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Effect of High-Pressure Liquid Phase Synthesis of Deep Red Emitting Mg_2TiO_4:Mn

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ABSTRACT

In this study, we attempted to synthesize deep-red luminescent Mg_2TiO_4:Mn under pressure and investigated the effect of the process on the phase formation. As a result, the formation of seed crystals under pressure was considered to be effective in controlling the particle size.

1 Introduction

Currently, Eu is widely used as a luminescent center in red light-emitting phosphors. However, since Eu is a rare earth element[1], its use is considered undesirable both economically and from an environmental point of view. Therefore, we focused our attention on Mn as an alternative luminescent center to Eu. Mn^{4+} exhibits red to deep red luminescence[2] and is expected to be a light source for plant growth[3] and a wavelength conversion material for solar cells[4]. Considering these applications, fine particles are desirable in terms of light conversion and transmission. Although it is possible to make fine particles by mechanical grinding, it is preferable to make fine particles during synthesis because of concerns about a decrease in luminous efficiency. In this study, we attempted to synthesize Mg_2TiO_4:Mn, a deep red luminescent material, under pressure[5] and investigated the effect of phase formation during the synthesis.

2 Experiment

$MgCl_2$, $TiCl_4$, and $MnCl_2$ were weighed according to their stoichiometric ratios, and the pH was adjusted using NH_4OH, and the mixture was stirred. 50 ml of the solution was adjusted to a 100 ml container, and the mixture was pressurized at 200 °C for 25 to 100 hours. Afterwards, the mixture was dried to form the $Mg_2Ti_{0.99}O_4$:$Mn_{0.01}$ phase was formed. The effect of pressurization time on nucleation was studied from these samples. The effect of the pressurization process was also investigated by calcining the pressurized samples at 1200°C and comparing them with samples prepared by calcination alone. In order to investigate the effect of the compound on the pressurization process, experiments were also conducted in which $TiCl_4$ was changed to TiO_2. These samples were characterized by X-ray diffraction (XRD), photoluminescence (PL), and scanning electron microscopy (SEM).

3 Results

3-1. Pressurization Process

The XRD results in Fig. 1 showed that the main components were $MgTiO_3$, TiO_2, and $Ti(ClO_4)_4$-like phases after pressure only, $MgTiO_3$ phase after calcination only, and Mg_2TiO_4 phase after pressure and calcination. It was also confirmed that the peak of Mg_2TiO_4 was clearly stronger in the sample calcined after pressurization than in the sample without pressurization. In the PL measurement results shown in Fig. 2, From the previous study, the emission peak around 670 nm is due to Mg_2TiO_4 phase, around 710 nm is due to $MgTi_2O_5$ phase, and around 760 nm is due to $MgTiO_3$ phase. The luminescence was mainly observed from the $MgTiO_3$ phase only in the sample with just pressure, from the $MgTi_2O_5$ and $MgTiO_3$ phases in the sample calcined after 25 hours of pressure, and from the Mg_2TiO_4 phase in the sample calcined after 50 hours of pressure. When the calcined samples were compared, the luminescence from the Mg_2TiO_4 phase, which is the target material, was more strongly observed in the sample with longer pressurization time. In the SEM images shown in Fig.3, in the pressure-only sample, extremely small particles were observed at 25 hours, and spherical particle agglomeration was observed at 50 hours. It was also confirmed that the majority of the post-firing samples had smooth primary particles with a surface profile of 2~3 nm, regardless of the pressurization time.

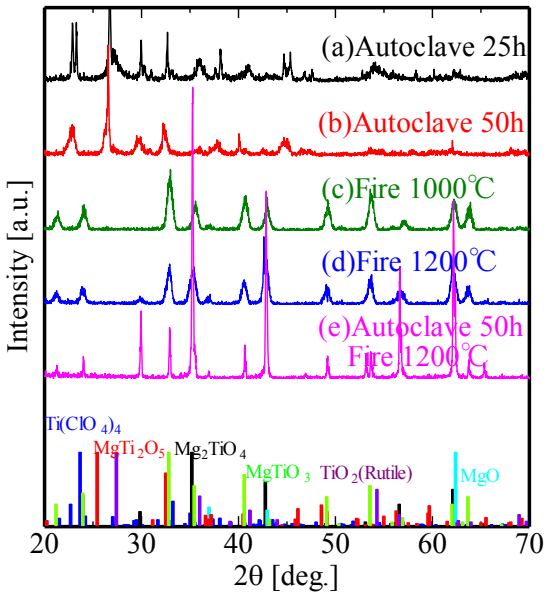

Fig.1 XRD patterns of Mg_2TiO_4:Mn phosphors.

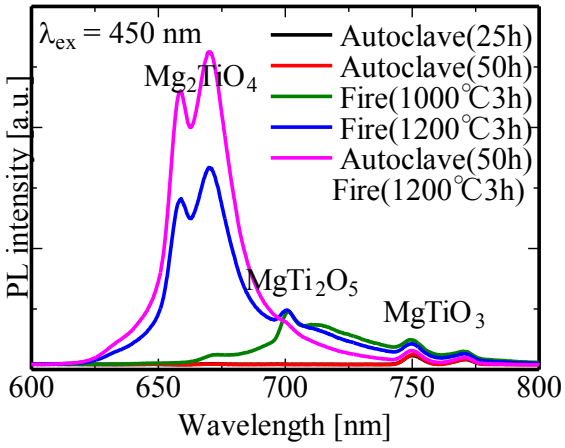

Fig.2 PL spectra of Mg_2TiO_4:Mn

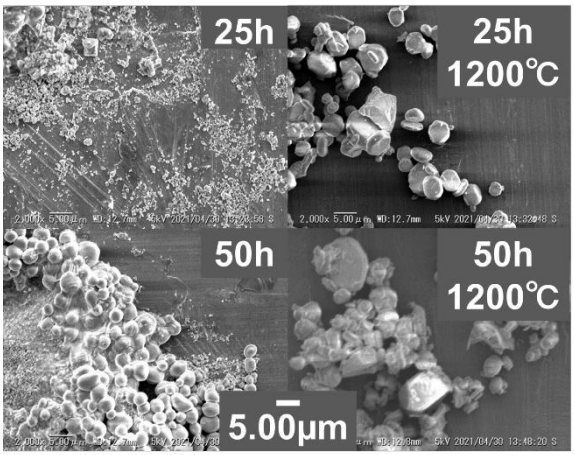

Fig.3 SEM images of Mg_2TiO_4:Mn phosphors

3-2. Raw Material TiO_2

The synthesis was carried out using TiO_2, which is thought to have been formed during the pressurization in 3-1. When TiO_2 was used, all the luminescent phases decreased with the extension of the pressurization time. It was also confirmed that the luminescence was weaker than that of the sample using $TiCl_2$ as the raw material.

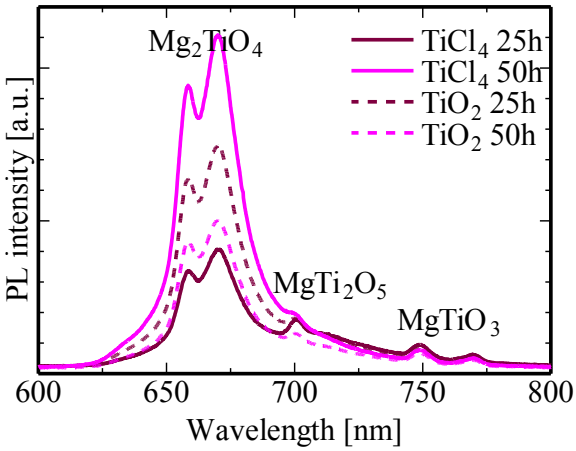

Fig.4 PL spectra for different raw materials

4 Discussion

4-1. Pressurization Process

The measurement results of XRD and PL suggest that the formation of Mg_2TiO_4 phase after calcination was accelerated by extending the pressurization time. This may be due to the formation of seed crystals similar to the TiO_2 Rutile phase and $Ti(ClO_4)_4$ formed during the oxidation process of Ti raw materials by pressure, which may have affected the phase formation by calcination. The formation of Mg_2TiO_4 is difficult by pressure synthesis alone, and it is assumed that the reaction of $MgTiO_3$ with residual Mg material leads to the phase formation of $MgTi_2O_5$ and Mg_2TiO_4. From these results, it is inferred that in the reaction process of Mg_2TiO_4, Ti-based oxides are first formed under pressure, and then Mg is synthesized stepwise. From the results of the SEM images, it was inferred that the raw materials had changed very little in the samples that were only synthesized under pressure for 25 hours. In the sample that was only pressurized for 50 hours, there were some nano-sized particles that seemed to be unreacted, but since the particles were mainly aggregates of micrometer-sized particles, it was inferred that some kind of reaction proceeded with the extension of the pressurization time. Comparison of the samples after calcination showed that the shape and particle size were almost the same, and no crystal growth was observed due to the extension of the pressurization time. PL measurements on the same samples showed no change in particle size, even though the luminescence of the Mg_2TiO_4 phase was enhanced by prolonging the pressurization time. This suggests that the extension of the pressurization time affected the enhancement of the formation of Mg_2TiO_4 while maintaining the particle size. Thus, the pressure reaction before calcination was considered to be effective in controlling the particle size and promoting the synthesis of Mg_2TiO_4.

4-2. Raw Material TiO_2

The decrease in luminescence with increasing pressurization time when TiO_2 was used as the raw material was thought to be due to the change in TiO_2 during pressurization. The luminescence intensity decreased in all the luminescent phases, and it was inferred that the reason was the decrease in the number of seed crystals, which are thought to promote the reaction. When comparing between the raw materials, the sample using TiO_2 as raw material showed better luminescence than the 25-hour pressurized sample, but the luminescence was clearly lower than that of the 50-hour pressurized sample. SEM images of the TiO_2 sample showed no particulate matter, as seen in the 25-hour pressurized sample shown in Fig. 3, suggesting that the synthesis reaction had proceeded. It was inferred that the formation of Ti-based oxides as seed crystals during the pressurization process was effective in promoting the reaction.

5 Conclusions

The purpose of this experiment was to investigate the effect of pressurization on phase formation during the synthesis of Mg_2TiO_4:Mn. The synthesized samples were evaluated by XRD, PL, and SEM measurements. From the measurement results, it is considered that Ti-based oxide seed crystals are synthesized during the pressurized synthesis process, and that these seed crystals are effective in controlling the particle size and promoting the reaction to the target material.

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