FULL PAPER

Emission properties of Zinc Gallate nanophosphors

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Nano-sized ZnGa_2O_4 , $\text{ZnGa}_2\text{O}_4\text{:Cr}$ and $\text{ZnGa}_2\text{O}_4\text{:Ti}$ phosphors were synthesized by low-temperature combustion method and the luminescent properties were studied in comparison with those from conventional solid-state reaction. The combustion reaction resulted in a single-phase spinel structure and the particles were 5–10 nm in size. Of all samples, undoped nano ZnGa_2O_4 exhibited an intrinsic blue emission and Ti-doped nano ZnGa_2O_4 had a tendency of white emission whereas Cr-doped nano ZnGa_2O_4 showed red emissions. Titanium ions in spinel structure was found to exist as in Ti^{3+} and Ti^{4+} , but favouring trivalent state. The oxidation state of Cr ions was confirmed as 3^+ in nano ZnGa_2O_4 .

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1. Introduction

ZnGa_2O_4 is a semiconducting material that crystallizes in a normal spinel AB_2O_4 structure (cubic spinel, Fd-3m) with an optical band gap of 4.4 eV.^{1),2)} The A site (Zn^{2+}) ions occupy tetrahedral sites with full T_d symmetry, and the B site (Ga^{3+}) ions are in octahedral sites with six-fold distorted octahedral coordination and D_{3d} point group. The trigonal axis of the B sites is coincident with the (111) axis and the site has a centre of inversion (No. 277 in the International Tables for Crystallography Volume A).³⁾

ZnGa_2O_4 has recently gained attention due to its potential as a phosphor host material with prospective uses such as an Ultraviolet (UV) and low-voltage emitter for application in diverse fields, field emission displays, thin-film electroluminescent devices, and vacuum fluorescent displays.^{4),5)} The recent development not only in advanced biological imaging technologies has further recognized the potential of ZnGa_2O_4 ,^{6)–8)} but also in the field of photocatalytic activities for water splitting and air purification.^{9)–12)} The oxide-based spinel structure of ZnGa_2O_4 provides advantageous physical and chemical properties as a phosphor since it is more stable under a high electric field and strong electron bombardment than conventional sulphide-based phosphors.⁴⁾

In general, UV or low-voltage electron excitation causes ZnGa_2O_4 to emit a strong blue emission owing to a transition via the self-activation centre at the Ga–O groups.^{5),13)} ZnGa_2O_4 acts as an excellent host for multicolour-emitting materials that shift its emission wavelength to different regions of visible spectrum.¹⁴⁾ For example, doping with a

transitional metal or rare-earth element, such as chromium or europium, shifts the emission from blue to red,^{15)–18)} whereas manganese or terbium cause green emission.^{19),20)}

Other applications, such as white lighting, employ a yellow-emitting phosphor like YAG:Ce^{3+} together with InGaN blue LED chips.²¹⁾ However, low colour rendering is the major drawback of such a system, arising from the lack of red emissions and different degradation rates of chip and phosphor. Therefore, the development of a single-composition white-emitting phosphor for UV or near-UV excitations has been suggested to improve the colour rendering and stability.²²⁾ However, such white emissions are rarely reported.²³⁾

Most oxide phosphors, including ZnGa_2O_4 , have generally been synthesized by a conventional solid-state reaction⁴⁾ at high temperatures (above 1000°C). For ZnGa_2O_4 , high-temperature processing often causes volatilization of ZnO with severe agglomeration and grain growth.⁵⁾ This prohibits the production of ultrafine and non-agglomerated nanopowders with narrow size distribution, which could be an essential characteristics of useful phosphors.²⁴⁾ A spherical shape and clean surface are also important for phosphor particles to minimize the scattering of light and to maximize their packing density.²⁵⁾ Therefore, wet chemistry, such as sol–gel,²⁶⁾ hydrothermal,²⁷⁾ use of polymeric precursor (Pechini),²⁸⁾ co-precipitation²⁹⁾ and combustion³⁰⁾ method, has been suggested as an alternative for the development of nano-sized phosphors.

This study reports the synthesis of nano-sized ZnGa_2O_4 spinel phosphors. Undoped, Cr^{3+} -doped, and Ti^{3+} -doped samples were made via a simple combustion method at temperatures lower than the conventional method. The phosphors were characterized in terms of size, photoluminescence and emission mechanism, using X-ray

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diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), photoluminescence emission (PLE) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

2. Experimental section

2.1 Materials

Zinc(II) nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (purity 98%), gallium(III) nitrate hydrate [$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$] (purity 99.9%), chromium(III) nitrate nonahydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (purity 99%), titanium(IV) oxyacetylacetonate [$\text{TiO}[\text{CH}_3\text{COCH}=\text{C}(\text{O})-\text{CH}_3]_2$] (purity 90%) and urea [$\text{CO}(\text{NH}_2)_2$] (purity 99%) were purchased from Sigma-Aldrich and used without further purification.

2.2 Synthesis

All reagents were purchased and used without further purification. Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, Reagent grade, 98%], gallium nitrate hydrate [$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, Sigma-Aldrich, 98% trace metals basis], urea (NH_2CONH_2 , Sigma-Aldrich, ACS reagent, 99.0–100.5%), chromium nitrate nonahydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99.99\%$ trace metals basis], and titanium oxyacetylacetonate [$\text{TiO}[\text{CH}_3\text{COCH}=\text{C}(\text{O})-\text{CH}_3]_2$, Aldrich, 90%) were used as starting materials.

Undoped and doped nano-sized ZnGa_2O_4 spinel compositions were synthesized by the combustion reaction of oxidizing and reducing agents.³¹⁾ For a typical synthesis of nano-sized undoped ZnGa_2O_4 , the stoichiometric amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (2 mmol) were mixed in distilled water in an alumina crucible, and gently stirred at room temperature for homogeneity until completely dissolved. An appropriate amount of urea (6.6 mmol) was added to the solution at room temperature.

The synthetic reaction was initiated by heating the solution to 150°C using a hot plate. This increased the viscosity of the solution with no precipitation, and NO_x gas evolved from nitrate decomposition. The mixture was held at 150°C to evaporate excess water until no gas was released. This formed a white gel-like precursor, which was then calcined in a pre-heated box furnace in the ambient atmosphere at various temperatures. The synthesized powders were ground in an agate mortar for powder characterization. The Cr^{3+} -doped and Ti^{3+} -doped ZnGa_2O_4 nanophosphors were synthesized by the same procedure as the undoped sample. Doping for the highest luminescence was achieved by adding 0.5 at.% $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{TiO}[\text{CH}_3\text{COCH}=\text{C}(\text{O})-\text{CH}_3]_2$ to the zinc and gallium precursors.

For a comparison micron-sized undoped ZnGa_2O_4 , Cr-doped ZnGa_2O_4 and Ti-doped ZnGa_2O_4 was also synthesized via the solid-state reaction using ZnO (Sigma-Aldrich, ACS reagent), Ga_2O_3 (Sigma-Aldrich, $\geq 99.99\%$ trace metals basis), Cr_2O_3 (Sigma-Aldrich, 99.9% trace metals basis), and TiO_2 (Sigma-Aldrich, 325 mesh, $\geq 99\%$ trace metals basis) powder as precursors. Stoichiometric amount

of precursors are mixed by ball-milling in ethanol media for 20 h. The suspension was dried in an oven at 90°C for overnight. The obtained powder were calcined at 1200°C for 4 h.

2.3 Characterization

Powder XRD analyses were used to identify the phases present and to calculate crystallite sizes. The diffractometer (D8-Advance, Bruker, Billerica, MA, USA) used monochromatized Cu-K α radiation ($\lambda = 1.54148 \text{ \AA}$). The powder samples were also analysed by HR-TEM (3000F, JEOL). The excitation and emission spectra were recorded at room temperature using a spectrofluorometer (QuantaMaster 300, PTI) equipped with a wavelength filter in the range of 400–800 nm. A CNO analyser (EC-200AC, LECO) was used to measure the oxygen content. To determine the oxidation states of the Cr and Ti dopant ions, XPS was conducted, and all measurements were calibrated to the binding energy of the C1s peak at 284.6 eV.

3. Results and discussion

3.1 Characteristics of ZnGa_2O_4

Figure 1 shows the XRD patterns of the undoped- ZnGa_2O_4 nanoparticles synthesized by combustion and calcined at various temperatures up to 1000°C for 1 h. Despite the significant peak broadening due to the nano-sized particles, all the diffraction peaks [Figs. 1(b)–1(e)],

Fig. 1. XRD patterns of spinel ZnGa_2O_4 (a) JCPDS 38-1240 standard reference, (b) as-synthesized ZnGa_2O_4 , and the samples calcined for 1 h at (c) 300, (d) 500, (e) 700°C and (f) 1000°C.

except for that of the as-prepared sample processed at 150°C [Fig. 1(a)], were well matched with the reference peaks for cubic spinel ZnGa_2O_4 (JCPDS #38-1240). This confirms the formation of single-phase ZnGa_2O_4 without any secondary phases.

XRD patterns of undoped ZnGa_2O_4 , 0.5 at.% Cr-doped ZnGa_2O_4 , and 0.5 at.% Ti-doped ZnGa_2O_4 are shown in Fig. 2. All samples were synthesized at 500°C for 1 h. It is interesting to note that the addition of Ti to ZnGa_2O_4 slows the crystallization of the powder while high crystallinity of the phosphors is obtained from undoped and Cr-

Fig. 2. XRD patterns of ZnGa_2O_4 . (a) undoped ZnGa_2O_4 , (b) Cr-doped ZnGa_2O_4 , (c) Ti-doped ZnGa_2O_4 synthesized at 500°C for 1 h.

doped ZnGa_2O_4 . The average crystallite sizes of undoped ZnGa_2O_4 , 0.5 at.% Cr-doped ZnGa_2O_4 , and 0.5 at.% Ti-doped ZnGa_2O_4 estimated from the XRD patterns by using Scherrer's equation are 27, 32, and 25 nm, respectively. It should be attributed to the size of ions replacing Ga site as will be discussed later. It is reported that the sizes of Ti^{3+} , Ti^{4+} and Cr^{3+} are 0.081, 0.0745 and 0.0615 nm, respectively, whereas that of Ga^{3+} is 0.062 nm. The large size Ti ions retard the crystallization process effectively in the nano structure.

The average crystallite sizes of undoped ZnGa_2O_4 heat-treated at different temperatures is shown in Fig. 3. The sample heat-treated at 300°C for 1 h showed the smallest calculated average crystallite size of 5.3 nm, whereas 1000°C heat treatment for 1 h produced 85 nm in size (Fig. 3, open circles). Lattice parameters were also estimated by using Bragg's law (Fig. 3, closed squares). Increasing the calcination temperature generally increased the parameter from 8.33 to 8.36 Å, which matches the ICSD value of 8.362 Å,^{32,33} indicating improved crystallinity of the powder at 1000°C.

Figure 4 shows HR-TEM images of undoped ZnGa_2O_4 [Figs. 4(a)–4(d)] synthesized at 300°C for 1 h along with that of bulk ZnGa_2O_4 [Figs. 4(e) and 4(f)]. The particles in Fig. 4(c) have an average size of ~5.0 nm, which is consistent with the size obtained from the XRD result. From the selected-area electron diffraction (SAED) patterns in Fig. 4(d), the (111), (311), and (220) spots of ZnGa_2O_4 were identified with the $[\bar{1}12]$ zone axis. The lattice parameter was calculated to be in the range of 0.8334–0.8364 nm using (311) d-spacings of 0.2513–0.2522 nm. TEM image of bulk ZnGa_2O_4 in Fig. 4(e), which was prepared by a conventional solid-state reaction at 1200°C for 4 h, shows particles much larger than the combustion synthesized ZnGa_2O_4 . The calculated lattice parameter for solid-state reacted ZnGa_2O_4 using (311) d-spacing of 0.2517 nm from

Fig. 3. Calculated lattice constants and crystallite sizes of various ZnGa_2O_4 calcined between 300 and 1000°C for 1 h.

Fig. 4. (a) TEM image, (b) XRD pattern, (c) HR-TEM image, and (d) SAED pattern of undoped ZnGa_2O_4 synthesized at 300°C for 1 h, (e) TEM image and (f) HR-TEM image of bulk ZnGa_2O_4 prepared by solid-state reaction at 1200°C for 4 h.

its HR-TEM [Fig. 4(f)] was 0.8348 nm, which is similar to the lattice parameter, 0.83349 nm, in JCPDS 38-1240.

3.2 Luminescence of ZnGa_2O_4 phosphors

Figure 5 shows the PLE spectra of undoped and doped samples prepared at 500°C for 1 h (solid-lines) and micron-sized sample prepared by solid-state reaction (dashed-lines). All undoped ZnGa_2O_4 generally exhibits the characteristic blue emission at 430 nm (2.88 eV) under 254 nm UV excitation that originates from charge transfer from O to Ga in the host material.²⁰⁾ However, the spectrum in Fig. 5(a) for nano-sized ZnGa_2O_4 exhibits several peaks at 420 (2.95 eV), 450 (2.75 eV), 470 (2.63 eV), 480 (2.58 eV), and 490 (2.53 eV) nm, a bell-shaped spectrum. The low crystallinity of the nano ZnGa_2O_4 along with a high defect density should be responsible for the various emission peaks. Emission at ~ 560 nm (2.21 eV) was also observed, which has previously been obtained by doping ZnGa_2O_4 with Mn^{2+} .³⁴⁾ Synthesis by combustion with an organic-containing precursor is known to provide a large number of oxygen vacancies, resulting in emission peak at 680 nm (1.82 eV).³⁵⁾ Based on these facts, it can be said that it is more probable for nano-sized ZnGa_2O_4 to provide white emission than micron-sized ones.

Fig. 5. PLE spectra of (a) pure micron and nano ZnGa_2O_4 , (b) 0.5 at.% Cr-doped micron and nano ZnGa_2O_4 , and (c) 0.5 at.% Ti-doped micron and nano ZnGa_2O_4 .

The PLE spectrum of Cr-doped ZnGa_2O_4 (0.5 at.%) excited at 254 nm [Fig. 5(b)] shows a high-intensity peak ~ 695 nm (1.78 eV) regardless of the powder size. The Cr^{3+} ions are reported to substitute Ga^{3+} ions at octahedral

Fig. 6. PLE spectra of combusted nano ZnGa_2O_4 doped with varying concentration levels of (a) Cr and (b) Ti excited under 254 nm excitation. The amounts of dopants are between 0.25 and 1.00 at.% for Cr and Ti-doped ZnGa_2O_4 .

sites to minimize charge and size variation.³⁶⁾ Their oxidation state is suggested to be +3. Excitation at 254 nm causes the charge transfer in CrO^{6+} ; the $^4\text{A}_2 \rightarrow ^4\text{T}_1$ transition of Cr^{3+} and the emission band around 695 nm are attributed to the $^2\text{E} \rightarrow ^4\text{A}_2$ transition of Cr^{3+} in the octahedral sites.^{6),15),36)} Furthermore, the intrinsic blue emission of pure ZnGa_2O_4 host material was largely suppressed, indicating that the energy to the Cr^{3+} ions was highly efficient, resulting in red emission only. On contrary, Cr-doped ZnGa_2O_4 synthesized by solid-state reaction exhibited the intrinsic blue emission peaks in addition to red emission, reducing the efficiency of red colour. The PLE spectrum of 0.5% Ti-doped ZnGa_2O_4 shows bluish-white emission, Fig. 5(c), with a broad peak that consisted of almost all three primary colours: blue, green, and red. Similar to undoped samples, Ti-doped nano ZnGa_2O_4 tends to have various emission wavelengths even if red one is relatively weak, resulting in a bluish-white emission.

Optimum concentrations were sought for both dopants at contents ranging between 0.25 and 1.00 at.% and the results are shown in Fig. 6. Excitation was at 254 nm with equal amounts of powder. In both cases, the PLE intensity increased with dopant concentration up to 0.5 at.%,

beyond which it decreased. The red emission of Cr-doped ZnGa_2O_4 decreased at concentrations greater than 0.5 at.%, and further addition of Cr ions led to the intrinsic blue emission of ZnGa_2O_4 [Fig. 6(a)]. There was no further suppression of the blue emission. In contrast, the Ti-doped ZnGa_2O_4 showed no notable PLE shift or shape change, except that increasing the dopant concentration decreased the emission intensity [Fig. 6(b)]. Doping at 0.3 to 0.5 at.% is generally considered acceptable.^{14),37),38)} Based on the results discussed to this point it can be concluded that ZnGa_2O_4 has potential as a host material to provide white emission, at least, by mixing singly-doped ZnGa_2O_4 in nano size.

3.3 Oxidation state of the dopants

Figure 7 shows the wide-scan XPS spectrum for undoped ZnGa_2O_4 and fine scans for both doped samples. The spectrum of undoped ZnGa_2O_4 in Fig. 7(a) indicates the presence of all three constituent elements. The spectra for the doped samples also show the presence of all the constituent elements without any observable contamination other than a very small peak for adsorbed carbon. The fine XPS spectrum in Fig. 7(b) shows the Cr $2p_{3/2}$ (574 eV) and Cr $2p_{1/2}$ (585 eV) peaks with an 11 eV difference between them. This binding energy corresponds to Cr^{3+} in a trivalent oxidation state. All the values and the gaps between them in the fine XPS of Ga, Zn, and Cr agreed with the reference values,³⁹⁾ confirming the existence of a Cr^{3+} trivalent oxidation state.

XPS spectra of Ti-doped ZnGa_2O_4 synthesized at 500 and 1000°C [Figs. 7(c) and 7(d)] were taken to verify the valence state of the titanium ions in the spinel structure. Titanium ions can have various valence states that affect their photoluminescence along with the doping sites. The wide spectra reveal the presence of all four elements (not shown), and the detailed scan in Fig. 7(c) shows peaks at 456.70 and 458.15 eV which correspond to reported values for the $\text{Ti}^{3+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$ states, respectively.^{39),40)} It confirms the co-existence of Ti^{3+} and Ti^{4+} in the spinel structure. We have previously reported similar results for Ti-doped MgAl_2O_4 spinel.⁴¹⁾ High-intensity Ti^{3+} signals are evident for samples heat-treated at both 500 and 1000°C, and are larger at 1000°C, indicating that the trivalent oxidation state is more favorable at higher temperatures.

4. Conclusions

Nano-sized undoped, Cr^{3+} -doped, and Ti^{3+} -doped ZnGa_2O_4 spinel particles were synthesized by a combustion method based on the nitrate–urea redox reaction. XRD and HR-TEM results identified 5–10 nm nanoparticles with a spinel structure. The blue PLE of the undoped ZnGa_2O_4 at room temperature originated from charge transfer between Ga and O was suppressed and the spectra became broadened when the phosphor particle size decreased. It is attributed to the presence of various defects and low crystallinity of nano phosphors. Ti-doped ZnGa_2O_4 exhibited a bluish-white emission consisting of blue,

Fig. 7. (a) Wide-scan XPS spectrum for pure ZnGa_2O_4 . Narrow-scan XPS spectra for (b) Cr^{3+} ions and (c) Ti^{3+} and Ti^{4+} ions in separately doped ZnGa_2O_4 synthesized at 500°C for 1 h and (d) Ti^{3+} and Ti^{4+} ions in doped ZnGa_2O_4 synthesized at 1000°C for 1 h.

green, and red emissions under excitation at 254 nm while intensive red emission at 695 nm (1.78 eV) was observed from Cr^{3+} -doped ZnGa_2O_4 . The XPS results indicate that the Ti dopant is present in both the trivalent (Ti^{3+}) and tetravalent (Ti^{4+}) oxidation states, with the trivalent state more favourable within ZnGa_2O_4 spinel structure at high temperature. Nano ZnGa_2O_4 exhibits potential as a host material to provide white emission.

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