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Luminescence studies of the rare earth ions-doped CaF_2 and MgF_2 films for wavelength conversion

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Abstract

The rare earth (RE) Eu, Yb ions-doped CaF_2 and MgF_2 films were prepared by the vacuum deposition and sol–gel methods. In the sol–gel method, the trifluoroacetic acid (TFA, CF_3COOH) was used as a source of fluorine. The RE doped CaF_2 and MgF_2 films were characterized by photoluminescence (PL), photoluminescence excitation (PLE), the X-ray diffraction (XRD) and the atomic force microscopy (AFM) measurements. By the vacuum deposition, the strong luminescence due to the electric dipole allowed $4f^n$–$4f^{n-1}5d^1$ transitions of Eu^{2+} and Yb^{2+} ions were observed similar with those of the crystalline bulks. The AFM surface images of sol–gel films revealed the formation of the nano-particles for alkaline earth fluorides.

Keywords: CaF_2; MgF_2; Eu; Yb; Sol–gel synthesis; Vapor deposition; Luminescence

1. Introduction

Rare earth (RE) ions have been studied as favorable luminescent materials, and were widely applied to phosphor, fiber amplifiers, solid-state laser, etc. [1,2]. We proposed the usefulness of the wavelength conversion conception for improvements of the conversion efficiencies of the solar cells by applying the RE (Eu, Sm) doped fluoride crystal discs [3,4]. The alkaline earth fluorides of CaF_2, MgF_2 are promising materials for the anti-reflection film owing to their high transmittances and low refractive indices in all wavelength region of the sunlight.

The optical characterization and sol–gel synthesis of porous alkaline earth and lanthanide fluoride films using the hydrofluoric acid (HF) [5] and the trifluoroacetic acid (TFA, CF_3COOH) [6–9] have been studied. In the present study, the Eu and Yb ions-doped CaF_2 and MgF_2 films as the UV to visible conversion layer were prepared by the vacuum deposition and the sol–gel methods.

2. Experimental details

The PL, PLE and the XRD and the AFM surface images were investigated for the RE doped CaF_2 and MgF_2 films. The PL and PLE spectra were obtained by the spectrophotometer (JASCO.FP-6500, Japan) in the spectral region of 220–750 nm. The film thickness was measured using the surface profiler (Dektak3ST, ULVAC, Japan). The XRD spectra was obtained by the X-ray diffractometer (XRD-DSC III LT, Rigaku, Japan). The AFM surface images were observed by scanning probe microscope (JEOL, JSTM-4200A, Japan).

2.1. Vapor deposition

To prepare the CaF_2:Eu^{2+}, MgF_2:Eu^{2+}, MgF_2:Yb^{2+} targets for vacuum deposition, the source powders of CaF_2 (99.99%), MgF_2 (99.99%) EuF_3 (99.9%) and YbF_3 (99.9%), were mixed in a glove-box equipped with N_2 gas (99.999%). The mixed powders were charged into a graphite crucible, and were pre-heated for 4 h at 500 °C, and then were melted flowing Ar gas (99.9999%) atmosphere. The melt was kept for 4 h

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and then was slowly cooled to room temperature during 8 h. The targets were directly vaporized to the fused silica glasses under the vacuum below 3×10^{-4} Pa. The vacuum deposition procedures are as follow; pre-deposition treatment for 10 min, deposition rate below 1.0 nm/s and substrate temperature of 200 °C.

2.2. Sol–gel synthesis

For the sol–gel synthesis of CaF_2 and MgF_2, $Ca(OH)_2$ (99.9%, Wako) and $Mg(OH)_2$ (99.9%, Wako) powders were dissolved into the mixed solutions of ethanol, distilled water and TFA. The $EuCl_3{\cdot}6H_2O$ and $YbCl_3{\cdot}6H_2O$ powders were dissolved into mixed solutions and stirred for 2 h in the ultra sonic bath. The concentrations of alkaline earth and rare earth compounds were 0.5, 0.0025 M, respectively. The molar ratio of TFA to alkaline earth was kept at 6.2. The solutions were spin-coated on fused silica glass with rotation speed of 2500 rpm, and then immediately heated at 400, 500 and 600 °C for 15 min. The spin coating and heating processes were repeated by five times.

3. Results and discussion

3.1. Vacuum deposited films

The optically transparent films were successfully obtained by vacuum deposition, and their PL an PLE spectra are shown in Fig. 1(i), for film thickness of 1 μm. The luminescence due to the intra f–f transition of Eu^{3+} ion was not observed at 575 and 613 nm predicted. On the other hand, the luminescence due to the $4f^7$–$4f^6 5d^1$ transitions of the Eu^{2+} ion were observed for $CaF_2{:}Eu^{2+}$, $MgF_2{:}Eu^{2+}$ at the wavelength peaks at 425, 438 nm, respectively, as shown in Fig. 1(i). For $MgF_2{:}Yb^{2+}$ films, the luminescence due to the $4f^{14}$–$4f^{13}5d^1$ transition of the Yb^{2+} ion appeared at 474 nm. These spectra provide a good coincidence with those of the crystalline bulks already reported [10–12]. It should be noted that the RE doped compounds are not decomposed during evaporation process, because the $4f^n$–$4f^{n-1}5d^1$ transitions of the rare earth ions are strongly influenced by the crystal fields of the ligand ions. This is also thought to be due to the high dissociation energies between alkaline earth and fluorine ions [13].

The Eu doped CaF_2 film showed the strongest PL intensity, and the large concentration quenching over 1 mol%, as shown in Fig. 1(ii). This is due to the similar ionic radius of Ca^{2+} (1.12 Å) to be substituted for Eu^{2+} (1.25 Å). On the other hand, Mg^{2+} ion (0.72 Å) would be too small to be substituted for Eu^{2+} ion. The $MgF_2{:}Yb^{2+}$ film showed very weak luminescence as compared to that of $MgF_2{:}Eu^{2+}$, though the ionic radius of Yb^{2+} (1.02 Å) is smaller than that of Eu^{2+} ion.

This may be caused from the high reduction potential ($Yb^{2+}/Yb^{3+} = 1.15$ eV) of Yb ion as compared to that ($Eu^{2+}/Eu^{3+} = 0.35$ eV) of Eu ion [14] and so the Yb ion is easy to be trivalent. Actually, it was comprehended that the luminescence of Yb^{3+} ion were not confirmed in the present study, because the luminescence due to the intra 4f–f transition ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) of Yb^{3+} ion is within infrared region around 1040 nm reported [1,2].

The XRD spectra of the vacuum deposited films are shown in Fig. 2. The strong diffraction peaks appeared for both pure and RE doped alkaline earth fluorides films. Especially, the CaF_2 films showed a much strong diffraction on (2 2 0), and this is connected with the relationship between the formation energy and substrate temperature [15].

3.2. Sol–gel synthesized films

The PL spectra of sol–gel synthesized films for each heating temperature are shown in Fig. 3, where the excitation wavelength is 300 nm. The luminescence peaks of the Eu^{3+} ion were observed at 575, 614, 631 nm, respectively, and increased with higher temperatures.

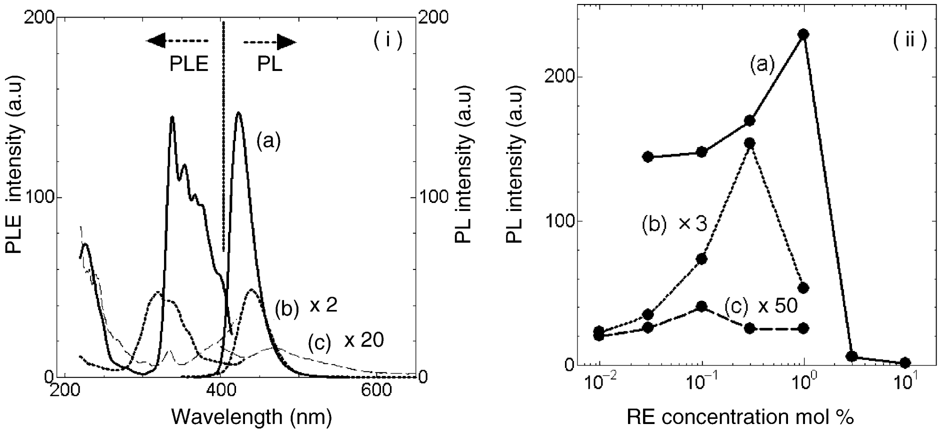

Fig. 1. (i) The PL and PLE spectra of the vacuum deposited films: (a) $CaF_2{:}Eu^{2+}$(0.1 mol%), (b) $MgF_2{:}Eu^{2+}$(0.1 mol%), (c) $MgF_2{:}Yb^{2+}$ (0.03 mol%). (ii) The concentration dependences: (a) $CaF_2{:}Eu^{2+}$, (b) $MgF_2{:}Eu^{2+}$ and (c) $MgF_2{:}Yb^{2+}$.

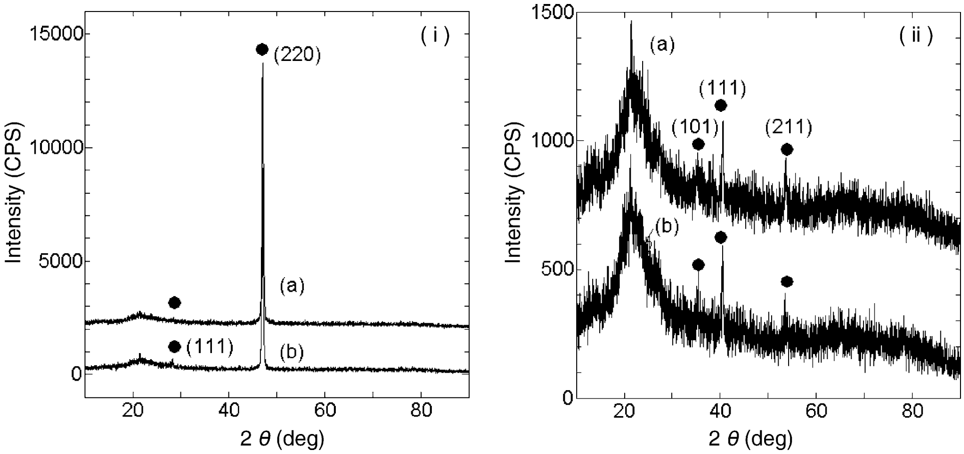

Fig. 2. XRD spectra for vacuum deposited films: (i), (a) pure CaF_2 and (b) CaF_2:Eu (1 mol%); (ii), (a) Pure MgF_2 and (b) MgF_2:Yb (0.1 mol%).

These emission peaks are assigned to the transitions of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_4$, respectively. The luminescence peak due to the electric dipole allowed $4f^7$–$4f^65d^1$ transitions of Eu^{2+} ion appeared at 439 nm for MgF_2:Eu film heated at 500 °C; however, decreased at 600 °C, though the luminescence of Eu^{3+} ion increased until 600 °C, as shown in Fig. 3(ii). It was not confirmed the luminescence of both Yb^{2+} and Yb^{3+} ions for MgF_2:Yb films. This is thought to be due to the high reduction potential of Yb ion and the luminescence at infrared region of the Yb^{3+}, as mentioned above.

The XRD spectra for sol–gel synthesized films are shown in Fig. 4, where the diffraction peaks from the alkaline earth oxides were observed when the films were heated at 600 °C. This evidence suggests that the oxidation have occurred in the high temperature, and is related to the changes of luminescence of Eu^{2+} and Eu^{3+} ions, as shown in Fig. 3. It was found that the oxidation of the alkaline earth and rare earth fluorides took place at high temperature of 600 °C by XRD measurements [7].

The diffraction patterns from the sol–gel synthesized films were different from the results of vacuum deposited films as compared Fig. 2 with Fig. 4. These differences are presumably due to the formation process of alkaline earth fluorides in sol–gel synthesis. It was studied that the decomposition of the alkaline earth and lanthanide trifluoroacetate gels by heating obeys following reactions [6–8]:

$$Ca(CF_3COO)_2 \rightarrow CaF_2 + gas$$

$$La(CF_3COO)_3 \rightarrow LaF_3 + gas$$

The AFM surface images of sol–gel synthesized films are shown in Fig. 5. The nano-particles were observed for CaF_2:Eu and MgF_2:Eu films heated at 500 °C, and the particle sizes are estimated as 180 and 120 nm, respectively. In contrast, the nano-particles were not confirmed for all films heated at 400 °C. For low temperatures below 400 °C, nanoparticles might be difficult to be formed [9].

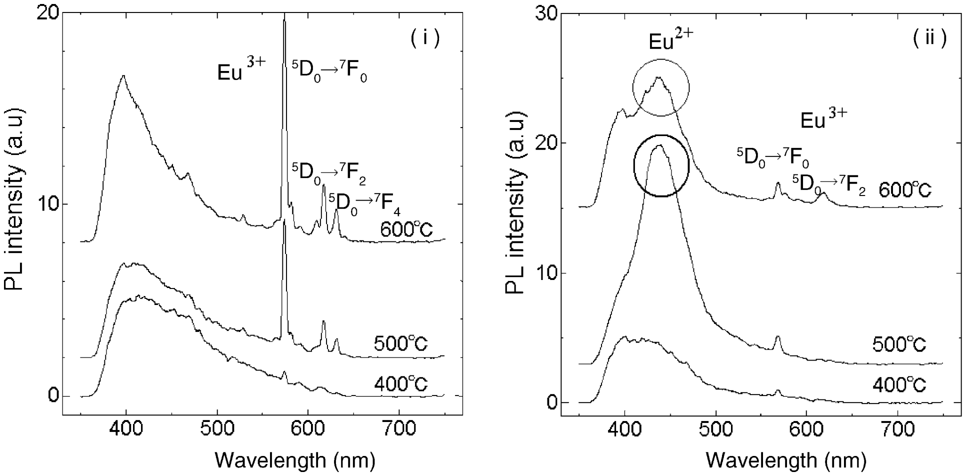

Fig. 3. PL spectra of sol–gel synthesized films: (i) CaF_2:Eu and (ii) MgF_2:Eu, where the Eu concentration of 0.5 mol% and film thickness are 610 and 620 nm, respectively.

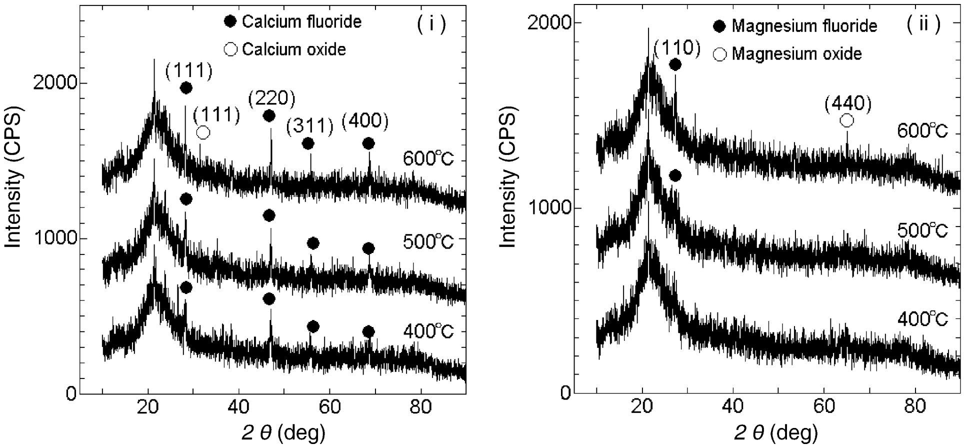

Fig. 4. The XRD spectra for sol–gel synthesized films: (i) CaF_2:Eu and (ii) MgF_2:Eu for both Eu concentrations at 0.5 mol%.

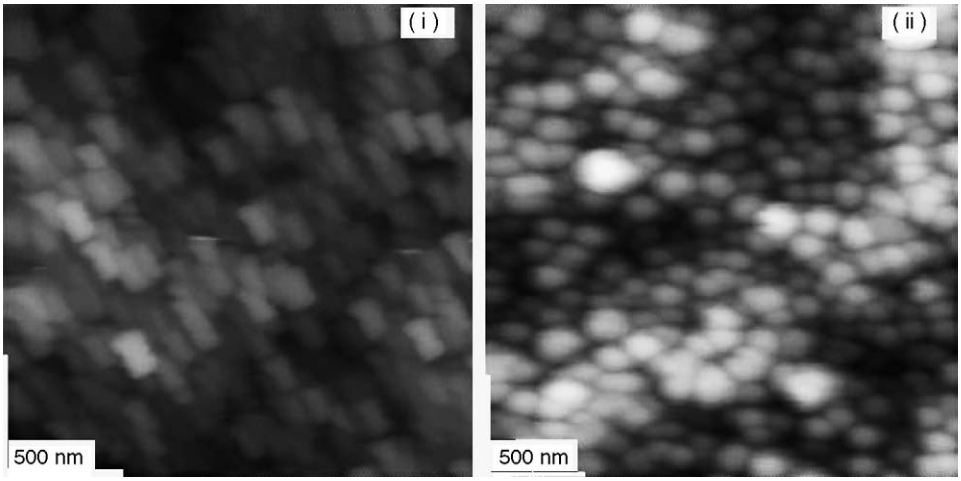

Fig. 5. AFM surface images of sol–gel synthesized films: (i) CaF_2:Eu and (ii) MgF_2:Eu for both Eu concentrations of 0.5 mol% and the heating temperature at 500 °C.

4. Conclusion

The Eu, Yb ions-doped CaF_2, MgF_2 films are synthesized by two procedures of vacuum deposition and sol–gel methods, and are characterized by the PL, PLE, XRD and AFM measurements. By the vacuum deposition, the luminescence due to the electric dipole allowed $4f^n$–$4f^{n-1}5d^1$ transitions of Eu^{2+} and Yb^{2+} ions were observed similar to those of the crystalline bulks. The divalent Eu ion doped CaF_2 film showed the strongest PL intensity in all measured samples, and exhibited the behavior of large concentration quenching. The sol–gel synthesized CaF_2, MgF_2 doped with Eu films resulted in the luminescence of Eu^{2+} and Eu^{3+} ions, respectively. From the AFM observations, it was found that the nano-particles of the Eu doped CaF_2, MgF_2 were successfully formed by sol–gel method.

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