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Phase formation and UV luminescence of Gd^{3+} doped perovskite-type $YScO_3$

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ABSTRACT

Synthesis of pure and Gd^{3+}doped perovskite-type $YScO_3$ was attempted by a polymerized complex (PC) method and solid state reaction (SSR) method. Crystalline phases and UV luminescence of samples were examined with varying heating temperatures. The perovskite-type single phase was not simply formed in the SSR method, as reported in some literatures, and two cubic C-type phases of starting oxide materials remained forming slightly mixed solid solutions. UV luminescence of Gd^{3+} doped samples increased with an increase in heating temperatures and volume of the perovskite-type phase. In contrast, a non-crystalline precursor was crystallized to a single C-type phase at 800 °C in the PC method forming a completely mixed solid solution. Then, the phase of perovskite-type $YScO_3$ formed at 1200 °C and its single phase was obtained at 1400 °C. It was revealed that high homogeneousness of cations was essential to generate the single perovskite-phase of $YScO_3$. Because Gd^{3+} ions were also dissolved into the single C-type phase in Gd^{3+} doped samples, intense UV luminescence was observed above 800 °C in both C-type phase and perovskite-type phase.

1. Introduction

Among many perovskite oxides, $YAlO_3$ has the largest energy gap, $E_g = 8.0$ eV [1], and is frequently used as a host material in optical application, especially in UV region. For instance, Ce^{3+} or Pr^{3+} doped $YAlO_3$ was investigated for application to a scintillator [2–5] and Gd^{3+} doped $YAlO_3$ was examined, as well as Gd^{3+} doped orthophosphate [6,7], aiming a UV light source for phototherapy and transilluminators [8,9]. Another Y based perovskite oxide with a large energy gap is $YScO_3$, which could be also a promising host material in UV application. C. Lu et al. reported that the energy gap of $YScO_3$ is approximately 6 eV [10], which is sufficiently larger than the energy of UV light from some emission centers such as Ce^{3+}, Pr^{3+} and Gd^{3+}. However, UV luminescent properties of $YScO_3$ have not been investigated extensively yet. This is not simply because Sc is a rare element, but also because synthesis of $YScO_3$ single phase was not as easy as that of $YAlO_3$.

Metal oxides of Y_2O_3 and Sc_2O_3 were usually used as starting materials for the synthesis of perovskite-type $YScO_3$ phase in solid state reaction (SSR). They are both cubic C-type structure, and form a complete solid solution of C-type $(Y,Sc)_2O_3$. The C-type structure is regarded as a defect-fluorite structure where eight unit cells of 1/4 anion-deficient fluorite structure are combined in an ordered way [11]. In an old phase equilibrium diagram of the binary system [12], only the C-type solid solution was shown but the trace of perovskite-type phase was indicated at high temperature of 1600 °C in non-equilibrium state [13]. Single phase of perovskite-type $YScO_3$ was successfully synthesized by SSR under high pressure of 2.0 GPa at 1000 °C for 1 h [13] or prepared in equilibrium under high temperature heating for a considerably long time without pressure [14,15]. The attempts of single crystal synthesis were reported previously by a flux method and a floating zone method [16,17]. Single crystals of perovskite-type $YScO_3$ were obtained by the flux method using a PbO/PbF_2 flux, but were not grown by a floating method [16,17].

The stability of perovskite-type structure ABX_3 is frequently discussed in terms of the Goldschmidt tolerance factor t, $t = (r_A+r_X)/\{2^{1/2}(r_B+r_X)\}$, where r_A, r_B, r_X are ionic radii of A-site cation, B-site cation and anion, respectively. The ideal cubic perovskite-type structure occurs for $t = 1$, and most known perovskite-type structures are present within the range $0.78 < t < 1.05$ [18]. Several discussions were reported about the phase stability on the basis of the t value [12,18–20]. The decrease of t from unity usually enlarges the structural distortion accompanying the tilting of the corner-sharing octahedra [21,22]. The t value for $YScO_3$ can be estimated to be $t = 0.797$ from the Shannon's effective ionic radii, 1.019 Å for Y^{3+}(VIII), 0.745 Å for Sc^{3+}(VI), 1.40 Å for O^{2-}(VI) [23]. Since the t value is substantially small and close to the lower limit of the stable range, it seems to be reasonable that the structure of $YScO_3$ is significantly distorted and the

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synthesis of the single phase is not simple and dependent on the synthesis methods.

In this study, a polymerized complex (PC) method [24] was adopted to synthesize the $YScO_3$ perovskite-type phase. In the PC method, it is anticipated that metal cations and chelating agents form chelate complexes and the complexes are dispersed homogeneously in solution. Furthermore, the homogeneous distribution is fixed in a polymer network by polymerization reaction. Because of the homogeneousness in cation distribution, single phases of pure and Gd^{3+} doped $YScO_3$ were obtained simply by heating the polymerized precursor. The formation of the perovskite-type crystalline phases by the PC method is reported along with the Gd^{3+} luminescence for Gd^{3+} doped samples.

2. Experiments

Powder samples of $(Y_{1-x}Gd_x)ScO_3$ ($x = 0.00, 0.07$) were prepared by a PC method and SSR method using Y_2O_3 (99.99%), Sc_2O_3 (99.9%), and Gd_2O_3 (99.9%) powder as starting materials. The starting materials were weighed stoichiometrically and the weighted powders were all dissolved into a slight amount of a heated mixed acid of HCl (36%) and HNO_3 (60%) in the PC method. Propylene glycol (PG) (99.0%) was poured into the solution as a total cation concentration in the PG solution became 0.2 M. Citric acid monohydrate (99.5%) was dissolved in warmed ethanol (99.5%) in another beaker as the concentration of the citric acid ethanol solution became 1.0 M. The PG solution and the citric acid ethanol solution were mixed as the molar ratio of the total cations to citric acid became 1:5. The obtained solution was stirred at 80 °C for 3 h, and then stirred at 150 °C for 8 h. Color of the solution changed gradually from colorless to dark brown and its viscosity increased largely indicating the formation of citric acid complexes and their polymerization with PG. Precursor powder, soot-like powder, was obtained by heating the viscous solution at 350 °C for 3 h. The precursor was calcined in air at 500 °C for 6 h to obtain white decarbonized powder. The calcined powder was isochronally heated in air for 6 h at temperatures from 600 to 1400 °C by every 200 °C step to obtain each sample powder. In the SSR method, the stoichiometrically weighted starting materials were mixed and ground in an agate mortar with ethanol. The mixed powder was dried and heated isochronally in air for 6 h at each temperature as done in the PC method.

XRD patterns of sample powders were measured at room temperature by an X-ray diffractometer (Rigaku, RINT 2500) with a Cu rotary target. Crystalline phases in samples were identified by comparing the observed patterns with calculated patterns simulated by RIETAN-FP [25] from crystal structural data of ICSD [14,26–28]. Rietveld analysis was conducted using RIETAN-FP to refine the crystal structures of the crystalline phases and evaluate their mole fractions in multi-phase samples. Morphology of samples was observed by a field emission scanning electron microscope (FE-SEM) (JEOL, JSM-6701F) under acceleration voltage of 2 kV. Photoluminescence (PL) spectra were measured at room temperature by a conventional spectrofluorometer (Jasco, FP-6500).

3. Results and discussion

3.1. Pure $YScO_3$ samples

Fig. 1(a) and (b) show XRD patterns of non-doped $YScO_3$ samples prepared by the PC and SSR method, respectively. The XRD patterns of the samples heated at every 200 °C from 600 to 1400 °C are shown. Calculated XRD patterns of Y_2O_3, Sc_2O_3, $(Y_{0.5}Sc_{0.5})_2O_3$, and perovskite-type $YScO_3$ are also shown in the bottom [14,26,27]. In Fig. 1(a), a sample prepared by the PC method (PC sample) was found to be non-crystalline at 600 °C without showing diffraction peaks. The PC sample heated at 800 °C gave distinct diffraction peaks, which suggested the sample was crystalized in a single C-type phase forming a completely mixed solid solution. The phase of perovskite-type $YScO_3$ was emerged from the C-type phase at 1200 °C and a pure perovskite-type phase was obtained at 1400 °C.

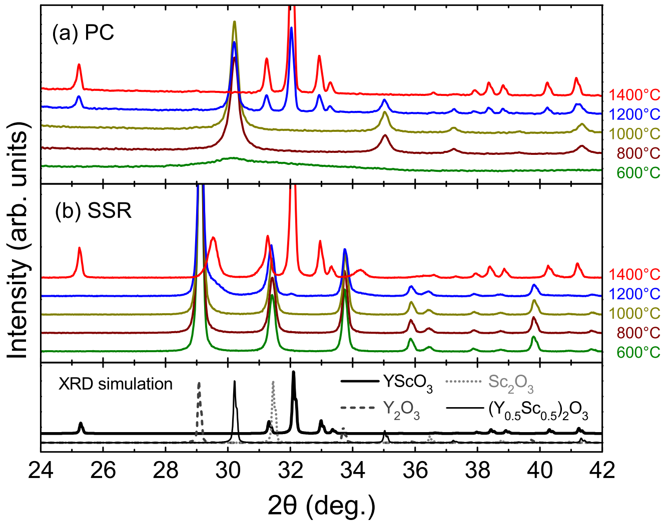

Fig. 1. XRD patterns of non-doped samples prepared by (a) a PC method and (b) a SSR method in the temperature range from 600 °C to 1400 °C. Calculated XRD patterns are shown in the bottom.

On the other hand, in Fig. 1(b), the XRD pattern for SSR at 600 °C was found to be a superposition of the patterns for Y_2O_3 and Sc_2O_3. Namely, a sample prepared by SSR method (SSR sample) was a mixture of the starting materials at 600 °C. The shapes of the XRD patterns were almost the same up to 1000 °C indicating no solid state reaction occurred obviously 1000 °C or below. A faint trace of a perovskite-type phase was observed at 1200 °C along with the broadened peak tails for the starting materials. The perovskite-type phase clearly increased at 1400 °C but the starting materials still remained in the SSR sample. Because the peak shift of the starting materials was observed, the remained stating materials were not pure Y_2O_3 and Sc_2O_3 but they formed slightly mixed solid solutions each other.

The chemical compositions of solid solutions were evaluated from observed lattice parameters as shown in Fig. 2. The dashed line was drawn first between the lattice parameters for the end members of pure C-type cubic Y_2O_3 ($a = 10.632$ Å [26]) and Sc_2O_3 ($a = 9.8459$ Å [27]). Then, observed lattice parameters for the C-type solid solution phases, namely slightly mixed solid solutions of Y_2O_3 or Sc_2O_3 in SSR samples (SSR Y_2O_3 s.s. or Sc_2O_3 s.s.) and highly mixed solid solutions in PC samples (PC s.s.), were evaluated from the XRD peak positions and plotted on the dashed line. Because the Y_2O_3-Sc_2O_3 system forms a complete solid solution, the horizontal axis gives approximate chemical composition of the solid solutions. From the plots in Fig. 2, the SSR Y_2O_3 s.s. or Sc_2O_3 s.s. were almost pure below 1200 °C and they are slightly mixed each other at 1400 °C. On the other hand, the chemical compositions of PC s.s. were approximately $(Y_{0.5}Sc_{0.5})_2O_3$ supporting the formation of highly mixed solid solutions even at crystalized temperature of 800 °C. These results verified the highly homogeneous mixing of component cations in the PC method.

To summarize the phase formation process observed in Fig. 1, mole fractions of crystalline phases in each sample were evaluated from the Rietveld refinement [29,30], assuming the chemical