Synthesis of blue-luminescent CaNb$_2$O$_6$ by using a biphasic liquid method at low temperatures

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We investigated a novel simple method to synthesize CaNb$_2$O$_6$ from precursors formed in immiscible liquid-liquid biphasic systems. Niobium pentaethoxide and calcium acetate monohydrate were used as starting materials, which were dissolved separately in hexane and water, respectively. After putting the hexane solution on the aqueous solution, they started to react at the interface of the two liquid phases and then a mixture of calcium acetate and amorphous niobate gels was precipitated in the aqueous solution at room temperature. The precipitates could be transformed to CaNb$_2$O$_6$ by heating at 700°C for 30 min. The morphology of the CaNb$_2$O$_6$ sample was characterized as rough and dimpled spheres 400–500 nm in size. The sample exhibited a blue emission upon excitation with ultraviolet light. A comparative study using a one-phase liquid method or a solid-state reaction method has strongly suggested that the biphasic liquid method is advantageous for obtaining highly luminescent CaNb$_2$O$_6$ at the lower processing temperatures.

Key-words : Calcium niobate, Phosphor, Sol–gel method, Biphasic liquid method, Morphology

1. Introduction

Metal niobate compounds that crystallize in the columbite-type structure (MNb$_2$O$_5$; M = calcium, magnesium, or transition metal elements) have attracted much attention due to their unique characteristics such as microwave dielectric properties, photo-catalytic activities, and a lithium insertion ability. Among them, CaNb$_2$O$_6$ is known as its interesting luminescence properties arising from electronic transitions between O 2p band and Nb 4d band of the NbO$_6$ units in the crystal structure. CaNb$_2$O$_6$ is known as one of the rare earth host crystals for doped activator ions. In the former self-activated CaNb$_2$O$_6$, the ordering of the Nb–O bonding influences strongly the intensity of luminescence. Thus the CaNb$_2$O$_6$ materials have been synthesized by a solid-state reaction method with high-temperature heating to obtain single-phase samples of good crystallinity.

Recently, a direct or an indirect liquid-phase synthesis is required even for luminescent materials from a view point of green processing of ceramics. Some of the advantages of a sol–gel processing, which is one of the representative liquid-phase synthesis methods, are suitable for the production of luminescent materials. That is, high homogeneity of precursor solutions makes it possible to lower the whole processing temperature necessary for the formation of solid-state materials. High controllability of shapes (powders or films) and microstructures (nanocrystals, nanocomposites, or hierarchically assembled structures) is also attractive for tuning both optical and luminescent properties in accordance with practical applications. Actually, luminescent materials synthesized by liquid-phase methods can show enhanced emission intensities through the appropriate microstructural control.

As for CaNb$_2$O$_6$, there have been only a few reports on its liquid-phase synthesis including a sol–gel method. The difficulty lies in the selection of raw materials and solvents, the control of grain growth, and the modulation of final morphology. Organic additives are usually employed for stabilizing precursor solutions, especially in the case of using highly reactive niobium alkoxides. However, this leads to complicated reactions in the solutions as well as multi-step thermal decompositions in the crystallization. In this article, we propose a new synthesis of CaNb$_2$O$_6$ through a biphasic liquid method. Niobium pentaethoxide [Nb(OC$_2$H$_5$)$_5$] was dissolved in an organic solvent and calcium acetate monohydrate [(CH$_3$COO)$_2$Ca·H$_2$O] was dissolved in water. The resultant solutions were immiscible and then biphasically separated after putting them together. White precipitates, which were formed at room temperature, were heat-treated typically at 700°C to obtain CaNb$_2$O$_6$ samples. Comparisons were made with different samples synthesized by a one-phase liquid method or a solid-state reaction method in terms of microstructure and optical properties. Our results then demonstrated that the biphasic liquid method without any additives was beneficial to the formation of samples with a characteristic morphology and an enhanced luminescence property.

2. Experimental procedure

In the biphasic liquid method, Nb(OC$_3$H$_7$)$_5$ (99.95% purity, 1.268 g cm$^{-3}$ in density, Sigma-Aldrich) was first diluted with ethanol 9 times in volume. The resultant solution was added to anhydrous hexane (96.0%, Wako Pure Chemical Industries) also 9 times in volume (Nb(OC$_3$H$_7$)$_5$-ethanol-hexane = 1:9:90 in a final volume ratio). A concentration of Nb(OC$_3$H$_7$)$_5$ was then 0.0398 mol dm$^{-3}$. Separately, an aqueous solution was prepared by dissolving (CH$_3$COO)$_2$Ca·H$_2$O (99.0%, Wako in ion-exchanged water. A concentration of (CH$_3$COO)$_2$Ca·H$_2$O was fixed at 1.0 mol dm$^{-3}$. 7 mL of the hexane solution was injected into 7 mL of the aqueous solution using a syringe, keeping disturbance minimal. Soon after a distinct liquid–liquid interface appeared, the hexane solution near the interface turned turbid, indicating that a certain reaction such as hydrolysis proceeded through delivering...
H₂O from the aqueous solution. Then, white precipitates that were formed in the organic phase fell from the interface region to the bottom of a container (filled with the aqueous phase) within 60 min. The precipitates were aged for 24 h before collecting by separation of the aqueous solution and subsequent centrifugation at 10,000 rpm for 10 min. All the above procedures were conducted at room temperature. The collected samples were dried at 60°C for 12 h and heated at 300, 500, or 700°C for 30 min with a heating rate of 25°C min⁻¹ in air, followed by a furnace cooling.

In the one-phase liquid method carried out for a comparative study, the equivalent amount of Nb(OC₂H₅)₅ was diluted with ethanol 9 times in volume and then dropped directly into an aqueous solution of (CH₃COO)₂Ca·H₂O at 0.5 mol dm⁻³ in concentration. White precipitates were formed immediately on the bottom of the container. The precipitates were aged for 24 h, collected by centrifugation at 10,000 rpm for 10 min, and then dried at 60°C for 12 h. The dried samples were heated at 300, 500, or 700°C for 30 min with the heating rate of 25°C min⁻¹ in air, followed by the furnace cooling.

For the solid-state reaction method, CaCO₃ (99%, Kojundo Chemical Laboratory) or (CH₃COO)₂Ca·H₂O and Nb₂O₅ (99.9%, Mitsui Mining & Smelting) powders (Ca:Nb = 1:2) were mixed in a mortar with the addition of acetone. The mixture was dried at 60°C and then heated at 700°C with the heating rate of 25°C min⁻¹ for 30 min in air, followed by the furnace cooling.

Crystalline phases of the samples were identified with an X-ray diffractometer (Bruker AXS D8 ADVANCE) by using CuKα radiation. The thermal decomposition behavior of the samples was examined by thermogravimetry-differential thermal analysis (TG-DTA; Shimadzu DTG-60) with a heating rate of 3°C min⁻¹ in flowing air. The morphology of the samples was observed with a field-emission scanning electron microscopy (FESEM; JEOL JSM-7600F) instrument. The microstructure was observed by transmission electron microscopy (TEM; Philips TECNAI F20). Diffuse reflectance spectra were recorded with a UV-visible spectrophotometer (JASCO V-670) using an integrating sphere unit (JASCO ISN-723). Photoluminescence (PL) spectra were measured at room temperature with a spectrofluorophotometer (JASCO FP-6500) using a xenon lamp (150 W) as a light source. Raman spectra were measured using a diode laser at 532 nm (CHROMEX Raman-One-CCD).

3. Results and discussion

3.1 Samples from the biphasic liquid method

Figure 1 shows X-ray diffraction (XRD) patterns of the dried precipitates through the biphasic liquid method and their heat-treated samples at 300, 500, or 700°C for 30 min in air. The pattern of the precipitates contains both sharp diffraction peaks and a broad amorphous hump. The sharp peaks coincide with those of (CH₃COO)₂Ca·nH₂O. It is known that calcium acetate has differing degree of hydration, depending on the sample history.¹⁹,²⁰ The exact hydration number (n) could not be determined in the precipitates because they were actually a mixture, as mentioned above. The hump in the pattern may be related to amorphous niobate gels.²¹ The sample heated at 300°C shows a different pattern with the decreased intensity of the peaks due to (CH₃COO)₂Ca·nH₂O and the increased amorphous nature. Sharp peaks appearing at lower 2θ angles are currently unidentified, but are probably due to another calcium acetate phase. A new XRD pattern is observed for the sample heated at 500°C, which is explained by the evolution of a CaCO₃ phase (ICDD No. 05-0586) by the thermal decomposition of (CH₃COO)₂Ca·nH₂O. It should be noted that the hump still remains in the

Fig. 1. XRD patterns of (a) the precipitates from the biphasic liquid method and their heated samples at (b) 300, (c) 500, and (d) 700°C.

Fig. 2. TG-DTA curves of the precipitates from the biphasic liquid method.

pattern. A pattern of the sample heated at 700°C can be indexed with an orthorhombic CaNb₂O₆ phase (ICDD No. 71-2406). A trace of CaO also appears in the pattern. It can be concluded from these results that the precipitates consist of crystalline (CH₃COO)₂Ca·nH₂O and amorphous niobate gels and CaNb₂O₆ is obtained by heating them at the relatively low temperature of 700°C for the short heating period of 30 min. As for the composition, the concentrations of Nb(OC₂H₅)₅ (0.0398 mol dm⁻³) and (CH₃COO)₂Ca·H₂O (1.0 mol dm⁻³) in the solutions had been preliminarily optimized to give the nearly single phase of CaNb₂O₆ after the heat treatment through the biphasic liquid method.

The conversion from the precipitates to the crystalline CaNb₂O₆ phase was examined further by TG-DTA, as shown in Fig. 2. A gradual weight loss, reaching 10.1%, is observed at elevated temperatures up to 220°C with minor DTA peaks. This loss is ascribed to the release of water molecules adsorbed in the precipitates as well as incorporated in the calcium acetate crystals.
A following weight loss is 15.3% at temperatures up to 431°C, accompanied by a sharp and strong exothermic peak. According to the literature, the decomposition of \((\text{CH}_3\text{COO})_2\text{Ca}\) to \(\text{CaCO}_3\) occurs at temperatures around 400°C. Our results in Fig. 1 also demonstrate that the decomposition is completed at 500°C. Therefore the second weight loss is the thermal conversion from the \(\text{CaCO}_3/\text{amorphous niobate gel mixture}\) to the \(\text{CaCO}_3/\text{amorphous niobate gel mixture}\). A final weight loss is 13.3% at temperatures up to 640°C. If we assume a following chemical reaction, a theoretical weight loss is calculated to be 12.0%.

$$\text{CaCO}_3 + \text{Nb}_2\text{O}_5 \rightarrow \text{CaNb}_2\text{O}_6 + \text{CO}_2 \uparrow$$

The discrepancy may come from the slightly larger calcium content in the precipitates, as noted in the XRD analysis with the appearance of the trace of \(\text{CaO}\) in the sample heated at 700°C. The morphology of the samples was observed with FESEM. As shown in Fig. 3(a1), the precipitates from the biphasic liquid method appear to be nearly spherical particles 400–500 nm in size. A magnified image in Fig. 3(a2) reveals that the surface of the particles is relatively smooth. Because the precipitates do not have distinct morphologies, each particle is supposed to be composed of the crystalline \((\text{CH}_3\text{COO})_2\text{Ca}_\text{nH}_2\text{O}\) and the amorphous niobate gels. The samples heated at 300 and 500°C (Figs. 3(b) and 3(c), respectively) have almost the same morphology as that of the precipitates. This indicates that the decomposition of calcium acetate does not provide an apparent volume contraction of the particles, probably owing to the coexistence of the amorphous niobate gels that help to relax the volume change. The \(\text{CaNb}_2\text{O}_6\) sample that was heated at 700°C still maintains the initial particle size, as shown in Fig. 3(d1). In addition, it is clear that the surface morphology becomes rough and dimpled after the heat-treatment when comparing Figs. 3(a2) and 3(d2). This change might be associated with the full crystallization of the particles.

3.2 Samples from the one-phase liquid and the solid-state reaction method

The samples from the one-phase liquid method were treated similarly to those from the biphasic liquid method to clarify their difference. Figure 4 shows XRD patterns of the dried precipitates through the one-phase liquid method and the heat-treated samples at 300, 500, or 700°C for 30 min in air. Although the precipitates also contain \((\text{CH}_3\text{COO})_2\text{Ca}_\text{nH}_2\text{O}\), an amorphous hump is much enhanced as compared to those from the biphasic liquid method. The discrepancy is supposed to come from the formation kinetics of the precipitates. In the one-phase liquid method, the white precipitates were formed soon after dropping \(\text{Nb(OC}_2\text{H}_5)_5\) into the aqueous solution. The solidification as the amorphous phase surpasses the crystallization under such the condition. In contrast, the reaction proceeded gradually in the organic solution probably through continuous delivery of the aqueous calcium acetate solution for the biphasic liquid method. The formation rate of the precipitates is therefore much smaller. The crystallization is also promoted in the organic solution where the solubility of calcium acetate is also much smaller. This would influence the morphology of the samples as mentioned below. The sample heated at 300°C shows a pattern with sharp peaks due to both anhydrous calcium acetate (ICDD No. 18-0293) and the same unidentified phase as that observed in the sample from the biphasic liquid method. The hump is also seen in the pattern. \(\text{CaCO}_3\) is formed in the sample heated at 500°C due to the decomposition of calcium acetates. Finally, \(\text{CaNb}_2\text{O}_6\) is obtained by heating the precipitates at 700°C for 30 min. This time a trace of \(\text{Ca}_4\text{Nb}_2\text{O}_9\) (ICDD No. 70-5420) is observed in the pattern.

Figure 5 shows FESEM images of the precipitates from the one-phase liquid method and the sample heated at 700°C. The precipitates consist of small particles approximately 40 nm in size. Some of the particles form larger secondary particles up to 250 nm in size. The heated sample shows a similar morphology without any specific shape. The difference in the morphology between the samples from the biphasic liquid method (Fig. 3) and those from the one-phase liquid method (Fig. 5) is also attributed to the formation kinetics of the precipitates. In the one-phase method, the hydrolysis of \(\text{Nb(OC}_2\text{H}_5)_5\) proceeds vigorously to form the amorphous niobate gels incorporating calcium.
acetate. The microstructural relaxation or stabilization is not expected in such the precipitation process without the time for aging. In contrast, there would be enough time to grow the particles into the large spherical shape under the suppressed hydrolysis of the alkoxide as well as the promoted crystallization of the acetate in the biphasic method.

A further comparison is made here between the liquid-phase and the solid-state reaction method. CaCO₃ or (CH₃COO)₂Ca·H₂O and Nb₂O₅ were mixed and heated at 700°C for 30 min in air for the solid-state reaction. XRD patterns of the products are shown in Fig. 6. When using CaCO₃, the product is a mixture of the decomposed CaO (ICDD No. 82-1690) and the unreacted Nb₂O₅ (ICDD No. 27-1003). Thus no complex oxide is formed under the same heating condition as that for the precipitates from the liquid-phase methods. In the case of (CH₃COO)₂Ca·H₂O, the product is a mixture of the unreacted Nb₂O₅ and another complex oxide (Ca₂Nb₂O₇; ICDD No. 74-0390). It is then concluded that the formation of CaNb₂O₆ is not possible at the low temperature of 700°C through the solid-state reaction.

3.3 Optical properties of the samples

Figure 7(a) shows diffuse reflectance spectra of the CaNb₂O₆ samples from the one-phase and the biphasic liquid method by heating at 700°C. In the visible region with wavelengths longer than 380 nm, both the samples exhibit high reflectance more than 85%, principally indicative of their high optical transparency. A close comparison of the spectra reveals that the sample from the biphasic method exhibits lower reflectance than that from the one-phase method. Generally, the diffuse reflectance is a measure of contributions from the specular reflection component (the reflection from the surface) and the diffusively scattered component (the reflection from inside). It is the specular reflection component that influences largely the spectral structure if the samples being measured are the same material. The fact that the sample from the biphasic method has lower reflectance indicates that it has the less specular reflection, probably due to its morphological character-

istic with the rough and dimpled surface of the larger particles.

In the UV region with wavelengths shorter than 380 nm, the reflectance of both the samples are considerably reduced, which is explained with light absorption by electronic transitions between the O 2p band and the Nb 4d band of the NbO₆ units. The absorption band is centered at approximately 250 nm, which is of fundamental significance for interpreting following luminescence properties.

PL excitation and emission spectra are compared in Fig. 7(b) for both the CaNb₂O₆ samples. Broad-band visible emissions centered at 458 nm are observed for both the samples. Actually the samples emitted blue light, which was visible to the eye, under the irradiation with the UV lamp (254 nm). The excitation band in Fig. 7(b) corresponds to the absorption band in Fig. 7(a). Therefore the photoluminescence of CaNb₂O₆ is generated by the O 2p–Nb 4d absorption and the subsequent Nb 4d–O 2p emission, as reported in the literature. It is also observed that the PL intensity is relatively larger for the sample from the biphasic method. One plausible reason for this PL enhancement is the morphological characteristic, as mentioned above. That is, the sample from the biphasic method could also show the less specular reflection of the emitted light, leading to the better light extraction from the particles.

In another consideration, the emission due to the Nb 4d–O 2p transition is known to be largely affected by ordering of the Nb–O bonding defects due to oxygen vacancies and grain boundaries would be a factor for changing the PL intensity. Crystallinity of the samples was then checked by TEM obser-
214 cm by Raman spectroscopy that can clarify the defect state and the core in the respective images, which evidences the similar interplaner distance of 0.29 nm are seen throughout the particle the change in the Nb peak shift is found in the spectra of both the samples and the evolved during the whole synthesis process.

4. Conclusions

The blue-emitting CaNb$_2$O$_6$ samples were synthesized by the biphasic liquid method using niobium pentaethoxide and calcium acetate monohydrate as the starting materials. The precursors obtained were the mixture of the calcium acetate and the niobate gels, which could be converted to CaNb$_2$O$_6$ by heating at 700°C for 30 min. The morphology of the samples was characterized as the rough and dimpled spheres 400–500 nm in size, which was beneficial to the enhancement of the blue emission. On the other hand, the usual one-phase liquid method was incapable of producing the samples with any defined morphology. Furthermore, CaNb$_2$O$_6$ was not formed in the solid-state reaction conducted under the same heating condition as that employed for the liquid-phase methods. Our results indicate that the liquid method with the controlled reactions can be adopted to synthesize the phosphor materials at the low temperatures.

Acknowledgment This work was supported by JSPS KAKENHI Grant Number 25420715.