ARTICLE IN PRESS

Nano-Structures & Nano-Objects ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

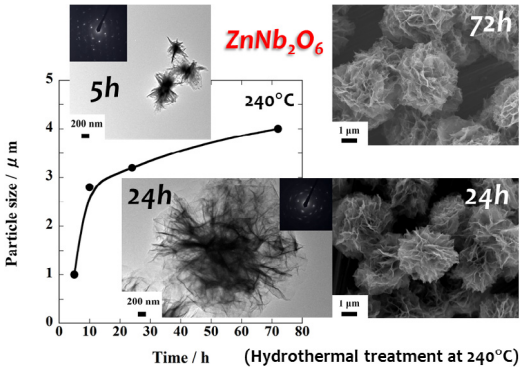
journal homepage: www.elsevier.com/locate/nanoso

Synthesis, morphology, and luminescence of $ZnNb_2O_6$ nanocrystals by hydrothermal method

Masanori Hirano *, Takaaki Okamoto

Department of Applied Chemistry, Faculty of Engineering, Aichi Institute of Technology, Yakusa, Toyota, 470-0392, Japan

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 May 2015
Accepted 3 November 2015
Available online xxxx

Keywords:
$ZnNb_2O_6$
Photoluminescence
Hydrothermal synthesis
Nanocrystal

ABSTRACT

The effect of hydrothermal treatment conditions on the formation, morphology, crystal growth, and photoluminescence of columbite-type $ZnNb_2O_6$ nanocrystals having rose-like morphology that were directly formed from aqueous precursor solutions of $ZnSO_4$ and $NbCl_5$ in the presence of aqueous ammonia was investigated. The crystallization of $ZnNb_2O_6$ nanocrystals was observed at 210 °C, but the hydrothermal treatment at 240 °C for 5 h under weakly basic condition around pH = 8.4 was necessary for the sufficient crystallite growth of columbite-type $ZnNb_2O_6$ phase. On the other hand, the solid product formed at 240 °C from the precursor solution at pH = 9.0 was almost amorphous. The observation by means of the transmission electron microscopy, selected area diffraction, and energy dispersive X-ray spectrometry showed that the $ZnNb_2O_6$ particles with the morphology like flower or rose consisted of arrayed nanosized-sheets having crystallite size of 11 nm. The $ZnNb_2O_6$ particles grew from about 1 to 4 μm accompanying crystal growth with morphological change into rose-like shape via the solution and precipitation mechanism as hydrothermal holding time at 240 °C increased from 5 to 72 h. The as-prepared $ZnNb_2O_6$ nanocrystals showed a broad-band emission in the UV-blue region centered at 420 nm (and peaked at 360 nm) under excitation at 276 nm.

1. Introduction

In recent years, great attention has been devoted to wet chemical routes to synthesize nanometer-sized particles of inorganic materials because their structures, crystalline phases, characteristics, and performances can be variously designed by controlling

* Corresponding author. Tel.: +81 565 48 8121; fax: +81 565 48 0076.
E-mail address: hirano@aitech.ac.jp (M. Hirano).

http://dx.doi.org/10.1016/j.nanoso.2015.11.001
2352-507X/

Please cite this article in press as: M. Hirano, T. Okamoto, Synthesis, morphology, and luminescence of $ZnNb_2O_6$ nanocrystals by hydrothermal method, Nano-Structures & Nano-Objects (2015), http://dx.doi.org/10.1016/j.nanoso.2015.11.001

their compositions and preparation conditions [1–3]. From a view point of green processing, the aqueous solution route including hydrothermal synthesis method is effective to form new compounds [4], solid solutions [5], and metastable phases [6] of complex oxides and oxide ceramics as nano-sized particles with peculiar morphological structures.

Zinc niobate ($ZnNb_2O_6$) that crystallizes in the columbite structure is one of representative members of orthorhombic columbite group, $M^{2+}Nb_2O_6$ where M^{2+} = calcium, magnesium, or transition metal elements. Zinc niobate has been of great interest in the field of microwave dielectric ceramics [7–9], photocatalyst materials [10–12], and sensor materials [13]. Zinc niobate is one of materials satisfying the demand for low-cost but nonetheless high-performance dielectric ceramics as dielectric resonators because it has a resonant frequency (f_r) in the microwave region and has high quality factor (Q) [7]. It has also been studied for the development of photocatalyst for water splitting with the aim at photon energy conversion [11]. On the other hand, $ZnNb_2O_6$ has interesting luminescence properties and shows self-activated luminescence under excitation with ultraviolet (UV) light. Thus, it works as one of host crystals for doping activator ions [14–17].

Many investigations on the preparation of zinc niobate and its application have been carried out using several synthesis techniques that include solid-state reaction [18,19], sol–gel [20], co-precipitation [21], molten salt [22], thermal decomposition [23], hydrothermal [24], glycothermal [25], citrate complex [12], Pechini [26], combustion [17], and mechanochemical [27]. However, there have been only a few studies on the direct synthesis of $ZnNb_2O_6$ nanocrystals through hydrothermal route. We have noticed that hydrothermally formed $ZnNb_2O_6$ nanocrystals possess characteristic morphology like rose and their formation, structures and properties fairly depend on the hydrothermal treatment conditions.

In this study, the effect of hydrothermal treatment conditions on the formation, morphology, crystal growth, and photoluminescence of $ZnNb_2O_6$ nanocrystals that are formed directly from aqueous precursor solutions of $ZnSO_4$ and $NbCl_5$ has been investigated. As a result, the behavior of change in phase, structure, and morphology of $ZnNb_2O_6$ nanocrystals depending on the treatment conditions has been clarified.

2. Experimental

2.1. Sample preparation

Reagent-grade $ZnSO_4 \cdot 7H_2O$ and $NbCl_5$ were used as starting materials. A mixture of an aqueous solution of $ZnSO_4 \cdot 7H_2O$ and ethanol solution of $NbCl_5$ in the ratio of Zn/Nb = 0.50 was prepared in a Teflon container. The solution mixture was controlled by the addition of aqueous ammonia to have a weakly basic condition in the end stage of hydrothermal treatment. This solution mixture with cation concentration of 0.20 mol/dm^3 (: Zn = 0.20 mol/dm^3, Nb = 0.40 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 180 ∼ 240 °C for 5 ∼ 72 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) measurements were performed at room temperature for the as-prepared powders using CuKα radiation (XRD; model RINT-2000, Rigaku, Tokyo, Japan). The morphology of the samples was observed using transmission electron microscopy (TEM; model JEM-2010, JEOL, Tokyo, Japan), selected area electron diffraction (SAED), and field emission scanning electron microscopy (FESEM; model JSM-6335FM, JEOL, Tokyo, Japan). Energy-dispersive X-ray spectrometer (EDS) was used to analyze the composition of samples.

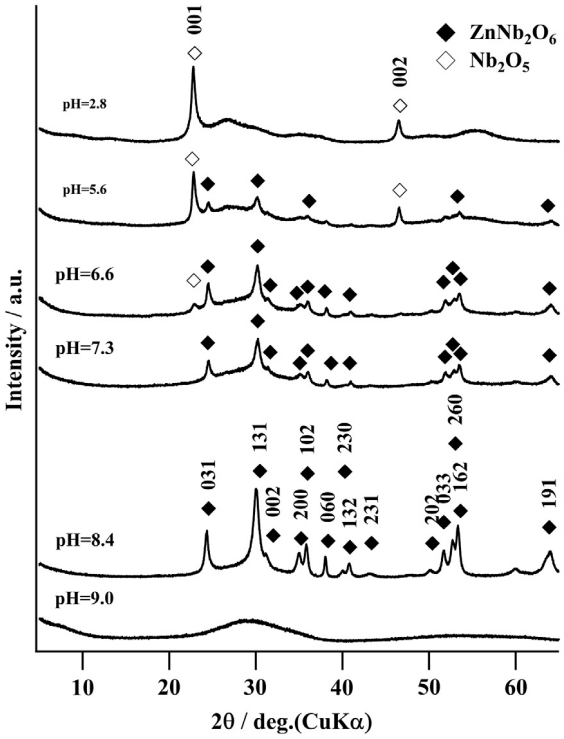


Fig. 1. XRD patterns of precipitates obtained from the precursor solutions with various pH under hydrothermal conditions at 240 °C for 5 h.

The crystallite size of $ZnNb_2O_6$ phase was estimated from the line broadening of 131 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 diffuse reflectance spectra measurements for powder samples have been made. The optical absorption of these prepared powders was measured using an ultraviolet–visible spectrophotometer (V-560, Nihon Bunko, Tokyo, Japan).

The photoluminescence (PL) emissions of samples were measured using a spectrofluorometer (F-2700, Hitachi High-Tech, Japan) with Xe lamp. Powder samples were excited with 276 nm radiation from a 150 W xenon lamp. The emission wavelength was scanned from 300 to 700 nm at a scanning rate of 60 nm/min.

3. Results and discussion

3.1. Effect of pH of the precursor solution

The effect of the pH of the precursor solution on the formation and crystallization of $ZnNb_2O_6$ has been investigated. The XRD patterns of precipitates formed from the precursor solutions with various pH under hydrothermal conditions at 240 °C for 5 h are shown in Fig. 1. The crystalline phases appeared in the solid precipitates excluding the case formed from the precursor solution of pH = 9.0. Amorphous-like precipitate was obtained from the precursor solution of pH = 9.0, and Nb_2O_5 phase appeared as the main phase at pH = 2.8. In the case of weakly acidic

Please cite this article in press as: M. Hirano, T. Okamoto, Synthesis, morphology, and luminescence of $ZnNb_2O_6$ nanocrystals by hydrothermal method, Nano-Structures & Nano-Objects (2015), http://dx.doi.org/10.1016/j.nanoso.2015.11.001