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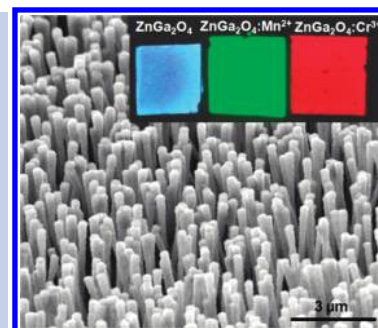
Red, Green, and Blue Luminescence from ZnGa_2O_4 Nanowire Arrays

Zhanjun Gu,^{†,‡} Feng Liu,[†] Xufan Li,[†] Jane Howe,[§] Jun Xu,[§] Yuliang Zhao,[†] and Zhengwei Pan^{*,†}

[†]Faculty of Engineering, Department of Physics and Astronomy, University of Georgia, Athens, Georgia 30602, [‡]Lab for Bio-Environmental Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China, and [§]Materials Science and Technology Division, Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

ABSTRACT Large-area ($>1\text{ cm}^2$), vertically aligned ZnGa_2O_4 , Mn^{2+} -doped ZnGa_2O_4 ($\text{ZnGa}_2\text{O}_4\cdot\text{Mn}^{2+}$) and Cr^{3+} -doped ZnGa_2O_4 ($\text{ZnGa}_2\text{O}_4\cdot\text{Cr}^{3+}$) nanowire arrays were synthesized by a two-step thermal evaporation method using ZnO nanowire arrays as the templates followed by reaction with Ga and/or dopant (Mn or Cr) vapors. Bright red, green, and blue luminescence was achieved, respectively, from $\text{ZnGa}_2\text{O}_4\cdot\text{Cr}^{3+}$, $\text{ZnGa}_2\text{O}_4\cdot\text{Mn}^{2+}$, and ZnGa_2O_4 nanowire arrays under ultraviolet light irradiation. The realization of three primary colors from one host material suggests that full color display based on ZnGa_2O_4 nanowires might be achievable.

SECTION Nanoparticles and Nanostructures



Future flat panel display technologies demand highly efficient and stable phosphor materials for better performance.¹ Zinc gallate (ZnGa_2O_4), a ternary spinel material with a band gap of 4.4–4.7 eV, has shown excellent potential for incorporation in future display system because of its prominent blue emission, high chemical and thermal stability, and good cathodoluminescence characteristics at low-voltage.^{2,3} ZnGa_2O_4 is naturally a very promising blue-emitting phosphor.⁴ It can also act as an excellent host material for high luminance multicolor-emitting phosphors when doped with appropriate activators: Mn-activated ZnGa_2O_4 ($\text{ZnGa}_2\text{O}_4\cdot\text{Mn}^{2+}$) for green emission^{5,6} and Cr-doped ZnGa_2O_4 ($\text{ZnGa}_2\text{O}_4\cdot\text{Cr}^{3+}$) for red emission.^{5,7} ZnGa_2O_4 phosphors (with or without doping) were usually used in the form of thin films.^{8–11} It is anticipated that when the phosphors are made into nanocrystals, the density of emission sites would be dramatically increased, which may lead to high-brightness and high-definition display.¹²

Considerable efforts have been spent in recent years to fabricate ZnGa_2O_4 nanowires and their arrays.^{13–15} Bae et al. synthesized aligned ZnGa_2O_4 nanowires by thermal evaporation of ZnO–Ga powders using Au as a catalyst.¹³ Chang and Wu reported a three-step process using Ga_2O_3 nanowires as the templates.¹⁴ All the so-far demonstrated ZnGa_2O_4 nanowires are undoped, so the observed luminescence is the self-activated blue emission stemming from the octahedral Ga–O groups in the spinel lattices.^{4,16} For applications in full color displays and nanoscale light sources, however, doping appropriate activators (e.g., Mn^{2+} and Cr^{3+}) into ZnGa_2O_4 nanowires is highly desirable.

Recently, ZnO nanowires were frequently used as templates to fabricate a series of ZnO-based ternary spinel

nanotubes (e.g., ZnAl_2O_4) or core/shell nanowires (e.g., $\text{ZnO}/\text{Zn}_2\text{TiO}_4$) using a three-step process,^{16–18} in which pre-synthesized ZnO nanowires were coated with an oxide (e.g., Al_2O_3 and TiO_2) shell by various deposition techniques (e.g., atomic layer deposition) followed by solid-state reaction of ZnO with oxide shell at high temperature. Depending on the oxide shell thickness and diffusion direction (outward or inward relative to the ZnO nanowire center), the resulting product is either in the tube form or in a core/shell structure. In this three-step process, an oxide shell deposition stage is needed, and the doping of the ternary nanotubes or core/shell nanowires has not yet been achieved. In this letter, we report the fabrication of highly aligned ZnGa_2O_4 nanowire arrays and the first doping of ZnGa_2O_4 nanowires with transition metals Mn and Cr using pre-synthesized ZnO nanowire arrays as the templates via a simpler two-step thermal evaporation method. The three primary colors (red, green, and blue: RGB) that are required for full color displays were realized from these doped and undoped ZnGa_2O_4 nanowire arrays: red from $\text{ZnGa}_2\text{O}_4\cdot\text{Cr}^{3+}$, green from $\text{ZnGa}_2\text{O}_4\cdot\text{Mn}^{2+}$, and blue from undoped ZnGa_2O_4 .

Figure 1a,b shows the scanning electron microscope (SEM) images of the aligned ZnO nanowire arrays and the ZnGa_2O_4 nanowire arrays fabricated at 1000 °C, respectively. It is clear that the ZnGa_2O_4 nanowires reserve the alignment and sizes of the ZnO nanowires very well. Depending on the ZnO nanowire templates, the obtained ZnGa_2O_4 nanowires have diameters in the range of 50–200 nm and lengths up to

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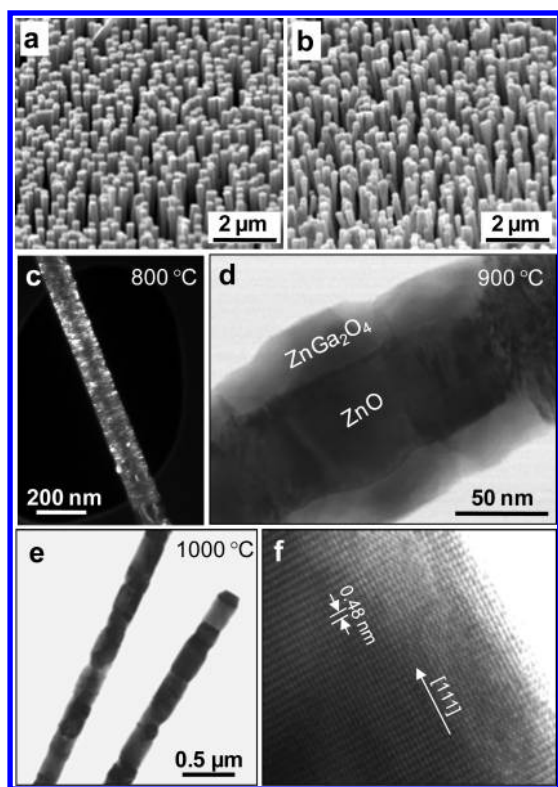


Figure 1. (a) SEM image of a ZnO nanowire array. (b) SEM image of a ZnGa₂O₄ nanowire array fabricated at 1000 °C. (c) Z-contrast TEM image of a ZnO/ZnGa₂O₄ core/shell nanowire obtained at 800 °C. The bright particles are ZnGa₂O₄. (d) TE mode of a ZnO/ZnGa₂O₄ core/shell nanowire formed at 900 °C. (e) Low-magnification TEM image of two ZnGa₂O₄ nanowires fabricated at 1000 °C. (f) HRTEM image of a ZnGa₂O₄ nanowire.

~5 μm . Transmission electron microscope (TEM) analyses of the samples formed at different temperatures (800°, 900°, and 1000 °C) show that the conversion reaction of $\text{ZnO} + \text{Ga} + \text{O}_2 \rightarrow \text{ZnGa}_2\text{O}_4$ is determined by the reaction temperature. At 800 °C, only a thin ZnGa₂O₄ particle layer was formed on the ZnO nanowire surface (Figure 1c). At 900 °C, about half of ZnO was converted to ZnGa₂O₄ (Figure 1d). At 1000 °C, the ZnO nanowires were completely converted to ZnGa₂O₄ nanowires (Figure 1e). Different from the starting ZnO nanowires which is a single crystal,¹⁹ the ZnGa₂O₄ nanowires are made of many 0.1–1 μm long crystallites that stack one-by-one along the nanowires' longitudinal direction (Figure 1e). Unlike the previously reported ZnO-based ternary nanowires and nanotubes prepared by the three-step process,^{16–18} no voids or tubular structures were observed in our ZnGa₂O₄ nanowires formed at 1000 °C. This means that the Ga–ZnO reaction at 1000 °C is very efficient and sufficient, and that the inward diffusion of Ga ions to the ZnO nanowire center is the dominant diffusion process.¹⁶ High-resolution TEM (HRTEM) analysis (Figure 1f) shows that each crystallite is a ZnGa₂O₄ single crystal with a growth direction along $\langle 111 \rangle$. The surfaces of the ZnGa₂O₄ nanowires are clean, atomically sharp, and without any sheathed secondary phases.

The temperature-dependent ZnO to ZnGa₂O₄ conversion was verified by X-ray diffraction (XRD) analyses, as that

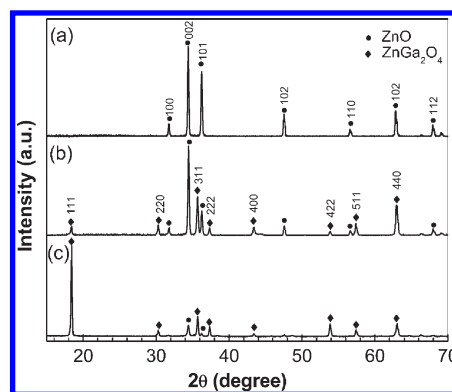


Figure 2. XRD patterns of (a) ZnO nanowire arrays, (b) a ZnO/ZnGa₂O₄ core/shell nanowire array prepared at 800 °C, and (c) a ZnGa₂O₄ nanowire array formed at 1000 °C.

shown in Figure 2. At 800 °C, only a small amount of ZnGa₂O₄ phases was formed in the product (Figure 2b), while, after 30 min of reaction at 1000 °C, the $\langle 001 \rangle$ -oriented wurtzite ZnO nanowires (Figure 2a) were totally converted to spinel ZnGa₂O₄ nanowires with a preferential growth direction along $\langle 111 \rangle$ (Figure 2c). The remaining small amount of ZnO phases in Figure 2c is believed to come from the ZnO layer located at the bottom of the nanowire array,¹⁹ where the penetration of Ga vapor is limited and thus the conversion reaction is incomplete. This temperature-dependent phase conversion is in good agreement with the results obtained by annealing Ga₂O₃ and ZnO powders in air at 500–1000 °C.²⁰

Intentional introduction of impurities (activators) into inorganic phosphors is fundamental to control their optical properties.²¹ This has worked very well for ZnGa₂O₄ powders: undoped ZnGa₂O₄ powder is a blue-emitting phosphor, while the Mn²⁺- and Cr³⁺-activated ZnGa₂O₄ powders emit bright green^{5,6} and red^{5,7} luminescence, respectively. Our present experiments further show that this doping principle is also true for ZnGa₂O₄ nanowires. Adding a small amount of MnCl₂ or CrCl₃ powder into the source does not affect the morphology, alignment, and crystal structures of the ZnGa₂O₄ nanowires. However, the optical properties of the ZnGa₂O₄ nanowires are hence dominated by the optically active Mn²⁺ or Cr³⁺ ions. Figure 3a is a digital image of the undoped, Mn-doped, and Cr-doped ZnGa₂O₄ nanowire arrays grown on Si substrates (size: ~1 cm × 1 cm). Under the excitation of a 254 nm ultraviolet (UV) lamp, bright blue, green, and red luminescence (Figure 3b) emits from the undoped ZnGa₂O₄, ZnGa₂O₄:Mn²⁺, and ZnGa₂O₄:Cr³⁺ nanowire arrays, respectively. The uniform luminescence brightness across the 1 cm² area suggests that the doping is very sufficient and uniform. Figure 3c is the room-temperature photoluminescence (PL) spectra of the three ZnGa₂O₄ nanowire arrays under 275 nm UV light excitation. The blue emission from the undoped ZnGa₂O₄ nanowires is broad and peaked at 452 nm, which can be attributed to the self-activation center of the octahedral Ga–O group in the spinel lattices.^{4,16} The green emission band from the ZnGa₂O₄:Mn²⁺ nanowire array is narrow and centered at 503 nm, which can be clearly assigned to the Mn²⁺⁴T₁–⁶A₁ characteristic transition.^{5,6} The red emission from the ZnGa₂O₄:Cr³⁺ nanowire array is peaked at 696 nm

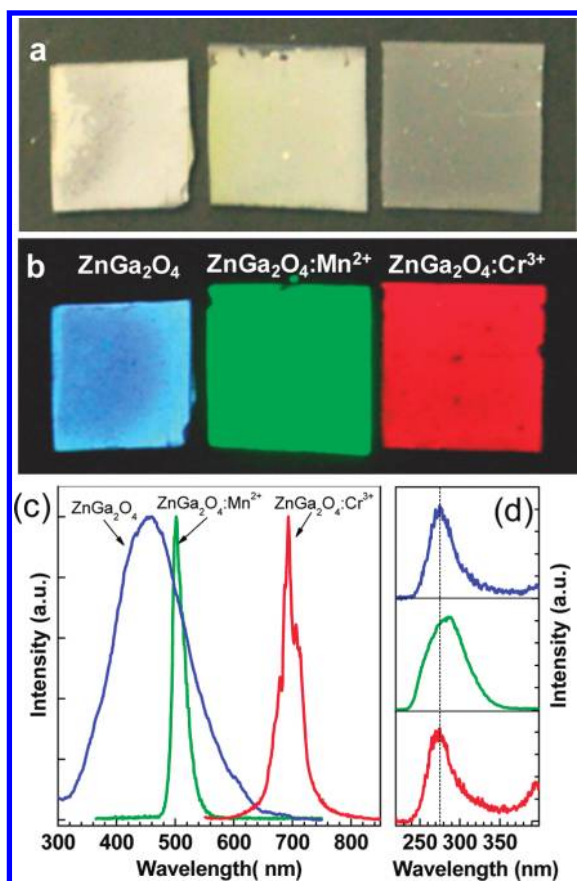


Figure 3. (a) Digital image of (from left to right) undoped ZnGa_2O_4 , $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$, and $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ nanowire arrays grown on Si substrates (size: 1 cm \times 1 cm). (b) Optical image of the samples in panel a under a 254 nm UV lamp irradiation. (c) PL spectra of the three ZnGa_2O_4 nanowire samples. The excitation wavelength is 275 nm. (d) Excitation spectra of (from top to bottom) ZnGa_2O_4 , $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$, and $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ nanowire arrays.

and can be assigned to the ${}^2\text{E}-{}^4\text{A}_2$ characteristic transition of Cr^{3+} ions.^{5,7} Meanwhile, when monitoring the emission maximum of the three ZnGa_2O_4 products, the characteristic excitation peak of the ZnGa_2O_4 host centered at 275 nm emerges in the respective excitation spectrum (Figure 3d), indicating that Mn^{2+} and Cr^{3+} ions have been effectively doped into the ZnGa_2O_4 nanowires and respectively substituted for the tetrahedral site of Zn^{2+} and the octahedral site of Ga^{3+} .^{22,23}

To determine the concentration and confirm the oxidation states of Mn and Cr ions in ZnGa_2O_4 nanowires, we conducted analyses using X-ray photoelectron spectroscopy (XPS). The XPS composition measurements show that the Mn or Cr concentration in the doped ZnGa_2O_4 nanowires is about 0.3–0.5 atom %, a reasonable level for an efficient phosphor.²¹ Figure 4a and 4b show the XPS spectra of Mn ions and Cr ions in doped ZnGa_2O_4 nanowires, respectively. For the Mn XPS spectrum shown in Figure 4a, the peaks at 653.4 and 641.4 eV can be attributed to $\text{Mn } 2p_{1/2}$ and $\text{Mn } 2p_{3/2}$ states, respectively. These binding energies are in good agreement with the reported values of Mn^{2+} ions,²⁴ indicating that the

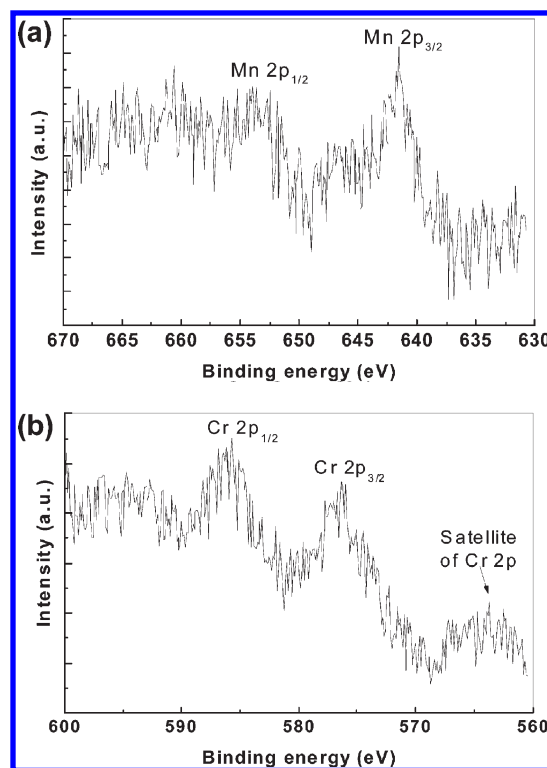


Figure 4. XPS spectra of (a) Mn^{2+} ions and (b) Cr^{3+} ions in ZnGa_2O_4 nanowires.

Mn ions in our ZnGa_2O_4 nanowires are in divalent (Mn^{2+}) oxidation state. For the Cr XPS spectrum shown in Figure 4b, the peaks at 585.8 and 576.3 eV correspond to $\text{Cr } 2p_{1/2}$ and $\text{Cr } 2p_{3/2}$ states, respectively. In addition to these two peaks, a low binding energy satellite peak of Cr 2p located at 563 eV was also observed. These peaks indicate that the Cr ions in the ZnGa_2O_4 nanowires are in the trivalent (Cr^{3+}) oxidation state.²⁵

In summary, using a simple two-step reaction process, we have demonstrated the synthesis of large-area ZnGa_2O_4 , $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$, and $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ nanowire arrays, which respectively emit bright blue, green, and red luminescence under UV light irradiation. The realization of three primary colors from one host material suggests that full color display based on ZnGa_2O_4 nanowires might be achievable. These luminescent nanowires could also be used in applications such as solid-state lighting as well as radiation detection. The cathodoluminescence properties of the ZnGa_2O_4 nanowires will be studied in future research. Moreover, the two-step methodology introduced in this letter may be applied to synthesize many other ZnO-based spinel oxides. For instance, our recent synthesis results show that undoped and Mn^{2+} -doped Zn_2GeO_4 nanowires can be readily synthesized using the two-step method.

Experimental Method

The two-step material synthesis process was conducted inside a well-controlled tube furnace system. Vertically aligned ZnO nanowires were first grown on a Si substrate (size: ~ 1 cm \times 1 cm) by a low-temperature (600 $^\circ\text{C}$) oxidation

method.¹⁹ ZnGa₂O₄ nanowire arrays were then fabricated through the reaction between ZnO nanowires and Ga vapor, where the pregrown ZnO nanowire arrays acted as the template, molten Ga (~1 g) was used as the Ga source, and the tiny amount of residue oxygen in the reaction chamber acted as the O source. The reaction was conducted at 800–1000 °C under an argon flow rate of 200 mL/min and a reaction chamber pressure of ~200 Torr for 30 min. For Mn or Cr doping, a tiny amount (~0.01 g) of MnCl₂ or CrCl₃ powders was added to the source. The products were analyzed by SEM (FEI Inspect F FEG-SEM), TEM (Hitachi HF-3300 FEG STEM at 300 kV), XRD (PANalytical X'Pert PRO diffractometer with Cu K α radiation), spectrofluorometry (Horiba FluoroLog3-2iHR320), and XPS [ESCALab220i-XL spectrometer with a twin-anode Al K α (1486.6 eV) X-ray source]. For XPS measurement, all spectra were calibrated to the binding energy of the adventitious C1s peak at 284.6 eV.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: panz@uga.edu.

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