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Defects and Impurities in Colloidal Ga₂O₃ Nanocrystals: New Opportunities for Photonics and Lighting

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Abstract

Defects, both native and extrinsic, critically determine functional properties of metal oxides. Gallium oxide has recently gained significant attention for its promise in microelectronics, owing to the unique combination of conductivity and high breakdown voltage, and solid-state lighting, owing to the strong photoluminescence in the visible spectral region. These properties are associated with the presence of native defects that can form both donor and acceptor states in Ga_2O_3 . Recently, Ga_2O_3 nanocrystal synthesis in solution and optical glasses has been developed, allowing for a range of new applications in photonics, lighting, and photocatalysis. This review focuses on the structure and properties of Ga_2O_3 nanocrystals with a particular emphasis on the electronic structure and interaction of defects in reduced dimensions and their role in the observed photoluminescence properties. In addition to native defects, the effect of selected external impurities, including lanthanide and aliovalent dopants, and alloying, on the emission properties of Ga_2O_3 nanocrystals are also discussed.

Key words: gallium oxide, nanocrystals, defects and dopants, photoluminescence, lanthanides

Introduction

Transparent metal oxides exhibit a range of unique functional properties, and are indispensable for many technological applications.¹⁻³ This richness of properties arises from their complex crystal and electronic structures,⁴⁻⁸ which can be further modulated by controlling native defect formation or incorporation of impurities (e.g., doping or alloying).⁹ One of the striking characteristics of most transparent metal oxides is their robust n-type conductivity.³ Although these materials possess wide band gaps and should be considered insulators, the presence of suitable native or impurity defects allows for the formation of shallow electron donor states. As an example, oxygen vacancies that are readily formed in metal oxides are often responsible for the formation of new electronic states below the conduction band minimum with reasonably small activation energy.¹⁰⁻¹² These states can donate up to two electrons to the conduction band,¹¹ allowing for the coexistence of optical transparency and electrical conductivity. Hence, this class of materials has become generally known as transparent conducting oxides (TCOs). Various point-defect-derived states can also give rise to appreciable visible-range photoluminescence (PL) in some transparent metal oxides.¹²⁻¹⁴ This combination of properties renders wide band-gap metal oxides applicable in a variety of technologies, including displays, touch panels, solar cells, and light emitting diodes.

The development of the colloidal synthesis methodology over the past two decades has greatly enhanced the range of metal oxides available in the nanocrystalline form, with controlled nanocrystal shape, size, uniformity, and morphology. These advances have led to the discovery of new phenomena and further expansion of the properties and potential applications of transparent metal oxides.⁹ Examples include the generation of localized surface plasmon resonance in TCO nanocrystals (NCs),¹⁵⁻¹⁷ room-temperature ferromagnetism in diluted

magnetic semiconductor oxide (DMSO) NCs,^{6, 18-22} size- and composition-tunable light emission,²³⁻²⁵ and selective and efficient photocatalysts.²⁶⁻³⁰

Among transparent metal oxides, Ga₂O₃ is considered the widest band gap semiconductor. Although the first systematic studies of Ga₂O₃ were reported back in 1950's and 1960's,^{7, 31, 32} it has been much less investigated over the ensuing decades compared to other oxides, such as ZnO, TiO₂, or SnO₂. However, it has recently attracted a significant attention in microelectronics community as a potential alternative to silicon, particularly in high-power and high-voltage applications.³³ The promise of Ga₂O₃ in microelectronics stems for a wide range of achievable conductivities (from metallic to insulating), as well as a high breakdown voltage enabled by the critical electric field strength. Gallium oxide is also characterized by persistent luminescence (often referred to as afterglow),^{12, 34} making it attractive for applications in photonics and lighting. Recent progress in the synthesis and investigation of Ga₂O₃ nanostructures has revealed the new ways to stabilize different polymorphs and manipulate their electronic structure and properties. In this review article, we focus on the electronic structure and properties of nanocrystalline Ga₂O₃. Particular emphasis is placed on the investigation of the defect formation and interactions in colloidal NCs using PL spectroscopic techniques. The ability to manipulate the electronic structure of defects opens up significant opportunities for applications in photonics and lighting.

Structure and Properties Gallium Oxide Nanocrystals

Crystal Structure of Ga₂O₃ Nanocrystals

Gallium oxide is an n-type semiconductor that has exceptionally large band gap, in the excess of 4.5 eV.³² There are 5 different polymorphs of Ga₂O₃, known as α , β , γ , δ , and ϵ phases.⁷

Majority of the studies of bulk Ga_2O_3 have focused on base-centered monoclinic β phase, which is thermodynamically most stable phase at room temperature, and therefore most readily attained.^{35, 36} The unit cell of $\beta\text{-Ga}_2\text{O}_3$ consists of 4 formula units, containing a total of 8 Ga and 12 O atoms (Figure 1a). It belongs to the $C2/m$ space group with the cell constants $a=12.23 \text{ \AA}$, $b=3.04 \text{ \AA}$, $c=5.80 \text{ \AA}$, and $\alpha=\gamma=90^\circ$, and $\beta=103.7^\circ$. Four Ga atoms have tetrahedral (Ga1), and the other four distorted octahedral coordination (Ga2). Other phases can be stabilized under specific conditions, including a treatment of $\beta\text{-Ga}_2\text{O}_3$ at high temperature and pressure. This is the case for bulk corundum-type Ga_2O_3 (α phase),^{37, 38} which is the second most studied polymorph.³⁹ Most of the nanostructured Ga_2O_3 samples have been synthesized by gas-phase methods, such as chemical vapor deposition (CVD) or physical vapor deposition (PVD) with or without a catalyst.⁴⁰⁻⁴⁴ These nanostructures (e.g., nanowires, nanobelts, nanoribbons, nanorods, and nanosheets) typically also have monoclinic crystal structure, similar to bulk.

However, it has been demonstrated that the colloidal synthesis in solution results in the formation of quasi-spherical NCs having cubic crystal structure (γ phase).²³ The reversal in the relative phase stability of different polymorphs at room temperature has been observed for related materials, specifically In_2O_3 , when colloidal NCs are below critical size (ca. 5 nm for In_2O_3).^{5, 45-47} This phenomenon has been associated with surface energy and surface stress effects, which can become dominant contributions to the phase stabilization Gibbs free energy when surface-to-volume ratio of NCs is sufficiently large. In comparison to β phase, $\gamma\text{-Ga}_2\text{O}_3$ has been much less investigated. Rietveld refinement of the neutron diffraction data has revealed that $\gamma\text{-Ga}_2\text{O}_3$ NCs have a defective spinel structure, and adopt $Fd\bar{3}m$ space group with the unit cell constant $a \approx 8.238 \text{ \AA}$ (Figure 1b).⁴⁸ In this lattice Ga(III) ions reside in 4 different sites. In addition to 8 tetrahedral and 16 octahedral sites characteristic for the ideal spinel lattice,

additional 48 tetrahedral and 16 octahedral sites have been identified. The overall octahedral-to-tetrahedral ratio for the refined structure is found to be 1.35.⁴⁸ This complex and inherently defective structure contains both gallium and oxygen vacancies, which critically determine the properties of this system, as we will discuss in the following subsection.

Figure 1. Unit cell structure of (a) β -Ga₂O₃ and (b) γ -Ga₂O₃. Tetrahedral Ga sites are shown as blue spheres, and octahedral Ga sites as red spheres. Oxygen sites are shown as red spheres.

Photoluminescence of Ga₂O₃

First optical studies of β -Ga₂O₃ were performed in 1965, and included optical absorption and photoconductivity measurements.³² These investigations allowed for the basic characterization of the Ga₂O₃ band structure, and established that the β -phase Ga₂O₃ has a band gap of 4.7 eV. A few years later a series of studies of the PL properties of β -Ga₂O₃ have been reported.^{34, 49} These reports have demonstrated blue and green emission in bulk β -Ga₂O₃ samples. Specifically, Herbert et al.⁴⁹ observed a blue emission of nominally undoped Ga₂O₃

after annealing, and a green emission of Si^{4+} - and Zn^{4+} -doped Ga_2O_3 . Although the specific origins of the observed spectral bands were not addressed in those early studies, they were associated with point defects, similarly to other transparent metal oxides. The UV emission of β - Ga_2O_3 has also been reported, although with much lower intensity relative to blue/green emission discussed in this review.^{12, 50} This intrinsic emission has been attributed to the recombination of a conduction-band electron and a self-trapped hole or, conversely, a valence-band hole and a self-trapped electron. Subsequent studies have suggested that the blue/green emission arises from the recombination of an electron trapped in an oxygen vacancy, which acts as a donor site, and a hole trapped in a gallium vacancy or, more likely, gallium-oxygen vacancy pair as an acceptor site.^{12, 51} Before the photon emission the donor and acceptor sites are presumed to be neutral, and the emission process can be described using the following Kröger-Vink notation:

The energy of the emitted photon is then defined as:

$$E = E_{\text{g}} - (E_{\text{D}} + E_{\text{A}}) + \frac{e^2}{4\pi\epsilon r} \quad (2)$$

where E_{g} is the band gap energy, E_{D} and E_{A} , respectively, are the donor and acceptor binding energy, and r is the average separation between donor and acceptor sites. The last term in eq 2 represents a Coulomb attraction between the charged donor and acceptor sites, where e and ϵ are the electron charge and medium permittivity, respectively. This charge recombination mechanism is known as the donor-

acceptor pair (DAP) recombination, and involves a tunnel capture of a donor-trapped electron by an acceptor site as the rate determining step.⁵² This step is responsible for a delayed emission of Ga_2O_3 which follows a non-exponential time-decay.¹² Colloidal Ga_2O_3 NCs dispersed in a non-polar organic solvent have also shown a strong blue-green emission,^{23, 53} suggesting that charge recombination mechanism in γ phase is analogous to that in β -phase Ga_2O_3 (Figure 2).

Surprisingly, this afterglow has been found to be dependent on the NC size and synthesis conditions,^{54, 55} despite that fact that Ga_2O_3 NCs do not exhibit quantum confinement in the available size regime (ca. 3-5 nm diameter NCs).

Figure 2. Schematic illustration of the charge carrier pathways resulting in blue DAP emission of γ - Ga_2O_3 NCs. Solid arrows indicate carrier trapping and dashed arrows carrier detrapping processes. Details of the emission mechanism are given in the text.

Size-Dependent Defect Interactions and Photoluminescence Properties of Ga₂O₃

Nanocrystals

The size dependence of the γ -Ga₂O₃ NC emission is a complex phenomenon which is predominantly attributed to the DAP interactions.⁵⁵ As the Coulomb interaction between oppositely charged defect sites is inversely proportional to their separation, a decrease in the distance between donors and acceptors causes a blue shift in the DAP emission energy. This correlation between the defect separation and the radiative DAP recombination allows for an effective tuning of the NC emission by modulating the synthesis conditions.^{23, 54} Specifically, reduced DAP separation can be achieved by adjusting the colloidal synthesis parameters such as reaction time and temperature. For example, synthesis at lower temperatures yields smaller average NC sizes.^{23, 55} It has been shown that with decreasing NC size DAP PL band shifts to higher energies and narrows down (Figure 3a,b), which has been associated with the reduction in the average and maximum donor-acceptor separation, respectively. The effect of the reaction time on the PL properties of γ -Ga₂O₃ NCs has also been investigated. A study by Wang et al.⁵⁴ compared the PL spectra of Ga₂O₃ NCs obtained for the same reaction temperatures (220 °C) but different durations, and observed ca. 40% decrease in the PL intensity for 30 hr compared to 1 hr synthesis (Figure 3c). This decrease in intensity was accompanied by a slight red shift of the DAP PL band. These results imply that Ga₂O₃ NCs undergo kinetic annealing in the solution phase and the subsequent reduction in defect concentration with increasing reaction time. The atmosphere or environment in which the reaction takes place also affects the PL properties of Ga₂O₃ NCs (Figure 3d).⁵⁴ As discussed above, PL of γ -Ga₂O₃ NCs depends on oxygen vacancies acting as electron traps. The amount of oxygen vacancies can be increased by performing NC synthesis in a reducing environment; conversely, an oxidizing environment decreases the

concentration of oxygen vacancies. By increasing the concentration of oxygen vacancies, the quantum yield of Ga_2O_3 NC emission is increased, and the DAP PL band is slightly blue-shifted.⁵⁴

Figure 3. (a) 300 K PL spectra of $\gamma\text{-Ga}_2\text{O}_3$ NCs ranging from 3.3 to 6.0 nm upon NC band edge excitation.²³ (b) Photograph of colloidal 3.3 and 6.0 nm $\gamma\text{-Ga}_2\text{O}_3$ NCs illuminated with 250 nm light.²³ (c) 300 K PL spectra of $\gamma\text{-Ga}_2\text{O}_3$ NCs synthesized in argon at 220 °C for 1 (red), 7 (green) and 30 h (blue).⁵⁴ (d) Integrated PL intensity of colloidal Ga_2O_3 NCs as a function of synthesis time in different chemical environments at 220 °C.⁵⁴

Oxygen vacancy concentration is also directly related to the lifetime of the NC blue emission. The DAP recombination in Ga_2O_3 occurs in three steps following an excitation above the band edge: 1) an electron trapping on a donor site and hole trapping on an acceptor site, 2) electron tunnel transfer from the donor to the acceptor, resulting in the formation of a bound electron-hole pair, 3) radiative recombination of the electron-hole pair on the acceptor site. The

rate determining process in the DAP emission is the tunnel transfer of the electron captured by a donor site, which is dependent on the distance between the donor and the corresponding acceptor. Variable separation between distant pairs gives rise to the long afterglow and non-exponential PL decay curves. The DAP radiative recombination rate decreases exponentially with increasing donor-acceptor distance. On the basis of this dependence Thomas et al.⁵² developed a model for the kinetics of DAP recombination for an ensemble of donor-acceptor pairs. This model has provided an excellent agreement with the measured emission intensity as a function of time after the excitation pulse for bulk β -Ga₂O₃ in which minority defects (acceptors) are surrounded by majority defects (donors).¹² We have further modified this kinetic model to simulate the PL time-decay data for Ga₂O₃ NCs for different spatial distribution of defects and exclusion volume around the acceptor where donors cannot be located.^{56, 57} In that context we considered two extreme cases – one in which multiple donors and a single acceptor are all located on the surface of a spherical particle (2D model), and the other in which a single acceptor is located in the center of a spherical particle and multiple donors are randomly distributed within the sphere (3D model).⁵⁶ The best fits to the PL decay profiles for different NC sizes suggest that the optimal exclusion distance is surprisingly large (ca. 1 nm),⁵⁷ with a possible tendency for defects to form in the vicinity of NC surfaces.

The ability to conveniently manipulate the defect formation in Ga₂O₃ NCs by adjusting the reaction parameters, such as temperature, time, and environment, allows for tuning the PL properties of Ga₂O₃ NCs to enhance their applicability as a nanomaterial. Importantly, Ga₂O₃ NCs can also be dispersed in condensed media such as polymer films and optical glasses. Golubev et al.⁵⁸ have demonstrated that γ -Ga₂O₃ NCs can be formed in Ga-containing alkali-germanosilicate glasses (Figure 4, inset). The NCs retain efficient light emission in the fully

transparent glass medium, allowing for the fabrication of UV-to-visible solar blind converters (Figure 4).

Figure 4. PL spectra of heat-treated glasses prepared from 50 cm³ (dashed line) and 250 cm³ (solid line) molten glass volume. Scaling up the volume to achieve sizes comparable to the commercial UV-viewers did not significantly change the quality of glass or the Ga₂O₃ DAP emission characteristics. The excitation wavelength is 250 nm.⁵⁸

Doping and Alloying Ga₂O₃ Nanocrystals

Intentional and controlled incorporation of foreign element impurities is an effective way to modulate the electronic structure and PL properties of semiconductor materials. The elemental impurities may either substitute for host lattice sites or occupy interstitial spaces. Incorporation of the relatively small amounts of impurities is referred to as doping, while the incorporation of foreign elements in a large concentration results in the formation of mixed semiconductor lattices. Semiconductor alloys typically refer to mixed semiconductors obtained by replacing host lattice ions by impurity ions having identical valence state.

In situ doping of colloidal NCs during their growth in solution has attracted much attention over the past two decades. Despite many challenges of doping NCs⁵⁹ caused, in part, by the large surface area of NCs and a tendency for dopant ions to segregate on NC surfaces, significant progress has been achieved. For detailed discussion on this topic we refer a reader to selected review articles that have been published in recent years.⁶⁰⁻⁶² In this article we will review representative examples of lanthanide dopants, as luminescence centers, in Ga₂O₃ NCs. Substitutional doping of lanthanides can introduce localized energy levels into the Ga₂O₃ band gap that undergo radiative recombination. On the other hand, substitutional incorporation of metal ions having relatively high solubility in the host lattice can substantially alter its electronic structure through energy level delocalization. This phenomenon allows for compositional tuning of the Ga₂O₃ DAP PL band.

Lanthanide-Doped Ga₂O₃ Nanocrystals

Lanthanide(III) ions are perhaps the most prominent example of substitutional dopants with localized electronic states. The electrons in 4f orbitals of lanthanide(III) dopants are shielded by fully occupied outer shells, making intra-4f PL transitions largely independent of the local coordination. Hence, the f-f emission peaks of lanthanide(III) dopants centers are sharp and resistant to photon-induced degradation. In addition, they have a lifetime on the order of microseconds to milliseconds, which can be attributed to the parity-forbidden nature of the f-f transitions. Owing to these unique properties, lanthanide-based solid-state materials have found diverse applications in telecommunication (as optical amplifiers), lasers (as optical gain media), lighting (as phosphors), and biotechnology (as luminescent probes in biological assays).⁶³ One of the negative consequences of parity-forbidden character of intra-4f transitions in lanthanide(III) ions is a small extinction coefficient and low absorptivity. An effective sensitization of

lanthanide dopants in semiconductors is usually achieved by energy transfer from the host lattice upon band-edge excitation.⁶³ Wide-band-gap semiconductors are particularly good host lattices because lanthanide(III) dopant emission intensity increases with the band gap energy.⁶⁴ Furthermore, transparent metal oxides tend to have higher chemical stability and charge carrier concentration relative to typical semiconductors, making lanthanide doped TCOs attractive optoelectronic materials.

Guided by those opportunities, bulk lanthanide-doped β -Ga₂O₃ samples have been grown by different methods, such as radio-frequency magnetron sputtering, ion implantation, pulsed laser deposition, and spray pyrolysis.⁶⁵⁻⁶⁹ Several lanthanide dopant ions, including Eu³⁺, Er³⁺, Tb³⁺, Tm³⁺, Pr³⁺, and Dy³⁺ have shown strong sensitization by the Ga₂O₃ host lattice.^{65-68, 70} Consequently, narrow PL bands from blue to near-infrared spectral range, arising from dopant intra-4f transitions, have been observed upon Ga₂O₃ band gap excitation. The combination of the unique properties of Ga₂O₃ and the possibility to sensitize rare-earth dopant ions through the band gap excitation allows for a range of possible applications of lanthanide-doped Ga₂O₃. As an example, Er³⁺-doped Ga₂O₃ thin films have been found to exhibit both photoconductance and Er³⁺ $^4I_{13/2} \rightarrow ^4I_{15/2}$ near-infrared emission upon excitation with UV light, making them very promising for the design of dual-mode deep-UV photodetectors.⁶⁹

Figure 5. (a) Schematic of possible mechanisms of energy transfer from $\gamma\text{-Ga}_2\text{O}_3$ NC host to Eu^{3+} and Tb^{3+} dopants including energy levels diagram for Eu^{3+} and Tb^{3+} ions with emission lines. (b) CIE 1931 chromaticity diagram indicating the coordinates of emission from undoped and lanthanide-doped Ga_2O_3 NCs. Codoped sample has chromaticity coordinates corresponding to white light.⁷¹

The recent advancements in the preparation and doping of colloidal NCs have further expanded the range of possible applications of lanthanide-doped Ga_2O_3 . These efforts have partly been motivated by the size-dependent structure and properties of metal oxides and the possibility of convenient integration of colloidal NCs into functional structures and devices. Similar to bulk lanthanide-doped Ga_2O_3 systems, effective dopant sensitization has been demonstrated in their NC counterparts.⁷¹⁻⁷⁴ As a result, simultaneous host lattice DAP and dopant 4f-4f emissions have been achieved upon Ga_2O_3 NC band gap excitation. The combination of blue (Ga_2O_3), green (Tb^{3+}), and red (Eu^{3+}) emission in Eu^{3+} and Tb^{3+} co-doped $\gamma\text{-Ga}_2\text{O}_3$ NCs upon UV excitation can generate bright white light,⁷¹ which has promising applications in lighting and displays (Figure 5). Gallium oxide NCs also have a relatively strong non-linear absorption coefficient, making it possible to obtain narrow band emissions corresponding to

lanthanide f-f transitions upon two-photon absorption processes in Eu^{3+} or Tb^{3+} -doped $\gamma\text{-Ga}_2\text{O}_3$ NCs.⁷¹ Consequently, lanthanide-doped Ga_2O_3 NCs have a considerable potential as nonlinear markers. Furthermore, certain lanthanide dopants can exist in different oxidation states, allowing for further manipulation of the optical properties of Ga_2O_3 NCs. Specifically, controlled *in situ* reduction of Eu^{3+} to Eu^{2+} during the synthesis of Eu-doped Ga_2O_3 NCs has been demonstrated.⁷³ Oxygen vacancies, which are responsible for the DAP emission, have also been proposed to play a crucial role in stabilizing Eu^{2+} . The resulting europium dual emission (Eu^{3+} and Eu^{2+}) in conjunction with the Ga_2O_3 luminescence can allow for the design and preparation of new complex photonic and light emitting materials, including the materials for applications in X-ray storage and counterfeiting. Some lanthanide dopants, such as Dy^{3+} , can also form additional electron trap states in Ga_2O_3 NCs which promote electrons to the conduction band with a delay, leading to an extension of the DAP afterglow.⁷⁵

Aliovalently-Doped Ga_2O_3 Nanocrystals

Aliovalent impurities are ions which have a different oxidation state from the native host lattice ions which they replace. Incorporation of aliovalent dopants causes the formation of new energy levels which are usually located within the band gap.^{76, 77} Substituting host lattice cations with higher oxidation-state cations results in the formation of new energy levels below the conduction band minimum (donor states). On the other hand, substituting host cations with cations having a lower oxidation state causes the formation of localized energy levels above the valence band minimum (acceptor states). Introducing aliovalent dopants can, therefore, provide free electrons (n-type doping) or holes (p-type doping) in a host material, affecting its optical, electrical, and morphological properties. Given the role of the donor and acceptor states in DAP recombination, aliovalent doping is expected to significantly influence the PL properties of

Ga₂O₃. Unfortunately, aliovalent dopants typically have low solubility in Ga₂O₃. Titanium(IV) can be incorporated up to 5 atom % by preferentially occupying octahedral sites in β -Ga₂O₃.⁷⁸ These dopants form deep donor states in the host lattice and induce a small red shift in the band edge absorption, attesting to the change in the electronic structure of the β -Ga₂O₃ lattice. Similarly, an increase in the concentration of n-type carriers (electrons) has been observed for Sn⁴⁺-doped Ga₂O₃ with increasing doping concentration.⁷⁹ This correlation suggests the formation of donor states by substitution of octahedral Ga³⁺ with Sn⁴⁺,⁸⁰ analogously to the well-known case of Sn⁴⁺-doped In₂O₃ (ITO) NCs.⁸¹

On the other hand, substitutional doping of Ga₂O₃ with Zn²⁺ introduces acceptor states which are located ca. 0.26 eV above the valence band maximum.⁸² This electronic configuration gives rise to a complex PL spectrum, consisting of ultraviolet (UV), blue (BL₁ and BL₂), and green (GL) luminescence (Figure 6).⁸² While UV emission has been attributed to the recombination of an electron in the conduction band with a self-trapped hole, both BL and GL bands originate from the dopant-related defect states. The two blue bands with the emission peaks at 415 nm (BL₁) and 455 nm (BL₂) have been assigned to electron transitions from oxygen vacancy (V_O) donor states to the valence band, and DAP recombination between V_O (donor) and Zn²⁺ substitutional dopant site (acceptor), respectively, while GL has been assigned to phonon replicas' emission of BL₂.

Figure 6. Cathodoluminescence spectra of undoped Ga_2O_3 film (trace a), and Zn^{2+} -doped Ga_2O_3 films with nominal Zn content of 3 at% (trace b), 5 at% (trace b), and 7 at% (trace c).⁸²

Recently reported study on colloidal gallium tin oxide (GTO) NCs represents a powerful example how the principles of aliovalent doping can be used to design light emitting materials and devices with targeted lighting characteristics.²⁵ As discussed above, substituting Sn^{4+} for Ga^{3+} in Ga_2O_3 fosters the formation of donor states. Conversely, aliovalent doping of SnO_2 with Ga^{3+} induces additional acceptor centers within the band gap of SnO_2 . The ability to control defect states in GTO NCs by aliovalent doping of either Ga_2O_3 or SnO_2 NCs allows for a broad tunability throughout the entire visible range, despite the low miscibility of the corresponding dopant impurity. The quantum efficiency also changes with NC composition. The maximum value of the quantum yield is achieved for highest doping concentration in Ga_2O_3 or SnO_2 lattices, consistent with the expected increase in the DAP recombination rate with an increase in either donor or acceptor concentration. The ability to precisely tune the PL energy together with band broadening allows for modulation of the lighting characteristics. One of the most effective ways to optimize the performance of the lighting devices is to adjust the scotopic to photopic (S/P) ratio of the active phosphor. Light sources with S/P values of ca. 2.5 can operate at lower

power, and hence are generally considered to be most efficient. Given the extent of DAP PL band broadening, and the ability to broadly tune the DAP emission energy of GTO NCs by changing the composition, optimal S/P can be readily achieved (Figure 7), making this material attractive for the fabrication of tunable LEDs and other lighting applications.

Figure 7. PL spectrum of optimized GTO NCs (green trace) covering both scotopic (S, blue trace) and photopic (P, red trace) luminosity functions. The function corresponding to S/P of 2.5 is shown as a brown trace. Inset: Photograph of the emission of colloidal GTO NCs excited into the GTO NC band gap.²⁵

Alloyed Ga_2O_3 Nanocrystals

Alloyed semiconductors offer the possibility to tune their electronic structure and properties with composition in addition to size. This approach has been particularly common for II-VI and III-V compound semiconductors, for which both cation and anion compositions could be controlled in a wide range.⁸³⁻⁸⁴ Alloyed group 13 (boron group) metal oxides have also been explored, although to a lesser degree.⁸⁵⁻⁸⁶ The prospects of controlling the optical properties of Ga_2O_3 NCs via composition modulation appear particularly attractive, given the lack of quantum confinement effect for Ga_2O_3 in the NC size regime achievable by colloidal synthesis.²³ Farvid et

al.⁸⁷ have reported a colloidal synthesis of mixed gallium indium oxide (GIO) NCs with varying crystal structure and Ga/In composition ratio, and demonstrated compositional dependence of their PL properties. The XRD patterns for mixed GIO NCs with different In content (from 0 to 100 %) is shown in Figure 8a. As the indium content increases the NC structure gradually changes from γ -Ga₂O₃ and *rh*-In₂O₃ (corundum-type In₂O₃), with both phases coexisting for intermediate compositions. Figure 8b shows the absorption spectra of GIO NCs having different compositions. The absorption spectra shift to lower energy with increasing In content indicating a decrease in the band gap energy. This phenomenon is accompanied by a red shift of the DAP PL band, allowing for a broad composition-induced emission tunability in the visible range (Figure 8c). The compositional tunability of the DAP emission energy has largely been attributed to the changes in the electronic states of the donors and acceptors (Figure 8d). More specifically, it has been suggested that the energy levels of the donors and acceptors follow a decrease in the band gap of GIO NCs with increasing amount of In³⁺ ions which tend to occupy octahedral sites in γ -Ga₂O₃ NCs. While pure γ -Ga₂O₃ NCs show purple emission, increasing indium content changes the emission color to blue-green for GIO NCs, and eventually to orange-red for pure corundum-type In₂O₃ NCs, as depicted in Figure 8e. Such broad tunability renders these GIO NCs promising materials for phosphors and optoelectronic devices, including tunable LEDs.

Figure 8. XRD patterns of GIO NCs having different In content, as indicated in the graph. The vertical lines represent XRD patterns of bulk γ -Ga₂O₃ (bottom, JCPDS 20-0426) and rh -In₂O₃ (top, JCPDS 21-0406). (b,c) Absorption (b) and PL (c) spectra of GIO NCs with varying atom % In content: 0 % (purple), 13 % (blue), 24 % (green), 47 % (olive), 84 % (orange), and 100 % (red). (d) Schematic of the possible origin of PL in pure γ -Ga₂O₃ NCs (left) and GIO NCs with a γ -Ga₂O₃ structure (right). The DAP recombination is indicated by arrows, and the labels correspond to the defect species described in the text. (e) Photograph of γ -Ga₂O₃ (left), GIO (24 at % In, middle), and rh -In₂O₃ (right) NCs.

Summary and Outlook

This review article showcases some recent progress on controlling the optical properties of Ga₂O₃ NCs for potential applications in photonics and lighting. At the heart of the PL properties of Ga₂O₃ is the native defect formation and interactions, which are dependent of the materials size, crystal structure, and composition. Therefore, by defect engineering via synthesis conditions and post-synthesis treatment, the physical, structural, and optical properties of gallium oxide can be manipulated for targeted applications. Furthermore, substitutional doping of Ga₂O₃

NC lattice with different metal ions changes the energy of the donor and acceptor states and Coulomb interactions. Doping with lanthanide ions also introduces localized intra-ionic energy levels that can impart new PL properties into colloidal Ga₂O₃ NCs. For high concentration of isovalent metal impurities (such as In³⁺) in Ga₂O₃ NCs the PL emission of the resulting mixed-compound NCs can be tuned over a broad spectral region. Although not a subject of this review, the PL properties of Ga₂O₃ NCs can also be expanded by functionalization of NCs with organic dye molecules with desired emission characteristics.⁸⁸

To improve the tunability and functionalization of Ga₂O₃ NCs in the future, well-designed synthetic methods and advanced characterization techniques must be used. Furthermore, the knowledge about defect engineering gained from the studies on colloidal Ga₂O₃ NCs can in principle also be used for other TCOs, opening the doors for future applications. The recent reports on nanocrystalline Ga₂O₃ have also demonstrated that this material is highly promising for a range of other applications, including photocatalysis, white-light-emitting phosphors, and UV sensitizers. The utility and versatility of this, once largely neglected material, in conjunction with the recent developments discussed in this Review article, highlight its remarkable potential. Despite the significant progress, we believe there will be many more exciting new developments in chemistry, physics, and application of Ga₂O₃ NCs in years to come.

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References

- (1) Hamberg, I.; Granqvist, C. G. *J. Appl. Phys.* **1986**, *60*, R123.
- (2). Fortunato, E.; Ginley, D.; Hosono, H.; Paine, D. C. *MRS Bul.* **2007**, *32*, 242.
- (3). Lewis, B. G.; Paine, D. C. *MRS Bull.* **2000**, *25*, 22.
- (4) Gurlo, A.; Kroll, P.; Riedel, R. *Chem. Eur. J.* **2008**, *14*, 3306.
- (5) Farvid, S. S.; Dave, N.; Radovanovic, P. V. *Chem. Mater.* **2010**, *22*, 9.
- (6) Farvid, S. S.; Hegde, M.; Radovanovic, P. V. *Chem. Mater.* **2013**, *25*, 233.
- (7) Roy, R.; Hill, V. G. *J. Am. Chem. Soc.* **1952**, *74*, 719.
- (8) Zhang, H.; Banfield, J. F. *J. Mater. Chem.* **1998**, *8*, 2073.
- (9) Radovanovic, P. V. Defect-Induced Optical and Magnetic Properties of Colloidal Transparent Conducting Oxide Nanocrystals. In *Functional Metal Oxides*, Ogale, S. B.; Venkatesan, T. V.; Blamire, M. G., Eds. Wiley-VCH: Weinheim, 2013; pp 163-194.
- (10) Kilic, C.; Zunger, A. *Phys. Rev. Lett.* **2002**, *88*, 095501.
- (11) Walsh, A. *Appl. Phys. Lett.* **2011**, *98*, 261910.
- (12) Binet, L.; Gourier, D. *J. Phys. Chem. Solids.* **1998**, *59*, 1241.
- (13) Das, S.; Ghorai, U. K.; Dey, R.; Ghosh, C. K.; Pal, M. *Phys. Chem. Chem. Phys.* **2017**, *19*, 22995.
- (14) Gu, F.; Wang, S. F.; Lü, M. K.; Cheng, X. F.; Liu, S. W.; Zhou, G. J.; Xu, D.; Yuan, D. R. *J. Cryst. Growth.* **2004**, *262*, 182.
- (15) Wang, T.; Radovanovic, P. V. *J. Phys. Chem. C.* **2011**, *115*, 406.

- (16) Buonsanti, R.; Llordes, A.; Aloni, S.; Helms, B. A.; Milliron, D. J. *Nano Lett.* **2011**, *11*, 4706.
- (17) Nutz, T.; zum Felde, U.; Haase, M. *J. Chem. Phys.* **1999**, *110*, 12142.
- (18) Farvid, S. S.; Ju, L.; Worden, M.; Radovanovic, P. V. *J. Phys. Chem. C* **2008**, *112*, 17755.
- (19) Radovanovic, P. V.; Gamelin, D. R. *Phys. Rev. Lett.* **2003**, *91*, 157202.
- (20) Dave, N.; Pautler, B. G.; Farvid, S. S.; Radovanovic, P. V. *Nanotechnology* **2010**, *21*, 134023.
- (21) Sundaresan, A.; Bhargavi, R.; Rangarajan, N.; Siddesh, U.; Rao, C. N. R. *Phys. Rev. B* **2006**, *74*, 161306(R).
- (22) Garnet, N. S.; Ghodsi, V.; Hutflus, L. N.; Yin, P.; Hegde, M.; Radovanovic, P. V. *J. Phys. Chem. C* **2017**, *12*, 1918.
- (23) Wang, T.; Farvid, S. S.; Abulikemu, M.; Radovanovic, P. V. *J. Am. Chem. Soc.* **2010**, *132*, 9250.
- (24) Layek, A.; Stanish, P. C.; Chirmanov, V.; Radovanovic, P. V. *Chem. Mater.* **2015**, *27*, 1021.
- (25) Ghodsi, V.; Radovanovic, P. V. *Chem. Mater.* **2018**, *30*, 3578.
- (26) Ghodsi, V.; Jin, S.; Byers, J. C.; Pan, Y.; Radovanovic, P. V. *J. Phys. Chem. C* **2017**, *121*, 9433.
- (27) Jin, S.; Lu, W.; Stanish, P. C.; Radovanovic, P. V. *Chem. Phys. Lett.* **2018**, *706*, 509.
- (28) Kong, M.; Li, Y.; Chen, X.; Tian, T.; Fang, P.; Zheng, F.; Zhao, X. *J. Am. Chem. Soc.* **2011**, *133*, 16414.
- (29) Ghodsi, V.; Lu, W.; Radovanovic, P. V. *J. Phys. Chem. C* **2019**, *123*, 433.
- (30) Sachs, M.; Pastor, E.; Kafizas, A.; Durrant, J. R. *J. Phys. Chem. Lett.* **2016**, *7*, 3742.
- (31) Lorenz, M. R.; Woods, J. F.; Gambino, R. J. *J. Phys. Chem. Solids* **1967**, *28*, 403.

- (32) Tippins, H. H. *Phys. Rev.* **1965**, *140*, 316.
- (33) Higashiwaki, M.; Jessen, G. H. *Appl. Phys. Lett.* **2018**, *112*, 060401.
- (34) Blasse, G.; Bril, A. J. *Phys. Chem. Solids* **1970**, *31*, 707.
- (35) Geller, S. *J. Chem. Phys.* **1960**, *33*, 676.
- (36) Lee, J.; Ganguli, S.; Roy, A. K.; Badescu, S. C. *J. Chem. Phys.* **2019**, *150*, 174706.
- (37) Remeika, J. P.; Marezio, M. *Appl. Phys. Lett.* **1966**, *8*, 87.
- (38) Foster, L. M.; Stumpf, H. C. *J. Am. Chem. Soc.* **1951**, *73*, 1590.
- (39) He, H.; Orlando, R.; Blanco, M. A.; Pandey, R.; Amzallag, E.; Baraille, I.; Rerat, M. *Phys. Rev. B* **2006**, *74*, 195123.
- (40) Choi, Y. C.; Kim, W. S.; Park, Y. S.; Lee, S. M.; Bae, D. J.; Lee, Y. H.; Park, G.-S.; Choi, W. B.; Lee, N. S.; Kim, J. M. *Adv. Mater.* **2000**, *12*, 746.
- (41) Hosein, I. D.; Hegde, M.; Jones, P. D.; Chirmanov, V.; Radovanovic, P. V. *J. Cryst. Growth* **2014**, *396*, 24.
- (42) Maximenko, S. I.; Mazeina, L.; Picard, Y. N.; Freitas Jr., J. A.; Bermudez, V. M.; Prokes, S. M. *Nano Lett.* **2009**, *9*, 3245.
- (43) Wang, G.; Park, J.; Kong, X.; Wilson, P. R.; Chen, Z.; Ahn, J.-h. *Cryst. Growth Des.* **2008**, *8*, 1940.
- (44) Vanithakumari, S. C.; Nanda, K. K. *Adv. Mater.* **2009**, *21*, 3581.
- (45) Farvid, S. S.; Dave, N.; Wang, T.; Radovanovic, P. V. *J. Phys. Chem. C* **2009**, *113*, 15928.
- (46) Farvid, S. S.; Radovanovic, P. V. *J. Am. Chem. Soc.* **2012**, *134*, 7015.
- (47) Hutflus, L. N.; Radovanovic, P. V. *J. Am. Chem. Soc.* **2015**, *137*, 1101.
- (48) Playford, H. Y.; Hannon, A. C.; Tucker, M. G.; Dawson, D. M.; Ashbrook, S. E.; Kastiban, R. J.; Sloan, J.; Walton, R. I. *J. Phys. Chem. C* **2014**, *118*, 16188.

- (49) Herbert, W. C.; Minnier, H. B.; Brown, Jr., J. J. *J. Electrochem. Soc.* **1969**, *116*, 1019.
- (50) Harwig, T.; Kellendonk, F.; Slappendel, S. *J. Phys. Chem. Solids.* **1978**, *39*, 675.
- (51) Harwig, T.; Kellendonk, F. *J. Solid State Chem.* **1978**, *24*, 255.
- (52) Thomas, D. G.; Hopfield, J. J.; Augustyniak, W. M. *Phys. Rev.* **1965**, *140*, A202.
- (53) Chen, T.; Tang, K. *Appl. Phys. Lett.* **2007**, *90*, 053104.
- (54) Wang, T.; Radovanovic, P. V. *Chem. Commun.* **2011**, *47*, 7161.
- (55) Wang, T.; Radovanovic, P. V. *J. Phys. Chem. C.* **2011**, *115*, 18473.
- (56) Hegde, M.; Wang, T.; Miskovic, Z. L.; Radovanovic, P. V. *Appl. Phys. Lett.* **2012**, *100*, 141903.
- (57) Fernandes, B.; Hegde, M.; Stanish, P. C.; Mišković, Z. L.; Radovanovic, P. V. *Chem. Phys. Lett.* **2017**, *684*, 135.
- (58) Golubev, N. V.; Ignat'eva, E. S.; Ziyatdinova, M. Z.; Sigaev, V. N. *Glass Ceram.* **2021**, *77*, 412.
- (59) Erwin, S. C.; Zu, L.; Haftel, M. I.; Efros, A. L.; Kennedy, T. A.; Norris, D. J. *Nature.* **2005**, *436*, 91.
- (60) Norris, D. J.; Efros, A. L.; Erwin, S. C. *Science.* **2008**, *319*, 1776.
- (61) Bryan, J. D.; Gamelin, D. R. *Prog. Inorg. Chem.* **2005**, *54*, 47.
- (62) Buonsanti, R.; Milliron, D. J. *Chem. Mater.* **2013**, *25*, 1305.
- (63) Eliseeva, S. V.; Bunzli, J.-C. G. *Chem. Soc. Rev.* **2010**, *39*, 189.
- (64) Liu, Y.; Luo, W.; Zhu, H.; Chen, X. *J. Lumin.* **2011**, *131*, 415.
- (65) Peres, M.; Lorenz, K.; Alves, E.; Nogales, E.; Méndez, B.; Biquard, X.; Daudin, B.; Villora, E. G.; Shimamura, K. *J. Phys. D: Appl. Phys.* **2017**, *50*, 325101.

- (66) Gollakota, P.; Dhawan, A.; Wellenius, P.; Lunardi, L. M.; Muth, J. F.; Saripalli, Y. N.; Peng, H. Y.; Everitt, H. O. *Appl. Phys. Lett.* **2006**, *88*, 221906.
- (67) Li, W.; Peng, Y.; Wang, C.; Zhao, X.; Zhi, Y.; Yan, H.; Li, L.; Li, P.; Yang, H.; Wu, Z.; Tang, W. *J. Alloys Compd.* **2017**, *697*, 388.
- (68) Hao, J.; Cocivera, M. *J. Phys. D: Appl. Phys.* **2002**, *35*, 433.
- (69) Wu, Z.; Bai, G.; Qu, Y.; Guo, D.; Li, L.; Li, P.; Hao, J.; Tang, W. *Appl. Phys. Lett.* **2016**, *108*, 211903.
- (70) Sommerdijk, J. L.; Bril, A. *J. Electrochem. Soc.* **1975**, *122*, 952.
- (71) Wawrzynczyk, D.; Nyk, M.; Samoc, M. *Chem. Phys.* **2015**, *456*, 73.
- (72) Wang, T.; Layek, A.; Hosein, I. D.; Chirmanov, V.; Radovanovic, P. V. *J. Mater. Chem. C.* **2014**, *2*, 3212.
- (73) Layek, A.; Yildirim, B.; Ghodsi, V.; Hutflus, L. N.; Hegde, M.; Wang, T.; Radovanovic, P. V. *Chem. Mater.* **2015**, *27*, 6030.
- (74) Lorenzi, R.; Paleari, A.; Golubev, N. V.; Ignat'eva, E. S.; Sigaev, V. N.; Niederberger, M.; Lauria, A. *J. Mater. Chem. C.* **2015**, *3*, 41.
- (75) Stanish, P. C.; Yin, P.; Radovanovic, P. V. *Chem. Mater.* **2020**, *32*, 7516.
- (76) Fang, H.; Hegde, M.; Yin, P.; Radovanovic, P. V. *Chem. Mater.* **2017**, *29*, 4970.
- (77) Chen, Z.; Huang, L.; Zhang, Q.; Xi, Y.; Li, R.; Li, W.; Xu, G.; Cheng, H. *J. Phys. Chem. C.* **2015**, *119*, 4789.
- (78) Bandi, M.; Zade, V.; Roy, S.; Nair, A. N.; Seacat, S.; Sreenivasan, S.; Shutthanandan, V.; Van de Walle, C. G.; Peelaers, H.; Ramana, C. V. *Cryst. Growth Des.* **2020**, *20*, 1422.
- (79) Suzuki, N.; Ohira, S.; Tanaka, M.; Sugawara, T.; Nakajima, K.; Shishido, T. *Phys. Status Solidi C* **2007**, *4*, 2310.

- (80) Siah, S. C.; Brandt, R. E.; Lim, K.; Schelhas, L. T.; Jaramillo, R.; Heinemann, M. D.; Chua, D.; Wright, J.; Perkins, J. D.; Segre, C. U.; Gordon, R. G.; Toney, M. F.; Buonassisi, T. *Appl. Phys. Lett.* **2015**, *107*, 252103.
- (81) Zervos, M.; Mihailescu, C. N.; Giapintzakis, J.; Luculescu, C. R.; Florini, N.; Komninou, P.; Kioseoglou, J.; Othonos, A. *APL Mater.* **2014**, *2*, 056104.
- (82) Wang, X. H.; Zhang, F. B.; Saito, K.; Tanaka, T.; Nishio, M.; Guo, Q. X. *J. Phys. Chem. Solids* **2014**, *75*, 1201.
- (83) Cizeron, J.; Pileni, M. P. *J. Phys. Chem. B* **1997**, *101*, 8887.
- (84) Hou, J. J.; Han, N.; Wang, F.; Xiu, F.; Yip, S.; Hui, A. T.; Hung, T.; Ho, J. C. *ACS Nano* **2012**, *6*, 3624.
- (85) Swallow, J. E. N.; Palgrave, R. G.; Murgatroyd, P. A. E.; Regoutz, A.; Lorenz, M.; Hassa, A.; Grundmann, M.; von Wenckstern, H.; Varley, J. B.; Veal, T. D. *ACS Appl. Mater. Interfaces* **2021**, *13*, 2807.
- (86) Cook, D. S.; Hooper, J. E.; Dawson, D. M.; Fisher, J. M.; Thompsett, D.; Ashbrook, S. E.; Walton, R. I. *Inorg. Chem.* **2020**, *59*, 3805.
- (87) Farvid, S. S.; Wang, T.; Radovanovic, P. V. *J. Am. Chem. Soc.* **2011**, *133*, 6711.
- (88) Wang, T.; Chirmanov, V.; Chiu, W. H. M.; Radovanovic, P. V. *J. Am. Chem. Soc.* **2013**, *135*, 14520.