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Formation of complete solid solutions, $Zn(Al_xGa_{1-x})_2O_4$ spinel nanocrystals via hydrothermal route

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Abstract

Spinel-structured complete solid solutions: $Zn(Al_xGa_{1-x})_2O_4$, $x=0$–1.0 were directly formed as nanocrystals from the aqueous precursor solutions of inorganic metal salts under hydrothermal conditions at 240 °C for 5 h in the presence of tetramethylammonium hydroxide. The crystallite size of the spinel varied from 14.5 to 5 nm with increased Al atomic ratio, x in the composition from $x=0$ to 1.0. The linear decrease in the lattice parameter of the spinel phase by the substitutional incorporation of Al into the lattice nearly followed the Vegard's law though a slight positive departure from the law was observed. The incorporation of Al into the lattice, $Zn(Al_xGa_{1-x})_2O_4$ resulted in wider optical band gap due to the blue shift of absorption spectra. The broad-band UV–visible blue light emission centered at around 480 nm that was observed under excitation at 270 nm Xe lamp in the $ZnGa_2O_4$ spinel showed blue shift by the incorporation of Al into the lattice, $Zn(Al_xGa_{1-x})_2O_4$.

Keywords: D. Spinel; $ZnAl_2O_4$; $ZnGa_2O_4$; Solid solution; Hydrothermal synthesis

1. Introduction

Materials based on the spinel structure, AB_2O_4, which can be described by means of a cubic close packed arrangement of anions with one-half of the octahedral holes and one-eighth of the tetrahedral holes occupied by cations, possess high potentials and unique properties and have played an important part in various uses, e.g. the optical [1], magnetic [2], biomagnetic [3], electrochemical [4], electrocatalytic [5], and catalytic [6] fields of applications. Zinc aluminate ($ZnAl_2O_4$) and zinc gallate ($ZnGa_2O_4$) have the same spinel structure of AB_2O_4 which belong to the wide-band-gap semiconductor materials [7], e.g. ZnO, In_2O_3, and SnO_2. Both of $ZnAl_2O_4$ and $ZnGa_2O_4$ are known to have a normal spinel structure with all the Zn^{2+} ions in tetrahedral sites and Ga^{3+} or Al^{3+} ions in octahedral sites [8].

In recent years, zinc gallate has attracted attention as one of excellent phosphor host materials for applications in thin film electroluminescent devices (TFED), vacuum fluorescent displays (VFD), and field emission displays (FED) [9–13]. A blue emission of $ZnGa_2O_4$ without any dopant via a self-activation center of Ga–O groups under excitation by both UV light and low-voltage electrons [10,14] changes to green or up to red when it is activated with Mn^{2+}, Cr^{3+}, Eu^{3+}, and Tb^{3+} [15–17]. The zinc aluminate also possesses unique properties and has been used as phosphor materials [18–20], reflective optical coatings [21], UV-transport electro conductive oxide [22], photocatalyst for the degradation of toluene [23], and catalysts for dehydration, hydrogenation, dehydrogenation, and synthesis of fine chemicals [24–27].

These days, there is considerable interest in producing nanometer-sized crystals of inorganic materials [28] via wet chemical synthesis route, since the properties and performance of inorganic materials are closely linked to their synthesis routes in general. The direct formation of nanocrystals of solid solutions and complex oxides [29,30] with a controlled size and various morphologies at low temperatures has been of technological and scientific interest. The hydrothermal method, which is one of representative wet chemical synthesis techniques,

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is known to be useful for the synthesis of fine inorganic materials, especially those based on oxide nanocrystals [31–33].

In the literature on the preparation of spinel-type $ZnGa_2O_4$, various synthetic methods such as the flux method [11,34,35], solid-state reaction [12,17], co-precipitation [11,36], homogeneous precipitation [37], the sol–gel method [38], low-temperature and direct crystallization at 25–90 °C [39,40], hydrothermal synthesis [41,42], and combustion synthesis [43] have been reported. Many synthetic techniques, for instance, solid-state reaction [44], co-precipitation [45], sol–gel [46,47], spray pyrolysis [20], hydrothermal synthesis [48–51], template-assisted synthesis [52], and glycothermal synthesis [53] have also been employed for the preparation of $ZnAl_2O_4$ spinel. However, in the most literature, the detail of the structure such as lattice parameter of as-prepared $ZnAl_2O_4$ spinel that was synthesized via hydrothermal route without post-heat treatment in air has not been shown. Moreover, the influence of the composition of $Zn(Al_xGa_{1-x})_2O_4$ on the structure and properties of the spinel nanocrystals formed through hydrothermal route has hardly been investigated. It has been reported that $ZnGa_2O_4$ has the optical band gap of approximately 4.4 eV [54,55]. This value relatively agrees with theoretically calculated band gap values [56]. On the other hand, the optical band gap of $ZnAl_2O_4$ in the polycrystalline form has been reported to be 3.8–3.9 eV [22], which seems to be lower than the theoretical band gap values and does not so coincide with most band gap values derived from various kinds of theories [56–59].

Here, we present spinel-structured complete solid solutions: $Zn(Al_xGa_{1-x})_2O_4$, x=0–1.0 in the $ZnAl_2O_4$–$ZnGa_2O_4$ system directly formed as nanocrystals from the aqueous precursor solutions of inorganic metal salts under mild hydrothermal conditions in the presence of tetramethylammonium hydroxide for a short period of time. We report the effect of the substitutional incorporation of aluminum into the spinel lattice on the formation, microstructure, lattice parameter, optical band gap, and luminescence property of the hydrothermally prepared spinel-structured solid solutions.

2. Experimental procedure

2.1. Synthesis

The spinel-type $Zn(Al_xGa_{1-x})_2O_4$ solid solutions were synthesized by a hydrothermal method using tetramethylammonium hydroxide ($N(CH_3)_4OH$, TMAH). In a typical synthesis, a mixture of an aqueous solution of reagent-grade $ZnSO_4$, $Al(NO_3)_3$ and $Ga(NO_3)_3$ in different ratios of Zn/Al/Ga (that was controlled to be the composition: $Zn(Al_xGa_{1-x})_2O_4$, x=0–1.0) was prepared in a Teflon container. Before hydrothermal treatment, $N(CH_3)_4OH$ solution was added into the solution mixture until the pH of the solution which was hydrothermally treated became weakly basic. This solution mixture with total cation concentrations (Zn+Al+Ga) of 0.20 mol/dm^3 in the Teflon container was then placed in a stainless-steel vessel. The vessel was tightly sealed and it was heated at 120–240 °C for 5 h under rotation at 1.5 rpm. After hydrothermal treatment, the precipitates were washed with distilled water until the pH value of the rinsed water became 7.0, separated from the solution by centrifugation, and dried in an oven at 60 °C.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were collected with a powder diffractometer using CuKα radiation (RINT-2000, Rigaku, Tokyo, Japan). The transmission electron microscopy (TEM) imaging of the as-prepared samples was performed with a microscope (JEM-2010, JEOL, Tokyo, Japan). The crystallite size of cubic phase was calculated from the line broadening of 311 diffraction peak, according to the Scherrer equation, $D_{XRD}=K\lambda/\beta\cos\theta$, where θ is the Bragg angle of diffraction lines; K is a shape factor (K=0.9 in this work); λ is the wavelength of incident X-rays, and β is the corrected half-width given by $\beta^2=\beta_m^2-\beta_s^2$, where β_m is the measured half-width and β_s is the half-width of a standard sample. The lattice parameter was measured using silicon as the internal standard. The thermogravimetric analysis was carried out in the air with a heating rate of 5 °C/min (Thermo plus TG8120, Rigaku, Tokyo, Japan).

UV–vis absorption (diffuse reflectance) spectra of the prepared powders were recorded at room temperature and in air by means of ultraviolet–visible spectrophotometer with an integrating sphere attachment (V-560, Nihon Bunko, Tokyo, Japan). The spectra were derived from the measured ones using the Kubelka–Munk equation [60]. Photoluminescence (PL) spectra of the samples were recorded with a fluorescence spectrophotometer (F-2700, Hitachi High-Tech, Japan) with Xe lamp. The sample powders were excited with 270 nm radiation from a 150 W xenon lamp. The emission wavelength was scanned from 280 nm to 800 nm at a scanning rate of 60 nm/min.

3. Results and discussion

3.1. Formation and structural characteristics of spinel solid solutions

The hydrothermal treatment of the precursor solution mixtures with compositions: $Zn(Al_xGa_{1-x})_2O_4$, x=0 and 1.0 was carried out under weakly basic and hydrothermal conditions at 120–240 °C using TMAH to get the information on the formation and crystallization of $ZnGa_2O_4$ and $ZnAl_2O_4$ spinel phase, respectively. The XRD patterns of the precipitates formed from the precursor solutions with compositions: x=0 and 1.0 under hydrothermal conditions at various temperatures are shown in Fig. 1(a) and (b), respectively. As the hydrothermal treatment temperature rises, the XRD lines become sharper and the crystallinity of the precipitates is improved. The precipitates formed at the temperature range of 120–240 °C (x=0) and 180–240 °C (x=1.0) were detected as almost a single phase of cubic spinel. The crystallite growth behavior of the cubic spinel phase of the samples (x=0 and 1.0) are shown in Fig. 2. It is evident that the crystallite growth