citric acid anhydrous (CA) as starting materials. Their purities were all over 99.9%. A sufficient amount of citric acid was added to the former solution as a chelating agent. The molar ratio of citric acid to the total metal ions was 3:2. EG was added to the above solution as a stabilizing agent. The precursors containing Li and Ga were dried in an oven at 120 °C for 10 h. $LiGaO_2$ powders were obtained after calcination at 500–700 °C for 3 h in air.

The phases were identified using X-ray powder diffraction (XRD, Rigaku Dmax-33). The morphology and microstructure were examined by high-resolution transmission electron microscopy (HR-TEM, HF-2000, Hitachi). The excitation and emission spectra were recorded on a Hitachi-4500 fluorescence spectrophotometer equipped with a xenon lamp. The absorption spectra were measured using a Hitachi U-3010 UV–vis spectrophotometer.

3. Results and discussion

The amorphous metal–organic gel was heat-treated to pyrolyze the organic components for crystallization. XRD patterns of the precursor powders at heat-treatment temperatures of 500–700 °C for 3 h are shown in Fig. 1. The sample calcined at a temperature of 500 °C exhibits a micro-crystallized structure due to the decomposition of the amorphous gel. $LiGaO_2$ formed directly from the amorphous precursor. When the precursor was sintered at temperatures above 600 °C, the peaks of (1 1 0) and (0 1 1) were separated, and all of the peaks were identified to be those of the orthorhombic $LiGaO_2$ phase (JCPDS card no., 22-0412). The intensity of the diffraction peaks, and thus the crystallinity of $LiGaO_2$, increased with annealing temperature. It is believed that an increase in

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[*] Corresponding author. Tel.: +886 7 381 4526x5336.
E-mail address: fang.tehua@msa.hinet.net (T.-H. Fang).

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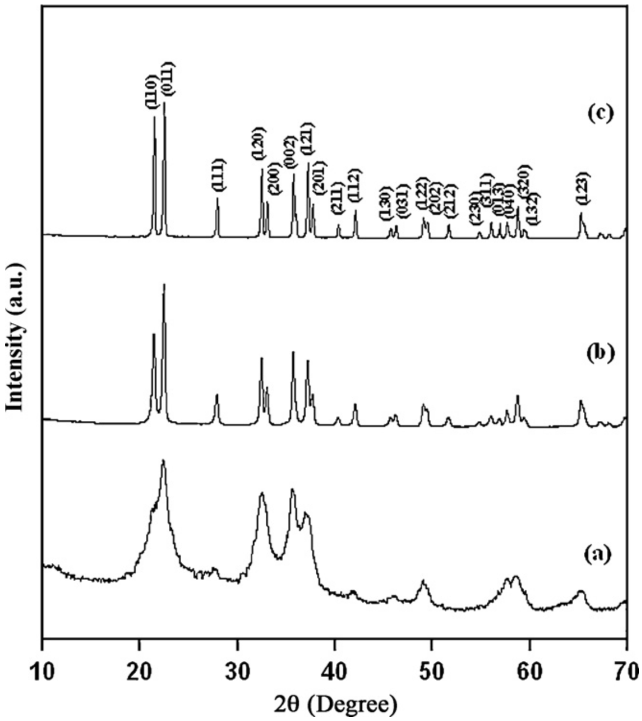

Fig. 1. X-ray diffraction patterns of $LiGaO_2$ precursor powders annealed at (a) 500, (b) 600, and (c) 700 °C for 3 h.

temperature increased atomic mobility and accelerated grain growth.

Fig. 2a shows scanning electron microscopy (SEM) images of the $LiGaO_2$ sample sintered at 600 °C. The microflakes are distributed homogeneously, the diameter of the sheet is 3–5 μm, and the thickness is 73–100 nm. The growth mechanism of the microflake structure is not yet fully understood. A wide variation in the crystal morphology of oxide films has been reported for samples synthesized using the sol–gel method. The shape and size of plates depend on the temperature, acid concentration, and immersion time [12,13].

Recently, nanostructured lithium aluminate (α-$LiAlO_2$) with plate-like crystals was synthesized using hydrothermal techniques [14]. Transmission electron microscopy (TEM) micrographs of the two-dimensional nanoflakes are shown in Fig. 2b. Many disordered mesopores were observed on the microflakes, as shown in the inset. The average diameter of the mesopores was 4–10 nm. The microflake growth is favored the aggregation of $LiGaO_2$ molecules as lamellar crystal template under hydrolysis process. Similar phenomena have been observed for α-$LiAlO_2$ nanoflakes [15].

Fig. 3a shows the excitation spectra of the $LiGaO_2$ samples calcined at temperatures of 500–700 °C. The photoluminescence results reveal that the sample prepared at 600 °C exhibits the greatest absorption intensity at 327 nm. These peaks are associated with the direct excitation of the $LiGaO_2$ host itself, via the charge transfer (CT) transition between Ga and O. The crystal structure of $LiGaO_2$ is an ordered variant of wurtzite, with Ga^{3+} ions in tetrahedral co-ordination [8]. Therefore, the main peaks of excitation, at about 327 nm, were associated with CT bands of the tetrahedral gallate group in the $LiGaO_2$ system.

The sample heat-treated at 600 °C has the most intense emission spectra (λ_{ex} = 327 nm) in Fig. 3b, associated with the higher absorbing intensity of the tetrahedral gallium group. The high photoluminescence performance may result from improved crystallinity leading to higher oscillating strengths [16] or reduced internal reflections of the emitted light due to rougher surfaces [17]. The compounds $LiGaO_2$ and $GaBO_3$ have luminescence centers at tetrahedral and octahedral sites, with broad emission bands at 360 and 460 nm, respectively [18]. Similar results were obtained for $LiGaO_2$, as shown in Fig. 3b. The sample prepared at 700 °C exhibits peaks at wavelengths of 383 and 450 nm, respectively associated with CT bands of Ga atoms at tetrahedral and octahedral sites.

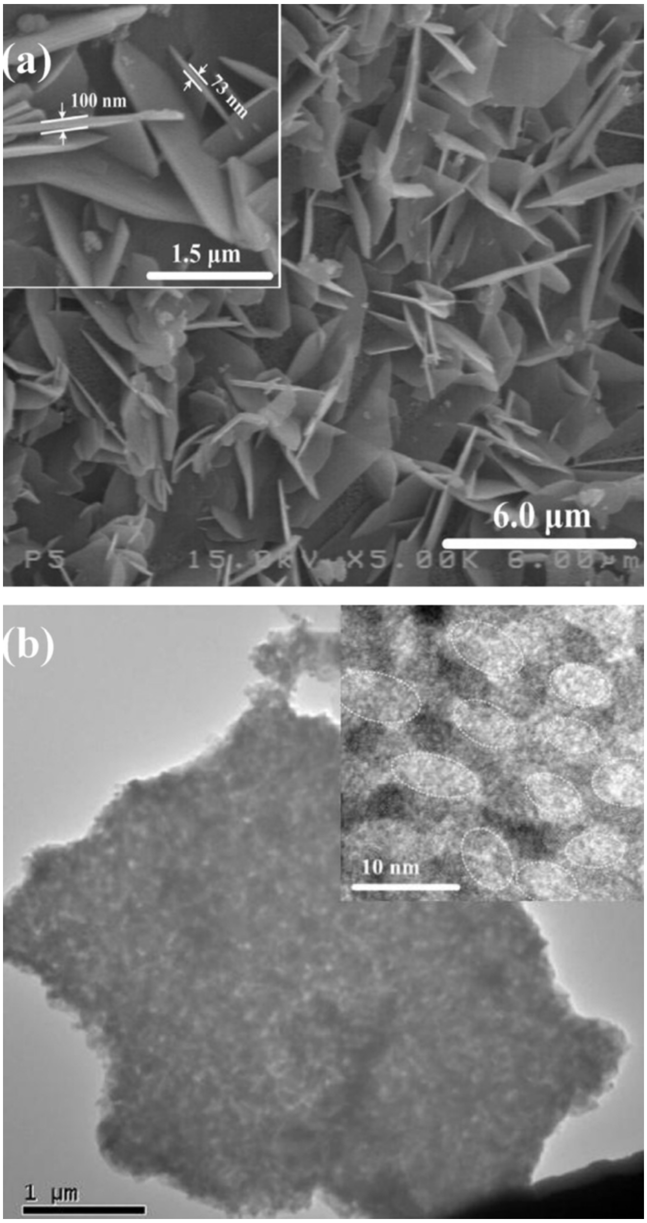

Fig. 2. (a) SEM micrograph of $LiGaO_2$ microflakes, (b) TEM image of an as-synthesized microflake with many mesopores.

The UV–vis absorption spectra of the as-prepared $LiGaO_2$ microflakes were measured and the band gap was estimated from the absorption onset; the results are shown in Fig. 4. The optical absorption band has a peak at 315 nm that corresponds to the excitation spectrum. For a direct-band-gap semiconductor, absorbance

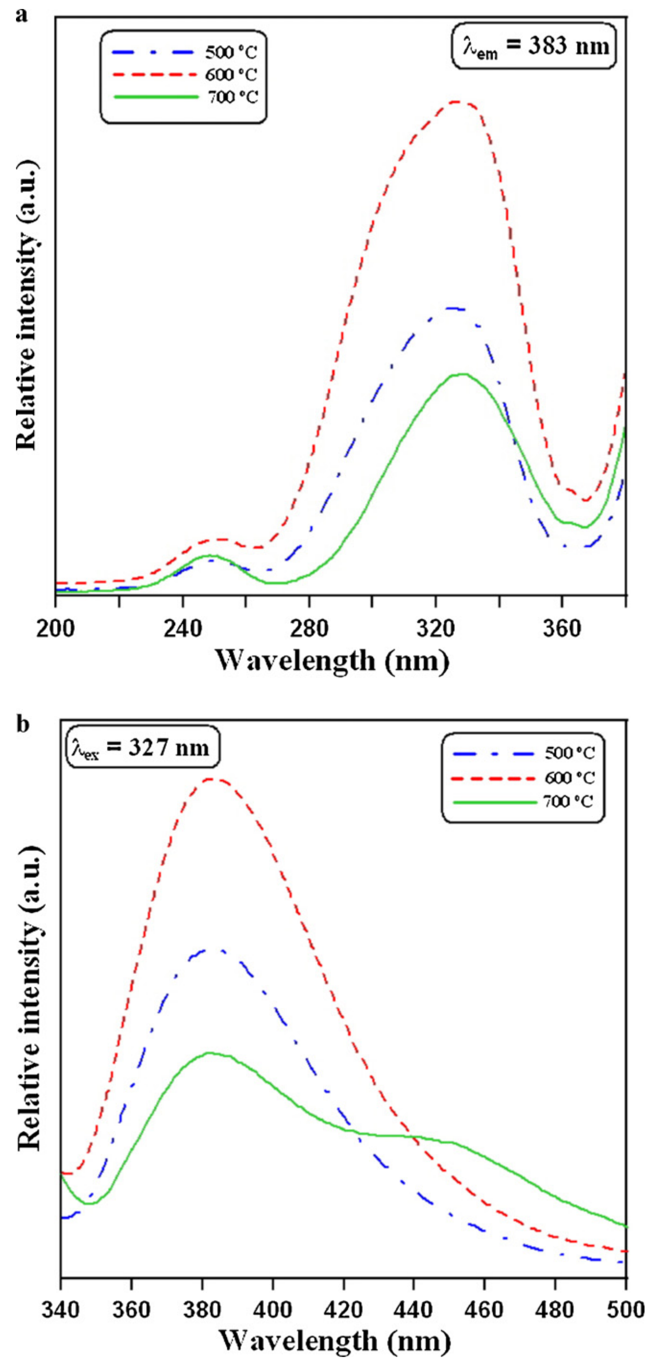

Fig. 3. (a) Room-temperature excitation (λ_{em} = 393 nm) and (b) emission (λ_{ex} = 327 nm) spectra of pure $LiGaO_2$ phosphors heat-treated at various temperatures.

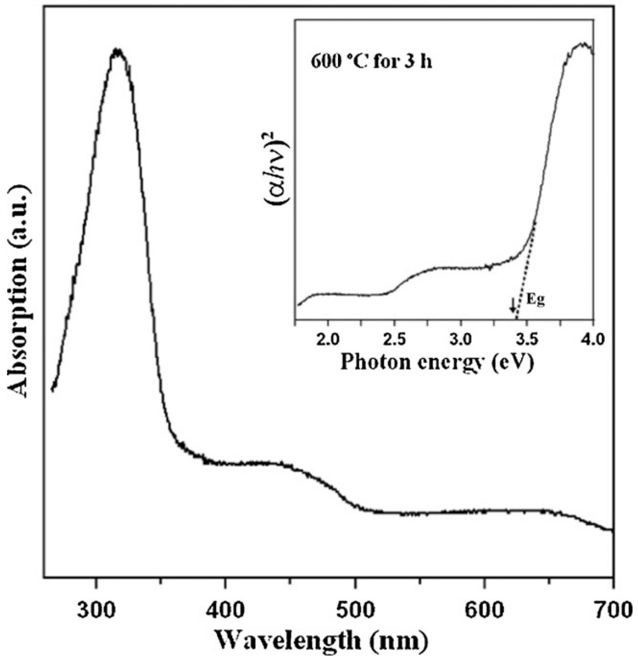

Fig. 4. Absorption spectra of $LiGaO_2$ powders annealed at 600 °C for 3 h at room temperature. The inset shows optical absorption as a function of photon energy for $LiGaO_2$ microflakes.

in the vicinity of the onset due to the electronic transition is given as:

$$\alpha = \frac{C(h\nu - E_g)^{1/2}}{h\nu} \qquad (1)$$

where α is the absorption coefficient, C is a constant, $h\nu$ is the photon energy, and E_g is the band-gap energy. The inset of Fig. 4 shows the relationship of $(\alpha h\nu)^2$ versus $h\nu$. Extrapolation of the linear region gives a band gap of 3.38 eV. The direct band-gap energy obtained from the experimental results is 3.38 eV, which is close to the result (3.14 eV) obtained using first-principles density function calculations [19]. Therefore, the sample of microflakes had a higher band gap than that of an ideal crystal structure of $LiGaO_2$.

4. Conclusion

Well-crystallized orthorhombic $LiGaO_2$ was obtained after heat treatment at above 500 °C, as determined from XRD. The excitation wavelengths at about 325 nm were associated with charge transfer between Ga and O with Ga^{3+} ions in tetrahedral co-ordination. The PL spectra under 325 nm excitation showed a broad and strong emission peak at about 383 nm, which originated from the tetrahedral gallium group. The absorption edge of the sampled calcined at 600 °C was at 367 nm, which corresponds to a band-gap energy of 3.38 eV.

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