

Preparation of Mn Doped Mg_2TiO_4 Deep Red Emitting Phosphor by Liquid Phase Synthesis

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Keywords: Liquid Phase Synthesis, Deep Red Emission, $Mg_2TiO_4:Mn$,

ABSTRACT

Mn doped deep red emitting phosphor $Mg_2TiO_4:Mn$ was synthesized by a liquid phase synthesis (LPS) method using urea and polyethylene glycol (PEG). Adding PEG and urea, the inhomogeneous and agglomeration of the particle decreased, and fine particle phosphor was obtained. The XRD results showed that the Mg_2TiO_4 phase was preferentially formed by LPS. PL and PLE results showed that it was observed at 658 nm and 670 nm under 450 nm excitation.

1 INTRODUCTION

Currently, deep red emitting phosphor has been developed as a light source for growing plants. This is also expected as a wavelength conversion material for solar cells. All of them need to absorb blue to ultraviolet light emit red light efficiently.

So far, Eu^{3+} has been widely used as a luminescent center of red phosphors. The emission wavelength of Eu doped phosphors are around 610 nm, therefore the phosphor which shows around 700 nm have been desired. More over in recent years, rare earth-free phosphors have been demanded because of environmental and economic backgrounds. However, suitable phosphors which shows deep red emission with good efficiency has not been developed yet. Furthermore, considering the application of phosphors, it is necessary to prepare fine particles. However, it is concerned that the luminescent efficiency may be decreased due to the fine particle formation.

In our previous work, $Mg_2TiO_4:Mn$ phosphor which tuned IV ions by Ge and Si prepared by solid phase synthesis was evaluated [1]. Mg_2TiO_4 has an inverse spinel structure. Mn^{4+} is replaced IV^{4+} site (Ti, Ge and Si) in the octahedral site adding a small amount of Mn. As a result, the 3d orbital of Mn^{4+} was affected by the ligand, splitting of crystal field occurs, and then the energy level difference is created. Deep red emission was caused from the energy transition between these energy level discharges [2].

Solid phase synthesis (SPS) has been widely used in the production of general phosphors. However, it is required by low temperature firing or using of chemical

additives to suppress of crystal growth to aim for fine particles [3]. Therefore, in this research, we have tried to prepare $Mg_2TiO_4:Mn$ fine particle phosphor by liquid phase synthesis (LPS) and control the particle size [4].

In this study, polyethylene glycol (PEG) and urea which were expected as surfactant and flocculant were used.

2 EXPERIMENT

Fig. 1 shows the experimental procedure for preparing the $Mg_2TiO_4:Mn$ phosphor powder.

Magnesium di-n-propoxide ($Mg(O-n-C_3H_7)_2$) was dissolved with ethanol at 80°C, and PEG20k of 0 ~ 40 mol% was added (precursor A). Titanium chloride ($TiCl_4$) and manganese chloride ($MnCl_2$) were dissolved in water (precursor B). Precursor A was added to precursor B, urea of 300 mol% was mixed and stirred for 24 hours to prepare a colloidal solution. Next, the solution was dried in oven at 130°C, and fired at 1200°C for 3 hours in air atmosphere using a muffle furnace to obtain phosphors. The concentration of Mn was maintained at 1 mol%.

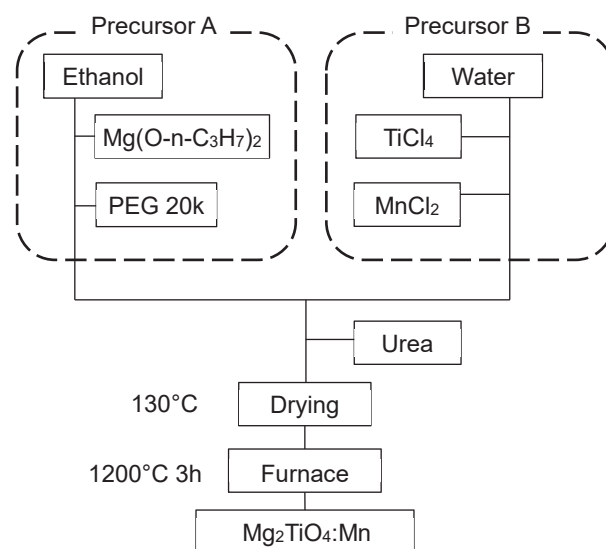


Fig. 1 Experiment flowchart preparation of $Mg_2TiO_4:Mn$ phosphor powder.

The structural property and the morphologies of the phosphors were evaluated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Photoluminescent (PL, PLE) properties were measured by Xe lamp. The phosphors prepared by SPS were measured for comparison.

3 RESULTS AND DISCUSSION

Fig. 2 shows the XRD patterns of the $Mg_2TiO_4:Mn$ phosphors synthesized by (a) solid phase synthesis, (b) without urea, (c) with urea 300 mol% and without PEG, and (d) with urea 300 mol% and PEG 40 mol%, respectively. The diffraction peaks from Mg_2TiO_4 phase were observed in all phosphors. In addition, the peak of $MgTiO_3$ phase appeared in SPS powder. It is thought that the dispersion of the raw materials was insufficient, and $MgTiO_3$ phases were formed preferentially by low-temperature firing at $1200^\circ C$. MgO phase was observed in the phosphor prepared without urea by liquid phase synthesis as shown in Fig.2 (b). By not using urea having a role as a dispersant and neutralizing agent, PH of Precursor B was biased to acidity, then the reaction of chlorides was delayed, it is considered that the priority MgO was formed. $MgTiO_3$ phase disappeared by preparation using urea, as shown in Fig.2(c) [5]. It is considered that the urea acted as neutralizer and promoted the reaction of the raw materials. These results suggested that urea was effective for low temperature synthesis. However, $MgTiO_3$ phase was observed again by addition of PEG, in Fig.2 (d), the phosphor prepared with urea and PEG. It is considered that the raw materials were not dispersed enough because the viscosity of the

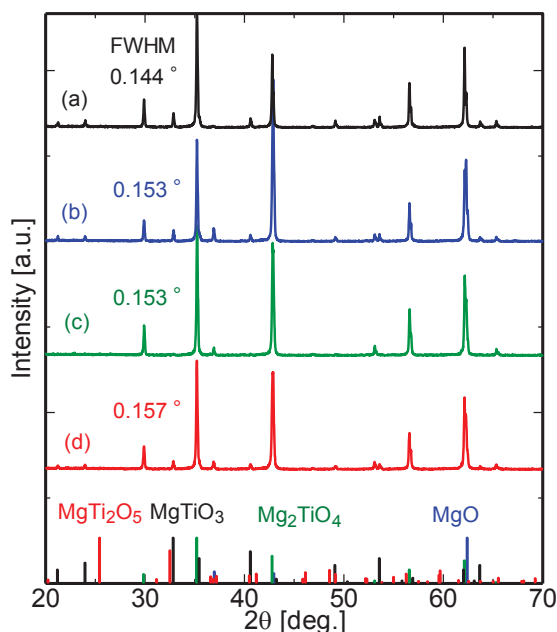


Fig. 2 XRD patterns of $Mg_2TiO_4:Mn$ phosphors prepared by (a) SPS, (b) without Urea and PEG, (c) with Urea 300 mol% and without PEG, and (d) with Urea 300 mol% and PEG 40 mol%.

precursor solution increased by addition of PEG.

Fig. 3 shows the SEM images of the phosphors synthesized by (a) solid phase synthesis, (b) without urea, (c) with urea 300 mol% and without PEG, and (d) with urea 300 mol% and PEG 40 mol%, respectively. From Fig. 3(a), prepared by SPS, the particle size was not uniform and aggregated. It was also observed agglomeration of particles in Fig.3(b), prepared without urea. The dried gel had viscosity, then stuck and adhered each particle during firing. The aggregation was reduced by preparation with urea and without PEG (Fig.3(c)). It is thought that the urea increased the dispersibility of raw materials. However, the uniformity of the particles and smoothness of the surface are insufficient. By adding PEG, highly uniformity was obtained as shown in Fig.3(d). It is considered that PEG affected as a surfactant and prevented aggregation of the precursors.

The crystallite diameter was calculated from the results of XRD measurement using Scherrer's formula. From the calculation, the diameters were (a) 57.93 nm, (b) and (c) 54.52 nm, and (d) 53.13 nm, respectively. From these results, it is considered that urea and PEG play an important role in controlling the particle shape.

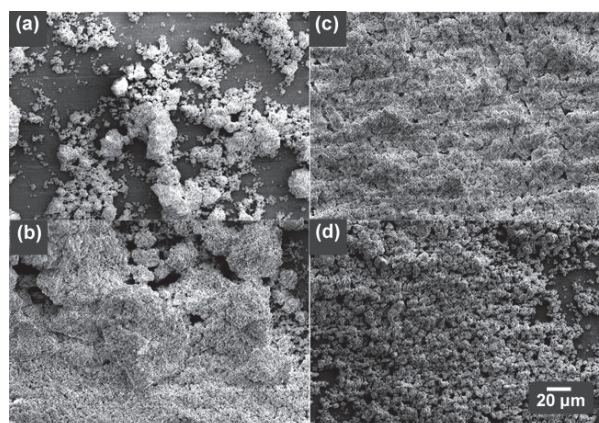


Fig. 3 SEM images of $Mg_2TiO_4:Mn$ phosphors prepared by (a) SPS, (b) without Urea and PEG, (c) with Urea 300 mol% and without PEG, and (d) with Urea 300 mol% and PEG 40 mol%.

Fig. 4 shows the PL and PLE spectra of $Mg_2TiO_4:Mn$ phosphors synthesized by (a) solid phase synthesis, (b) without urea, (c) with urea 300 mol% and without PEG, and (d) with urea 300 mol% and PEG 40 mol%, respectively, excited by 450 nm and monitored at 658 nm. From the PL results, all phosphors showed deep red emission peaked at 658 nm and 670 nm, which is considered to be emission due to the ${}^2E - {}^4A_2$ transition of Mn^{4+} . There was no emission of $MgTiO_3:Mn$ around 700 nm, luminescent center Mn^{4+} was replaced in Ti^{4+} site of Mg_2TiO_4 phase preferentially [4]. The phosphor by

SPS showed the highest luminance by excitation under 450 nm. On the other hand, PL intensity became weakened by liquid phase synthesis. It is considered that the particle size of the phosphor of SPS was larger than the others, then longer excitation wavelength such as 450 nm penetrated deeper and excited because of aggregated particles.

From PLE spectra, two excitation bands of around 500 and 320 nm were observed in all phosphors. The phosphor prepared with urea showed stronger excitation at UV region. It seems that Mn^{4+} was difficult to excite directly by longer wavelength due to its small particle size, however, the host excitation was easily induced by UV excitation.

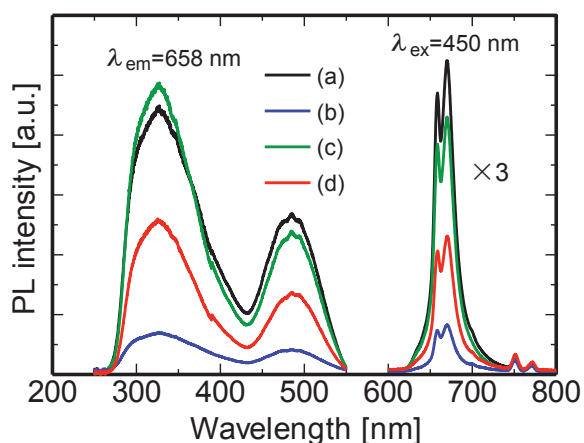


Fig. 4 PL and PLE spectra of $Mg_2TiO_4:Mn$ phosphors prepared by (a) SPS, (b) without Urea and PEG, (c) with Urea 300 mol% and without PEG, and (d) with Urea 300 mol% and PEG 40 mol%, excited by 450 nm and monitored at 658 nm.

4 CONCLUSIONS

Mn doped deep red emission phosphor $Mg_2TiO_4:Mn$ was prepared by liquid phase synthesis with urea and polyethylene glycol.

Mg_2TiO_4 phase were confirmed in all phosphors. However, the peak of $MgTiO_3$ and MgO phases appeared because the dispersions of the raw materials were insufficient, and the reaction of chlorides was delayed. The urea acted as neutralizer and promoted the reaction of the raw materials.

From the SEM images, the urea increased the dispersibility of raw materials. And PEG affected as a surfactant and prevented aggregation of the precursors.

All phosphors showed deep red emission peaked at 658 nm and 670 nm. It indicates that the luminescent center Mn^{4+} was replaced in Ti^{4+} site of Mg_2TiO_4 phase preferentially. From PLE spectra, Mn^{4+} was difficult to excite directly by longer wavelength due to its small particle size, however, the host excitation was easily induced by UV excitation.

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