Hydrothermal formation of luminescent nanoparticles based on zirconia and europium niobate

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Luminescent nanoparticles based on zirconia (ZrO$_2$) and europium niobate (Eu$_3$NbO$_7$) were directly formed as a single phase of structure corresponding to cubic phase from the precursor solutions of NbCl$_5$, ZrOCl$_2$, and EuCl$_3$ under mild hydrothermal conditions at temperatures more than 180°C. The lattice parameter corresponding to cubic phase decreased with increase in the concentration of ZrO$_2$. The optical band gap of the nanoparticles with composition 50 and 90 mol % ZrO$_2$ in the ZrO$_2$ – 1/4(Eu$_3$NbO$_7$) system was 3.5 and 3.6 eV, respectively. The nanoparticles can be excited by ultraviolet light 395 nm (f transition) and emit orange (590 nm) and red light (610 nm) corresponding to Eu$^{3+}$ from $^5$D$_{0}$ $\rightarrow$ $^7$F$_{1}$ and $^5$D$_{0}$ $\rightarrow$ $^7$F$_{2}$ transitions, respectively. The photoluminescence intensity of the sample containing larger amount of ZrO$_2$ was superior to that of the sample, 50 mol % ZrO$_2$.

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1. Introduction

Inorganic compounds doped with rare-earth ions possess great scientific and interesting properties and have played an important part in various uses, e.g. the optical, magnetic, electrical, chemical, structural, and catalytic fields of applications. Much attention has been paid to compounds containing lanthanide ions, especially niobate of rare-earth metals due to their interesting characteristics such as luminescence, ionic conductivity, photo-catalytic activity, magnetic properties, crystal structures, and phase stability. Niobate compounds, Ln$_3$NbO$_7$ (Ln = lanthanes and yttrium) have a fluorite-related structure. The compounds with small cations crystallize as fluorite or pyrochlore-types of structure. Niobates with larger cations have an orthorhombic unit cell. On the other hand, zirconium oxide (zirconia, ZrO$_2$) is well known to have three polymorphs based on the fluorite structure: monoclinic, tetragonal, and cubic phase. The zirconia has been used for many applications such as oxygen sensors, an electrolyte for solid-oxide fuel cells, a high-temperature heater, cutting tools and structural materials, dental materials and biomatertials, luminescent materials, high-temperature refractories, and so on.

The characteristic of luminescence of rare-earth-doped substances is affected by the host materials. Recently, many Eu$^{3+}$-doped materials have been extensively studied because of the intra-4f-shell transitions that occur from the excited level down to the lower levels: $^5$D$_{0}$ $\rightarrow$ $^7$F$_{1}$ (I = 1, 2, 3, 4) for Eu$^{2+}$ ions. The investigation on the synthesis routes of materials is one of the approaches for the improvement of performance and their properties. The niobate, Ln$_3$NbO$_7$ has been synthesized through a variety of preparation techniques such as solid state reaction, epitaxial growth, flux method, the Pechini-type polymerizable complex method, etc. The hydrothermal method is known to be able to directly synthesize new compounds, metastable phases, solid solutions, and composite nanoparticles.©2013 The Ceramic Society of Japan
High-Tech, Japan) with Xe lamp. Powder samples were excited with 395 nm radiation from a 150 W Xe lamp. The emission wavelength was scanned from 500 to 750 nm at a scanning rate of 60 nm/min.

3. Results and discussion

Hydrothermal treatment of the precursor solution mixture with composition \(x\text{Zr}_4\text{O}_8 \cdot (100-x)\text{Eu}_3\text{NbO}_7\) was carried out at 240°C under weakly basic conditions in the presence of aqueous ammonia. The pH of the solution mixture after hydrothermal treatment was in the range of 9.5–11.0. Figure 1(a) shows the XRD patterns of the as-prepared precipitates. A single phase of crystalline product was not formed at the composition \(\text{ZrO}_2 \leq 30\) (mol %) under hydrothermal condition at 240°C in this study, though co-existence of sharp XRD lines of \(\text{Eu(OH)}_3\) and broad peak around \(2\theta = 30^\circ\) was detected as shown in the sample \(x = 30\). In the present study, the structure and property of solid precipitates were investigated by the comparison of the sample \(x = 50\) and 90. The precipitates with composition \(x = 50\) and 90 prepared under hydrothermal condition at 240°C were detected as almost a single phase of cubic structure although co-presence of very slight amount of monoclinic phase was detected around \(2\theta = 30^\circ\) in the sample \(x = 90\). Figure 1(b) shows the details of region around 50° 2\(\theta\), i.e., a shift of the 220 line in the XRD patterns of the precipitates formed directly via hydrothermal treatment at 240°C, together with the XRD lines of the internal standard Si around 50° 2\(\theta\). It is clearly observed that the XRD lines of 220 shift in accordance with increase in the \(\text{ZrO}_2\) content in the system. The lattice parameter of the as-prepared samples estimated as cubic structure is shown in Table 1. The lattice parameter of cubic phase decreased with increase in the \(\text{ZrO}_2\) content in the sample. It is considered that the samples were formed as solid solution in the zirconia-niobate system.

Hydrothermal treatment of the precursor solution mixture with composition \(x = 50\) was carried out at 150–240°C in order to get the information on the formation temperature of the material. The XRD patterns of the precipitates formed at various temperatures are shown in Figure 2. The diffraction lines become sharper and the crystallinity of the product increases with increasing hydrothermal treatment temperature. All the precipitates formed at the temperature more than 180°C were detected as almost a single-phase corresponding to cubic structure, and no diffraction peaks are shown in Figure 2. The diffraction lines become sharper and the crystallinity of the product increases with increasing hydrothermal treatment temperature. All the precipitates formed at the temperature more than 180°C were detected as almost a single-phase corresponding to cubic structure, and no diffraction peaks

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**Table 1.** Lattice parameter, optical band gap, and crystallite size of the samples \([x = 50\) and 90 in \(x\text{Zr}_4\text{O}_8 \cdot (100-x)\text{Eu}_3\text{NbO}_7\)] prepared under hydrothermal condition at 240°C for 5 h

| Sample \(x\) (mol %) | Lattice parameter (nm) | Band gap (eV) | Crystallite size (nm) |
|-----------------------|------------------------|--------------|----------------------|
| 50                    | 0.5181                 | 3.46         | 6.0                  |
| 90                    | 0.5138                 | 3.63         | 7.6                  |

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**Fig. 1.** (a) X-ray diffraction patterns of the sample \(x = 30, 50\) and 90 obtained under hydrothermal conditions at 240°C for 5 h. (b) Close-up of the region around 50° 2\(\theta\) of the X-ray diffraction patterns of precipitates formed at the compositions of \(x = 50\) and 90.

**Fig. 2.** X-ray diffraction patterns of the sample \(x = 50\) obtained under hydrothermal conditions at various temperatures for 5 h.
The diffuse reflectance spectra of the samples $x = 50$ and 90.

due to another crystalline phases was detected, although the crystallinity of cubic phases was low. To prepare the product with relatively sufficient crystallinity hydrothermal treatment at 240°C is found to be necessary.

As shown in Table 1, the crystallite sizes of the samples with cubic phase $x = 50$ and 90 formed at 240°C are 6.0 and 7.6 nm, respectively. The crystallite of cubic phase of the sample with higher content of ZrO$_2$ was apt to grow larger at lower temperature than that of the sample with smaller content of ZrO$_2$ as can be seen from the difference in 220 XRD line broadness between the sample $x = 50$ and 90 in Fig. 1(b). The presence of zirconia assisted the formation of the material, i.e. solid solution based on niobate, Eu$_3$NbO$_7$ under hydrothermal condition. The phase stability of the samples with cubic phase that were hydrothermally synthesized was investigated via heating in air. In the samples: $x = 50$ and 90 after heating at the temperature up to 800°C, little change in the crystalline phase of the samples was observed.

The diffuse reflectance spectra of the as-prepared samples are shown in Fig. 3. A shift of the onset of absorption to shorter wavelengths was observed in the sample containing large amount of ZrO$_2$. In Table 1, the optical band-gap values of samples are shown. The optical band-gap values of the solid solutions were determined from the energy intercept by extrapolating the straight regions of the plot of $\alpha(h\nu)^{1/2}$ versus the photon energy $h\nu$ for a direct allowed transition ($E_g$).

The photoluminescence spectra (excited at 395 nm) of nanoparticles with composition: 50 and 90 mol% ZrO$_2$ in the ZrO$_2$ - 1/4(Eu$_3$NbO$_7$) system were formed as cubic phase from precursor solutions of EuCl$_3$, ZrOCl$_2$, and NbCl$_5$ under hydrothermal conditions in the presence of aqueous ammonia. The crystallite size of the cubic-phase nanoparticles with composition 50 and 90 mol% ZrO$_2$ synthesized at 240°C was 6.0 and 7.6 nm, respectively. The presence of zirconia assisted the formation of nano-sized niobate, Eu$_3$NbO$_7$ under hydrothermal condition as the formation of solid solution with cubic phase in the ZrO$_2$ - 1/4(Eu$_3$NbO$_7$) system. The photoluminescence spectra of the nanoparticles showed orange and red luminescence with main peaks at 590 and 610 nm corresponding to Eu$^{3+}$ from $^3\text{D}_0 \rightarrow ^7\text{F}_1$ and $^3\text{D}_0 \rightarrow ^7\text{F}_2$ transitions, respectively under excitation with 395 nm.

### 4. Summary

Nanoparticles with composition: 50 and 90 mol% ZrO$_2$ in the ZrO$_2$ - 1/4(Eu$_3$NbO$_7$) system were formed as cubic phase from precursor solutions of EuCl$_3$, ZrOCl$_2$, and NbCl$_5$ under hydrothermal conditions in the presence of aqueous ammonia. The crystallite size of the cubic-phase nanoparticles with composition 50 and 90 mol% ZrO$_2$ synthesized at 240°C was 6.0 and 7.6 nm, respectively. The presence of zirconia assisted the formation of nano-sized niobate, Eu$_3$NbO$_7$ under hydrothermal condition as the formation of solid solution with cubic phase in the ZrO$_2$ - 1/4(Eu$_3$NbO$_7$) system. The photoluminescence spectra of the nanoparticles showed orange and red luminescence with main peaks at 590 and 610 nm corresponding to Eu$^{3+}$ from $^3\text{D}_0 \rightarrow ^7\text{F}_1$ and $^3\text{D}_0 \rightarrow ^7\text{F}_2$ transitions, respectively under excitation with 395 nm.

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