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Preparation of undoped and Tb^{3+}-doped fluorescent HfO_2 spherical particles

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Undoped and Tb^{3+}-doped HfO_2 spherical particles were prepared by a sol–gel method, by using hafnium tetra-*t*-butoxide ($Hf(O\text{-}t\text{-}C_4H_9)_4$) as a precursor of hafnium dioxide, SPAN85® as a surfactant, mixed solvent of C_2H_5OH and $n\text{-}C_4H_9OH$, and H_2O, followed by investigation of their structural and optical properties. Spherical particles with good morphology and comparatively high dispersibility were obtained from solutions with the molar ratio SPAN85®:H_2O = 1:8–17.5, their sizes being 0.2–5 μm in diameter. Particles became small and aggregated when the molar ratio of H_2O was more than 17.5, but became large when it was less than 8. Spherical particles heat treated at 400°C or below were amorphous, and those heat treated at 600°C or above were crystallized. Tb^{3+}-doped HfO_2 spherical particles showed green luminescence due to the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions of the Tb^{3+} ion, and relatively strong luminescence was observed both in dried gel particles and particles heat treated at 1000°C. These Tb^{3+}-doped HfO_2 spherical particles can be expected for new optical materials.

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1. Introduction

Spherical particle phosphors of small sizes may be packed easily to produce various types of high-resolution optical displays and panels, and are therefore expected as new phosphors. The Tb^{3+} ion is the typical rare earth ion showing green luminescence. Therefore, Tb^{3+}-doped spherical particles can be expected for applications in green spherical-particle phosphors.

HfO_2 has low phonon energy (about 780 cm^{-1} [1),2)]) and is considered to be a host material suitable for luminescence of rare earth ions. HfO_2 is the substance with high hardness, high permittivity and large band gap, therefore, it is technically important for new generation materials. Compared with zirconium dioxide ZrO_2 which has similar structural features, HfO_2 has low thermal expansion coefficient[3)] and high phase transition temperatures: monoclinic to tetragonal (1720°C), tetragonal to cubic (2600°C), and cubic to liquid (2800°C).[4)]

Especially, tetragonal HfO_2 has the outstanding hardness and high chemical stability comparable as a diamond, and the high density of HfO_2 when crystallizing to tetragonal is suitable for host lattice of rare earth ions, and is attractive for a scintillating substance.[5)] There have been some reports on optical properties of HfO_2 doped with transition metal ions such as Mn^{2+}, Eu^{3+}, Tb^{3+}, Sm^{3+}, and Ce^{3+} ions.[6)–10)]

The preparation of HfO_2 particles by hydrothermal method has been reported.[11)–13)] Spherical particles of amorphous HfO_2 have been prepared by hydrolysis of hafnium-*t*-butoxide both in the aerosol phase and in ethanolic solutions.[3)] Moreover, uniform elongated colloidal HfO_2 particles have been fabricated.[14)]

To our knowledge, there have been no reports on the preparation and properties of HfO_2 spherical particles doped with rare earth ions such as Tb^{3+}. In the present study, we first established a sol–gel preparation method of undoped HfO_2 spherical particles, and then produced Tb^{3+}-doped HfO_2 spherical particles by applying this method. Structural and luminescence properties of the particles were investigated.

2. Experimental procedure

Undoped and Tb^{3+}-doped HfO_2 spherical particles were prepared by a sol–gel method. A starting solution consisted of hafnium tetra-*t*-butoxide ($Hf(O\text{-}t\text{-}C_4H_9)_4$) as a precursor of hafnium dioxide, sorbitan trioleate ($C_{60}H_{108}O_8$; SPAN85®, available from ICI America's Inc.) as a surfactant, H_2O, and C_2H_5OH and $n\text{-}C_4H_9OH$ as solvents, with the molar ratio $Hf(O\text{-}t\text{-}C_4H_9)_4$:SPAN85®:$H_2O$:$C_2H_5OH$:$n\text{-}C_4H_9OH$ = 1:0.01–1:2–10:22:55.

Undoped particles were prepared as follows: C_2H_5OH, $n\text{-}C_4H_9OH$, SPAN85® and H_2O were mixed and stirred for 15 min to prepare a solution. $Hf(O\text{-}t\text{-}C_4H_9)_4$ was added into the mixed solvent of C_2H_5OH and $n\text{-}C_4H_9OH$ under N_2 atmosphere to prepare another solution. These two solutions were mixed with stirring for 30 min in the air, and then kept for 24 h. Tb^{3+}-doped HfO_2 particles of the system $1Tb_2O_3 \cdot 99HfO_2$ were prepared by the same method, except for dissolving $Tb(C_5H_7O_2)_3 \cdot H_2O$ into the former solution containing SPAN85® described above. Gel powders prepared in the solution were filtered with suction and washed with C_2H_5OH, followed by drying at 100°C for 24 h to obtain dried gel powders. The heat treatment was carried out for the dried gel powders at 200–1000°C in the air.

The morphology and particle size of spherical particles were measured with a scanning electron microscope (SEM: KEYENCE VE–8800) and a field emission scanning electron microscope (FE-SEM: Hitachi S–4800). IR spectra were taken

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on a Fourier transform infrared spectrometer (FT-IR: Shimadzu FT-IR 8600). X-ray diffraction (XRD) patterns were measured with an X-ray diffractometer (Rigaku RINT–2200) with Cu Kα radiation. Luminescence and excitation spectra were recorded on a fluorescence spectrometer (Hitachi F–4500) with an Xe lamp as an excitation source. Luminescence quantum yield (*QY*) values were obtained by an absolute photoluminescence quantum yield measurement system (Hamamatsu C9920-02), under excitation at 254 nm with an Xe lamp as an excitation source. X-band ESR spectra were recorded on an instrument (JEOL FE2XG) at room temperature.

3. Results and discussion

Samples were prepared by changing the molar ratios of SPAN85® and H_2O with respect to $Hf(O\text{-}t\text{-}C_4H_9)_4$ in starting solutions. The molar ratios of C_2H_5OH and $n\text{-}C_4H_9OH$ have been constant in all samples.

The relation between the molar ratios in the starting solutions and the morphology of undoped HfO_2 dried gel particles is summarized in **Fig. 1**. The marks indicate different types of particles obtained: ● (good spherical particles), ▲ (spherical and bulky particles), and ■ (bulky and aggregated particles).

Figure 2 shows SEM photographs of dried gel particles of undoped HfO_2 prepared from starting solutions with various molar ratios. In comparison of Figs. 2(a) with 2(b), where the molar ratio of $Hf(O\text{-}t\text{-}C_4H_9)_4$ in the starting solution was doubled, it is found that aggregation of particles decreases and the particle size becomes large. In comparison of Fig. 2(c) and 2(d), where the molar ratio of H_2O in the starting solution was dou-

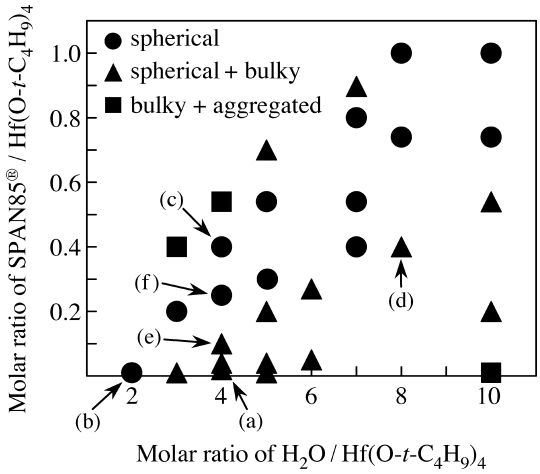
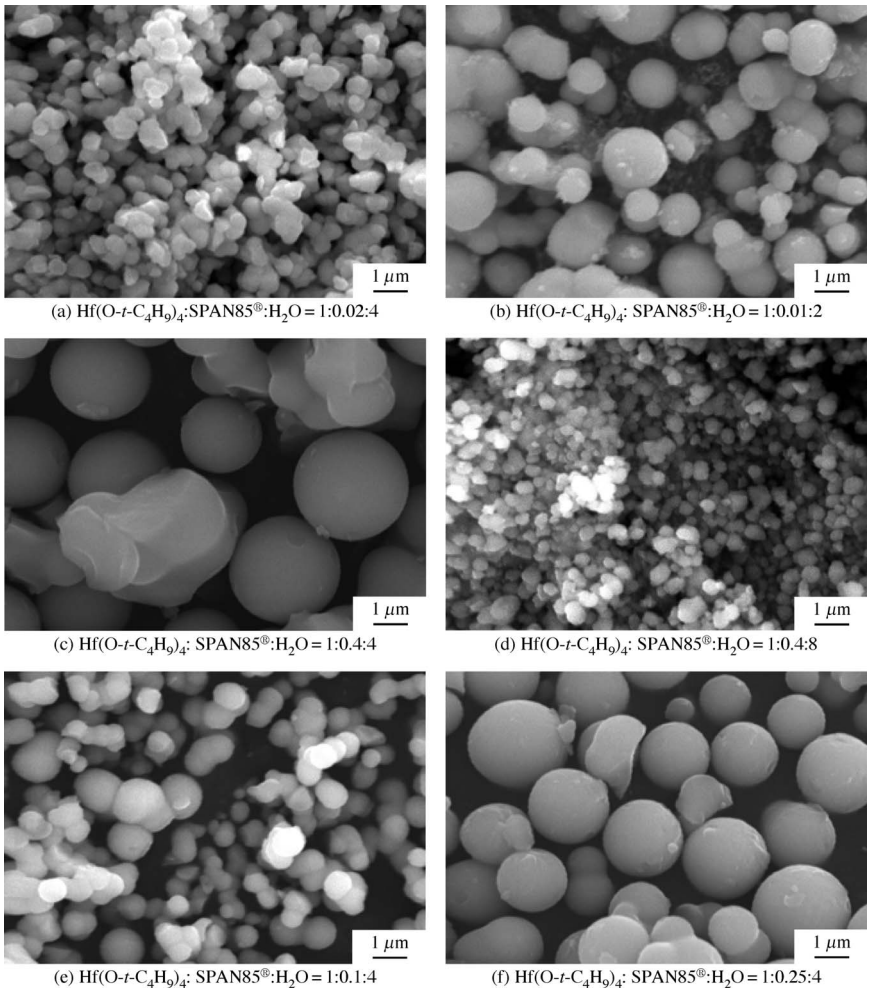


Fig. 1. Relationship between the molar ratio of starting solution and morphology of HfO_2 dried gel particles. Samples (a)–(f) correspond to those in Fig. 2 below.



(a) $Hf(O\text{-}t\text{-}C_4H_9)_4$:SPAN85®:$H_2O$ = 1:0.02:4
(b) $Hf(O\text{-}t\text{-}C_4H_9)_4$: SPAN85®:$H_2O$ = 1:0.01:2
(c) $Hf(O\text{-}t\text{-}C_4H_9)_4$: SPAN85®:$H_2O$ = 1:0.4:4
(d) $Hf(O\text{-}t\text{-}C_4H_9)_4$: SPAN85®:$H_2O$ = 1:0.4:8
(e) $Hf(O\text{-}t\text{-}C_4H_9)_4$: SPAN85®:$H_2O$ = 1:0.1:4
(f) $Hf(O\text{-}t\text{-}C_4H_9)_4$: SPAN85®:$H_2O$ = 1:0.25:4

Fig. 2. SEM photographs of HfO_2 dried gel particles prepared from starting solutions with various molar ratios of starting materials.

bled, aggregation of particles increased and the particle size became small. Comparing Figs. 2(e) with 2(f), where the molar ratio of SPAN85® in the starting solution was changed by a factor of 2.5, aggregation of particles decreased and the particle size became large.

Spherical particles with good morphology and dispersion were obtained from the starting solutions with the molar ratios of H_2O/SPAN85® = 8–17.5; the most favorable spherical particles were obtained with the molar ratio Hf(O-*t*-C_4H_9)$_4$:SPAN85®:H_2O = 1:0.25:4, as shown in Figs. 1(f) and 2(f).

The effect of SPAN85® for obtaining good spherical particles is considered to be as follows: when a large excess of SPAN85® is used, the viscosity of sol solution increases enormously, leading to less dispersion and inhomogeneous concentration of Hf(O-*t*-C_4H_9)$_4$. As a result, it is likely that particles of large size are obtained, and aggregation occurs. As the concentration of SPAN85® is too low, the viscosity of sol solution decreases, which results in collisions of small particles to lead to aggregation before the precursor particle growth. When appropriate concentrations of SPAN85® are used, as shown in Fig. 1, molecules of SPAN85® cover the surface of the spherical particles considerably, and then the precursor particles can grow maintaining the spherical shape without aggregation.

Figure 3 shows heat-treatment effects of XRD patterns for undoped HfO_2 spherical particles prepared from the starting solution with the molar ratio Hf(O-*t*-C_4H_9)$_4$:SPAN85®:H_2O = 1:0.25:4. It is found that cubic HfO_2 dominates in the spherical

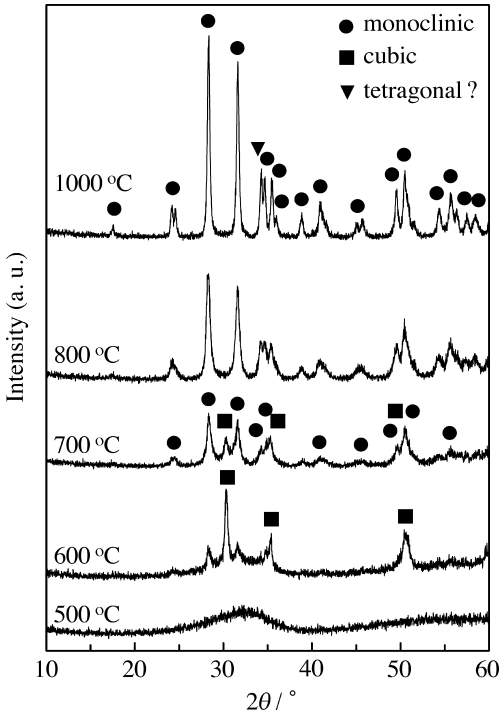


Fig. 3. XRD patterns of undoped HfO_2 spherical particles heat treated at various temperatures.

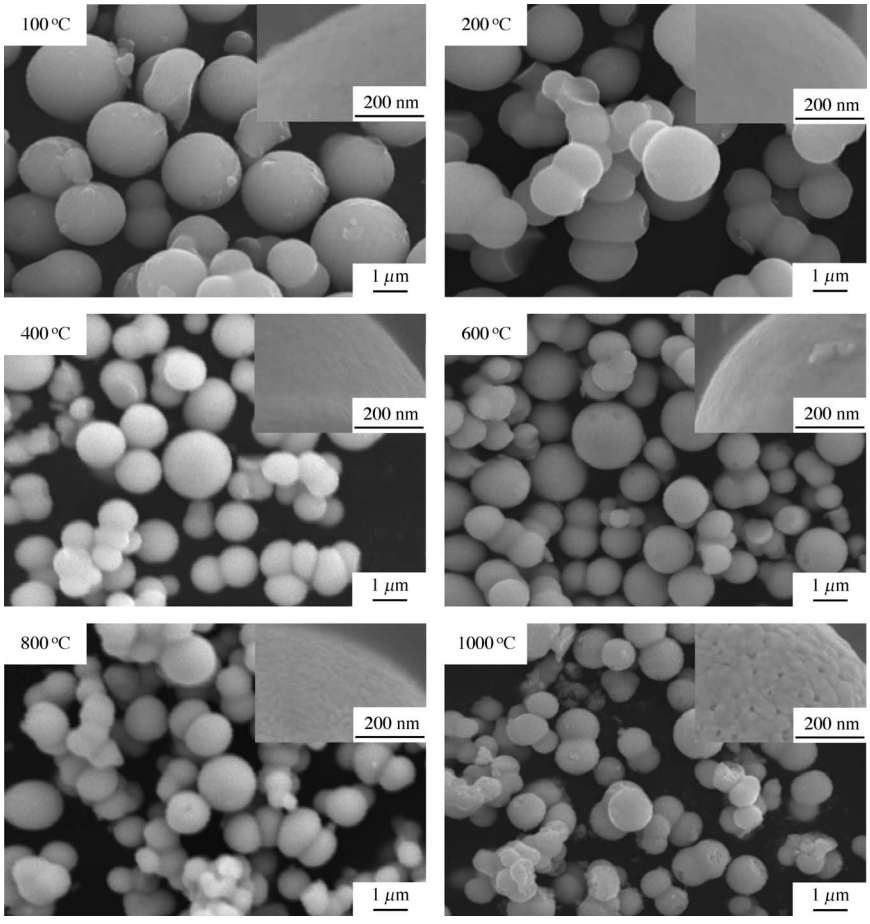


Fig. 4. SEM photographs of undoped HfO_2 spherical particles heat treated at various temperatures. Insets are FE-SEM photographs of surfaces of the particles.

particles heat treated at 600°C, cubic and monoclinic HfO_2 phases coexist in those heat treated at 700°C, and monoclinic HfO_2 becomes dominant in those heat treated at 800°C or above. Moreover, weak diffraction peaks, considered to be due to tetragonal HfO_2, are observed in the spherical particles heat treated at 1000°C. Similar diffraction peaks have also been observed in rare earth-doped yttrium-hafnium sol–gel oxide powders heat treated at 1000°C.[6] Usually, monoclinic HfO_2 was obtained by the heat treatment at lower temperatures such as several hundred °C,[4),13),15),16] while it is considered that tetragonal HfO_2 becomes dominant by the heat treatment at 1000°C or above, and by adding Y_2O_3 into HfO_2.[6] Cubic HfO_2 as well as monoclinic HfO_2 were observed in the spherical particles heat treated at 600 and 700°C. As described in the section of Introduction, cubic HfO_2 can be obtained by phase transition from tetragonal HfO_2 at the high temperature of about 2600°C.[4] It is thermodynamically metastable at low temperatures, and therefore seems to appear only under special conditions like ion beam assisted deposition at low temperatures.[17] Since cubic HfO_2 is attractive as high dielectric constant material, preparing cubic HfO_2 by such a simple sol–gel method in the present study will be of value.

Figure 4 shows SEM photographs of undoped HfO_2 spherical particles heat treated at various temperatures. These particle sizes were about 1 μm in diameter, and the sizes decreased and surfaces of the spherical particles became coarse with increasing the heat-treatment temperature. Especially, it is found that surfaces of the spherical particles heat treated at 800 and 1000°C are quite coarse with some hollows. This is probably caused by burning out of residual organics and by densification of the spherical particles with the surface grain growth during the heat treatment at high temperatures. Similar coarsening has been reported for Co_3O_4 particles prepared from cobalt alkoxides.[18]

SEM photographs of $1Tb_2O_3$-$99HfO_2$ samples, dried (100°C) gels and spherical particles heat treated at 1000°C, are shown in **Fig. 5**. These doped particles are found to be spherical, however their morphology is somewhat inferior to the undoped HfO_2 spherical particles.

Figure 6 shows luminescence and excitation spectra of $1Tb_2O_3$-$99HfO_2$ spherical particles heat treated at various temperatures. Under UV excitation at 254 nm, green luminescence due to the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions of Tb^{3+} ions was observed (Fig. 6(a)). The luminescence was strong in the dried gel particles (QY = 1.3 ± 0.1%) and the spherical particles heat treated at 1000°C (QY = 0.9 ± 0.1%).

Some investigations for optical properties of rare earth ions

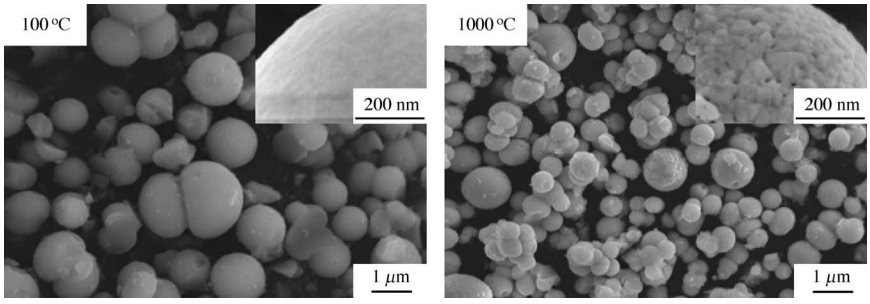


Fig. 5. SEM photographs of $1Tb_2O_3$·$99HfO_2$ dried (100°C) gels and spherical particles heat treated at 1000°C. Insets are FE-SEM photographs of surfaces of the particles.

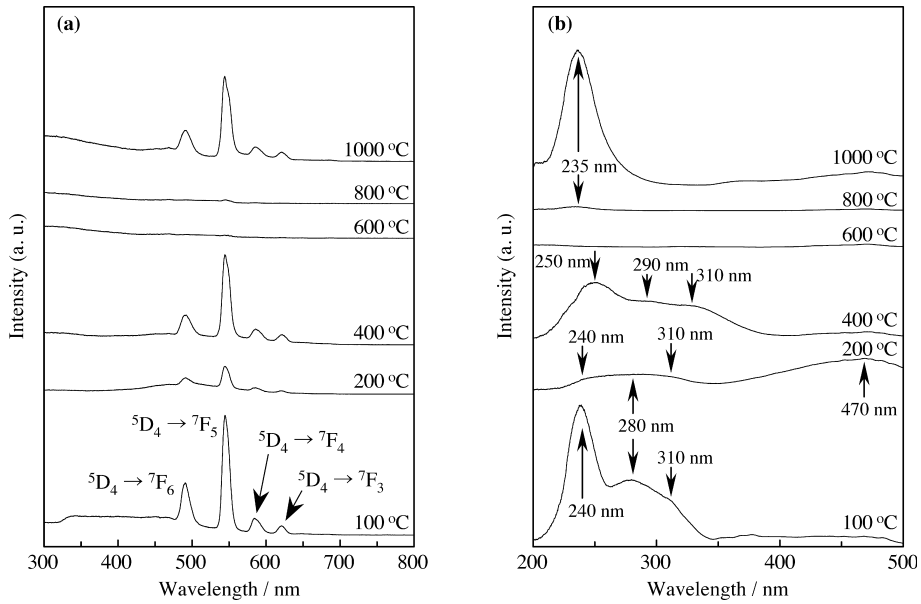


Fig. 6. Luminescence spectra (a) under excitation at 254 nm and excitation spectra (b) for the 545-nm luminescence of $1Tb_2O_3$·$99HfO_2$ spherical particles heat treated at various temperatures.

doped in HfO_2 have been reported, as mentioned in the section of Introduction. The relation between the luminescence intensity and the heat-treatment temperature has been reported in Ce^{3+}-doped HfO_2 materials.[10),19)] In monoclinic HfO_2 layers heat treated at 300–500°C, the luminescence due to Ce^{3+} ions weakens with increasing the heat-treatment temperature,[10)] while in strontium hafnate powders containing orthorhombic $SrHfO_3$ and monoclinic HfO_2 that were heat treated at 800–1200°C, the Ce^{3+} ion showed the strongest luminescence in a sample heat treated at the high temperature of 1200°C.[19)] These results somewhat resemble the result in the present study; the Tb^{3+} ion showed strong luminescence both in the samples heat treated at low temperatures and in the monoclinic HfO_2 spherical particles heat treated at 1000°C.

The reason why the luminescence intensity of the Tb^{3+} ion is low in the monoclinic HfO_2 spherical particles heat treated at 600 and 800°C is that the particles heat treated at 600°C are dark brown-colored due to residual carbon species resulted from combustion of organics during the heat treatment and that the crystallinity of the spherical particles heat treated at 800°C is incomplete. The oxidation of Tb^{3+} ions to Tb^{4+} ions has been reported to occur in oxide samples during the heat treatment, and those Tb^{4+} ions have been detected by optical absorption[20)] and ESR[21),22)] spectra. In the present study, no XRD data for mixed oxides like Tb_4O_7 containing Tb^{3+} and Tb^{4+} ions were obtained, and no ESR signal due to Tb^{4+} ions were obtained, therefore the oxidation of Tb^{3+} ions is not likely to occur. In addition, an ESR signal with g value of about 2.002 which is due to carbon-related radicals[23),24)] was observed in the spherical particles heat treated at 200, 400 and 600°C, where the dark brown spherical particles heat treated at 600°C had the strongest intensity.

Figure 6(b) shows excitation spectra of $1Tb_2O_3{\cdot}99HfO_2$ spherical particles heat treated at various temperatures. All of the excitation bands and shoulders observed in the range of 240 to 350 nm are probably due to the $4f^8$ to $4f^75d^1$ transitions of Tb^{3+}.[25),26)] No band gap transition in HfO_2 may appear in Fig. 6(b) because of its large band gap energy of 6.15 eV (201 nm).[27)] According to the previous report,[28)] the peaks and shoulders observed in Fig. 6(b) are considered to be due to Tb^{3+}-containing small-size particles (235 and 240 nm) and agglomerated particles (280, 290, 310 and 330 nm).

As mentioned above, both the doped dried gel particles and the spherical particles heat treated at 1000°C are found to be favorable for the Tb^{3+} luminescence in the present study. Further study will be needed to produce Tb^{3+}-doped HfO_2 spherical particles with high QY values.

4. Conclusion

We established the sol–gel preparation method of undoped HfO_2 spherical particles, and then produced Tb^{3+}-doped HfO_2 spherical particles with green luminescence by applying this method. Spherical particles with good morphology and comparatively high dispersibility were obtained from solutions with the molar ratio SPAN85®:H_2O = 1:8–17.5, their sizes being 0.2–5 μm in diameter. It is found that SPAN85® plays an important role in obtaining HfO_2 spherical particles without aggregation. Spherical particles heat treated at 400°C or below were amorphous, and those heat treated at 600°C or above were crystallized. Cubic HfO_2 is dominant in the spherical particles heat treated at 600°C, cubic and monoclinic HfO_2 coexist in those heat treated at 700°C, and monoclinic HfO_2 becomes dominant in those heat treated at 800°C or above. Crystallization and phase transition temperatures of $1Tb_2O_3{\cdot}99HfO_2$ spherical particle were slightly lower than those of undoped spherical particle. $1Tb_2O_3{\cdot}99HfO_2$ spherical particle showed green luminescence due to the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions of the Tb^{3+} ion. The luminescence was strong in both the $1Tb_2O_3{\cdot}99HfO_2$ dried gel particles ($QY = 1.3 \pm 0.1\%$) and the spherical particle heat treated at 1000°C ($QY = 0.9 \pm 0.1\%$).

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