Synthesis of colloidal solution of β -LiGaO₂ nanocrystals capped with organic surfactant

Kazuyuki TAKAHASHI, Yasuhiro MAEDA, Takashi SUEHIRO, Masao KITA* and Takahisa OMATA†

Division of Material and Manufacturing Science, Graduate School of Engineering, Osaka University,
2–1 Yamadaoka, Suita, Osaka 565–0871, Japan

*Department of Mechanical Engineering, Toyama National College of Technology, 13 Hongo-machi, Toyama 939–8630, Japan

We studied a means of synthesizing colloidal nanocrystals (NCs) of β -LiGaO₂, a wide-band gap semiconductor oxide, by reacting lithium hydroxide (LiOH) with gallium tri-iso-propoxide [Ga(OiPr)₃] in benzylamine. This reaction yielded near-stoichiometric β -LiGaO₂ NCs, 4–5 nm in diameter and capped with *n*-octylamine, which were highly dispersible in an organic solvent. We proposed that the LiOH and Ga(OiPr)₃ reacted via electrophilic attack of Li⁺ on the bridging oxygen of Ga(OiPr)₃ and/or nucleophilic attack of OH[−] on the α -carbon of Ga(OiPr)₃. This reaction formed Li–O–Ga bonds and contributed to the near-stoichiometry of the resultant β -LiGaO₂ NCs.

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1. Introduction

The size-dependent optical properties of colloidal semiconductor nanocrystals (NCs) capped with organic surfactant are very attractive as light-emitters and -absorbers in optoelectronic devices.¹⁾ Most studies of colloidal semiconductor NCs have focused on cadmium-based chalcogenides because these materials emit visible light at high intensity. The size-dependent properties of semiconductor NCs, of course, allow for their use in the infrared and ultraviolet (UV) regions, when the NCs consist of materials possessing an appropriate energy band gap. ZnO is one of the materials applicable to UV-light emitting devices because of its wide energy band gap of 3.37 eV;²⁾ however, size-dependent and high-intensity UV emission of colloidal ZnO NCs has not yet been demonstrated.³⁾ According to studies on colloidal CdSe NCs, fabrication of core/shell nanostructure significantly improves their emission intensity because of passivation of surface states, i.e., photoluminescence quantum yield exceeding 80% has been demonstrated for CdSe/ZnSe core/shell NCs.⁴⁾ For the case of ZnO NCs, β -LiGaO₂ with a wurtzite-derived structure has been proposed as a suitable shell material that improves UV emission intensity of ZnO NCs.⁵⁾

Two synthesis routes to colloidal β -LiGaO₂ NCs have been reported so far;⁵⁾ however, these routes cannot be used to form appropriate β -LiGaO₂ shells on ZnO NCs because of the formation of a byproduct that is highly corrosive to ZnO and significant deviation from the stoichiometry of the resultant β -LiGaO₂. To fabricate ZnO/ β -LiGaO₂ core/shell NCs, developing a synthesis route to colloidal β -LiGaO₂ NCs that does not form corrosive byproduct to ZnO, such as alkyl halides,⁵⁾ and achieves stoichiometric composition is extremely important. For this purpose we studied the synthesis of colloidal β -LiGaO₂ NCs capped with organic amines using a reaction between LiOH and Ga(OiPr)₃ in benzylalcohol (BZA), because the byproduct of this

reaction is expected to be 2-propanol that is not corrosive to ZnO based on the mechanism of previous alkyl halide elimination reaction.

2. Experimental

2.1 Chemicals

LiOH (99.995%), Ga(OiPr)₃ (99.9%), BZA (99.5%), oleylamine (OLA, 70%), and *n*-octylamine (OCA, 98%) were acquired from commercial sources. The OLA was purified by distillation before use, while all other chemicals were used without further purification. Water impurities in the BZA, OLA, and OCA were reduced to 50 ppm by molecular sieve to avoid hydrolytic reaction.

2.2 Reaction between LiOH and Ga(OiPr)₃

Prior to studying the reaction between LiOH and Ga(OiPr)₃, we explored organic solvent that dissolves both LiOH and Ga(OiPr)₃ and found that BZA is a suitable solvent. We first dissolved 0.03–0.2 mmol of LiOH and 0.1 mmol of Ga(OiPr)₃ in 3 mL of BZA. After mixing both the lithium- and gallium-source solutions in a glass vial, we held it at room temperature to study the reactivity between LiOH and Ga(OiPr)₃.

To form a colloidal solution of β -LiGaO₂ NCs, we substituted either an OLA or OCA for a portion of the BZA. In this case, 0.12 mmol of LiOH was dissolved in 1.5 mL of BZA; it was then mixed with 1.5 mL of OLA or OCA and heated at 60°C for 1 h. For gallium source solution, we dissolved 0.1 mmol of Ga(OiPr)₃ in 3 mL of OLA. Both the lithium- and gallium-source solutions were mixed in a glass vial, it was then held at room temperature for reaction. The solution was then heated at 100°C for 5 h to ensure that the surfactant capped the surfaces of the NCs.

2.3 Characterization

Powder samples were extracted from the colloidal solution by adding ethanol, washing the precipitate successively with acetone, hexane, ethanol, and methanol, and then drying it under vacuum at room temperature. To identify the crystalline phase, we used

† Corresponding author: T. Omata; E-mail: omata@mat.eng.osaka-u.ac.jp

powder X-ray diffraction (XRD; Rigaku, RINT2500, Cu-K α radiation). The average grain size was evaluated using the Debye–Scherrer equation from the full-width at half-maximum (FWHM) of the (120) diffraction peak of β -LiGaO₂ that is obtained from the left-side FWHM of the peak at $2\theta \sim 32.5^\circ$. The stoichiometries of the β -LiGaO₂ NCs were determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES; SII, SPS7800). High-resolution transmission electron microscopy (HRTEM) was performed with a JEOL JEM-2010 microscope.

3. Results and discussion

We first studied the reactivity between LiOH and Ga(OiPr)₃. We used a lithium-source solution dissolving 0.12 mmol of LiOH in 3 mL of BZA, which produced an atomic ratio ($X_{\text{Li}}/X_{\text{Ga}}$) of 1.2 in the starting solution. Approximately 30 min after we mixed both source solutions, it turned from colorless and transparent to white and turbid. **Figure 1(a)** shows the XRD profile of the resultant powder. Although the diffraction peaks were very broad, we matched all of them to the β -LiGaO₂ phase. Additionally, ICP-AES indicated that the $X_{\text{Li}}/X_{\text{Ga}}$ of the NCs was 1.10; thus, the resultant β -LiGaO₂ NCs were nearly stoichiometric.

The stoichiometry of ternary compounds sometimes depends on the composition of the source solution;^{5),6)} thus, we studied how the stoichiometry changed as we changed the composition of the starting solution. For a starting solution with $X_{\text{Li}}/X_{\text{Ga}} = 0.3$, the product was not β -LiGaO₂ but rather Ga₂O₃; the β -LiGaO₂ phase was only obtained from solutions with $0.5 \leq X_{\text{Li}}/X_{\text{Ga}} \leq 2.0$. For starting solutions with $0.5 \leq X_{\text{Li}}/X_{\text{Ga}} \leq 1.2$, the $X_{\text{Li}}/X_{\text{Ga}}$ of the resultant NCs was nearly constant, in the range of $1.05 \leq X_{\text{Li}}/X_{\text{Ga}} \leq 1.10$. For a starting solution with $X_{\text{Li}}/X_{\text{Ga}} = 2.0$, the $X_{\text{Li}}/X_{\text{Ga}}$ of the resultant NCs was 1.19, slightly Li-rich. These results indicate that the reaction between LiOH and Ga(OiPr)₃ in BZA produces near-stoichiometric β -LiGaO₂ NCs when the starting solution contains approximately equal amounts of lithium and gallium.

Fig. 1. XRD profiles of β -LiGaO₂ NCs obtained from the reaction between LiOH and Ga(OiPr)₃ in BZA (a) without surfactant, (b) with OLA, and (c) with OCA. Profile (d) is of β -LiGaO₂ polycrystalline powder obtained by solid-state reaction between Li₂CO₃ and β -Ga₂O₃ for comparison.

When we added OLA or OCA surfactant, the solution remained colorless and transparent even 30 min after mixing the source solutions and heating at 100°C for 5 h. In this case we identified the resultant NCs as a single phase of β -LiGaO₂, as shown in Figs. 1(b) and 1(c). For NCs produced from solutions with either the OLA or OCA surfactant, the average crystal size of the resultant NCs was ~ 4.5 nm; additionally, we determined their composition to be $X_{\text{Li}}/X_{\text{Ga}} = 1.07$. This value is nearly identical with that for the NCs produced without surfactant, and adding additional surfactant did not affect the stoichiometry of the resultant β -LiGaO₂ NCs. We were able to colloiddally disperse in chloroform the NCs produced from the solution with OCA; however, when we added the NCs produced from the solution with OLA to chloroform, a viscous and gel-like liquid formed. Thus, we conclude that OCA is a suitable surfactant to disperse β -LiGaO₂ NCs in this method, although the mechanism of gel formation for the NCs using OLA surfactant is currently unknown.

Figure 2 shows an HRTEM image of NCs capped with OCA. In this image we see NCs with diameters of 4–5 nm. We also see single-crystalline features with clear fringes discretely spread across the TEM grid; thus, the OCA effectively caps the surfaces of the NCs and prevents their aggregation.

Table 1 summarizes the average crystal sizes and mass yields of β -LiGaO₂ NCs synthesized using various reaction times at room temperature with OCA surfactant. We did not heat the samples to 100°C for 5 h to observe the effect of time held at room temperature. In this case the average crystal size gradually increased over time; however, the yield remained nearly constant at ~ 5.6 mg regardless of holding time. Complete reaction between LiOH and Ga(OiPr)₃ produces 4.5 mg of β -LiGaO₂; thus, masses exceeding 4.5 mg might be attributable to organics not removed by washing. Taking this experimental error into account, these observed yields indicate that all the source material reacted within 15 min, probably immediately, after mixing the source solutions.

In order to apply the NC formation reaction to the core/shell NC fabrication, the shell material has to deposit on seed NCs that consist of core material. This requests heterogeneous nucleation

Fig. 2. HRTEM image of colloidal β -LiGaO₂ NCs obtained from reaction between LiOH and Ga(OiPr)₃ in BZA with OCA as a surfactant.

Table 1. Average crystal size and yield of β -LiGaO₂ NCs synthesized at room temperature for various reaction times. Atomic ratio, $X_{\text{Li}}/X_{\text{Ga}}$, in the starting solution is 1.2, and the surfactant used is OCA in these syntheses

Reaction time at room temperature	Average crystal size, d_{120} /nm	Yield /mg
15 min	3.4	6.1
30 min	3.6	5.8
1 h	4.0	5.6
2 h	4.1	5.2
3 h	4.2	5.4

of shell material at the seed NC surfaces and growth to shell-layer by sequentially precipitation from the reaction solution. For instance, the supersaturation level or reactivity for the formation of the shell material should be suppressed low level, at which homogeneous nucleation of the shell material can be avoided.

In the present β -LiGaO₂ NC formation, almost all lithium and gallium sources reacted immediately after both source solutions mixed based on the yields summarized in Table 1. This indicates that the reactivity between LiOH and Ga(OiPr)₃ is too high to avoid homogeneous nucleation of β -LiGaO₂ phase, i.e., heterogeneous nucleation of β -LiGaO₂ at the core NC surfaces is hardly expected. Actually, according to our preliminary test to fabricate ZnO/ β -LiGaO₂ core/shell NCs using the present reaction, we obtained mixed NCs of ZnO and β -LiGaO₂ and could not obtain core/shell NCs. Therefore, we conclude that the synthesis route described here is difficult to apply to β -LiGaO₂ shell-layer formation on ZnO NCs. The reactivity between LiOH and Ga(OiPr)₃ should be suppressed by controlling source material concentration or adding some complex ligands that increase stability of LiOH and Ga(OiPr)₃.

Finally, we briefly discuss the reaction mechanism. Non-aqueous synthesis of BaTiO₃ using a reaction of alkoxide in BZA that involves similar source materials in the reaction presented here has been previously reported;⁷⁾ in this case, the Ti–O–Ti bond forms via reaction between Ti(OiPr)₄ and BZA, as shown in **Scheme 1(a)**. The crystalline framework of BaTiO₃ is configured as corner-shared TiO₆ octahedra; therefore, the formation of the Ti–O–Ti bond is necessary and sufficient for BaTiO₃ formation. However, the framework of β -LiGaO₂ is configured by alternatively corner-shared LiO₄ and GaO₄ tetrahedra, as illustrated in Fig. 1 in Ref. 6. This structural feature requires the formation of Li–O–Ga bonds. The formation reaction of β -LiGaO₂, in this sense, must have been triggered by LiOH attacking the Ga(OiPr)₃ and vice versa. The electrophilic attack of Li⁺ on the bridging oxygen of Ga(OiPr)₃ and/or nucleophilic attack of OH[−] on the α -carbon in Ga(OiPr)₃, as indicated in Scheme 1(b), is a plausible reaction. This reaction forms Li–O–Ga bonds and should contribute to the near-stoichiometry of the resultant β -LiGaO₂ NCs.

4. Conclusion

We developed a means of synthesizing colloidal solution of β -LiGaO₂ NCs by reacting LiOH and Ga(OiPr)₃. Using this process, we obtained near-stoichiometric β -LiGaO₂ NCs capped with *n*-octylamine, which are highly dispersible in chloroform. The reactivity between LiOH and Ga(OiPr)₃ is too high to avoid homogeneous nucleation of β -LiGaO₂ phase, i.e., heterogeneous nucleation of β -LiGaO₂ at the core NC surfaces is hardly expected; therefore, the present method is not applicable when

Scheme 1. Proposed formation reaction mechanism of (a) BaTiO₃ NCs in ⁷⁾ and (b) the β -LiGaO₂ NCs for the present method.

fabricating ZnO/ β -LiGaO₂ core/shell nanostructures. Thus, we still require developing a synthesis route to β -LiGaO₂ NCs that is applicable to forming a shell on ZnO NCs.

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