

Phase Control in The Pressurization Process of MgTiOF : Mn for Deep Red Emission

Naoki Uesugi¹, Masayuki Endo¹, Hiroko Kominami², Kazuhiko Hara²

E-mail: kominami.hiroko@shizuoka.ac.jp

1. Graduate School of Integrated Science and Technology, Shizuoka Univ.

2. Research Institute of Electronics, Shizuoka Univ.

3-5-1, Johoku, Naka-ku, Hamamatsu 432-8561, Japan

Keywords: Red emitting phosphor, High-pressure synthesis, Fine-particle, Hydrothermal synthesis, Mn⁴⁺ emission

ABSTRACT

We attempted to prepare MgTiOF:Mn for deep red light emission using a pressure vessel in the liquid phase synthesis method. However, Mg is stable as a fluoride and Ti is stable as an oxide, and the formation of a luminescent phase was not confirmed. Since the emission of Mn⁴⁺ was confirmed from the PL measurement results, a slight MgTiOF-based phase was formed, and it is considered possible to control the precipitates by adjusting the amount of HF to be added.

1 Introduction

Currently, Eu, which is a rare earth element^[1], is widely used as a luminescent center in red light-emitting phosphors, but rare earth-free phosphors using transition metal elements are desired from the economical and environmental viewpoints. In recent years, the application of Mn-activated red phosphors is expanding, such as the use of K₂SiF₆:Mn as white LEDs for backlights. The Mn⁴⁺-activated red phosphor is expected to have a longer wavelength^[2] due to the crystal field of the host material. Deep red phosphors are expected to be applied as light sources for growing plants^[3] and as wavelength conversion materials for solar cells^[4]. All of them need to absorb short-wavelength ultraviolet to blue light and emit long-wavelength red light. In addition, it is expected that excitation light is taken into the interior of the phosphor while light other than the excitation light is transmitted, and that the dispersibility and coatibility are high. From such a point of view, micro-particulation is necessary, but there is a concern that the luminous efficiency may be lowered due to the micro-particulation. Compared to the conventional solid-phase synthesis method, the liquid-phase method enables low-temperature synthesis, so it is thought that it is possible to suppress crystal growth and improve the dispersibility of the luminescent center, thereby improving the luminescent properties. In this research, so far, we have studied the synthesis of Mg₂TiO₄:Mn⁴⁺ phosphors^[5] by the liquid-phase synthesis method. In order to synthesize materials at a lower temperature than before, we attempted to synthesize fluoride phosphors (MgTiOF:Mn) using a pressurized vessel^[6], and investigated the phase control during the pressurization process.

2 Experiment

In this study, Manganese chloride (MgCl₂,4N), Titanium chloride (TiCl₄,4N), and Manganese chloride (MnCl₂,3N) were weighed according to their stoichiometric ratios. After that, each powder was dissolved in pure water and stirred for 1 hour. After stirring, HF(46–48 %) was

added. 50 ml of the solution was adjusted to a 100 ml container, and the mixture was pressurized at 200 °C for 50 hours. After that, the samples obtained by centrifugation (2000 rpm, 10 min, 3times, Pure water cleaning) were dried at 80°C. By changing the amount of HF to be added, the effect on phase control was investigated by X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM) and Photoluminescence (PL).

3 Results

From the XRD measurement results shown in Fig.1, a peak of MgF₂ was confirmed in samples with an HF content of 10 % or more relative to pure water. On the other hand, a TiO₂ peak was confirmed in the 0.2 % sample. In addition, two peaks of MgF₂ and TiO₂ were confirmed in the 2 - 4% sample.

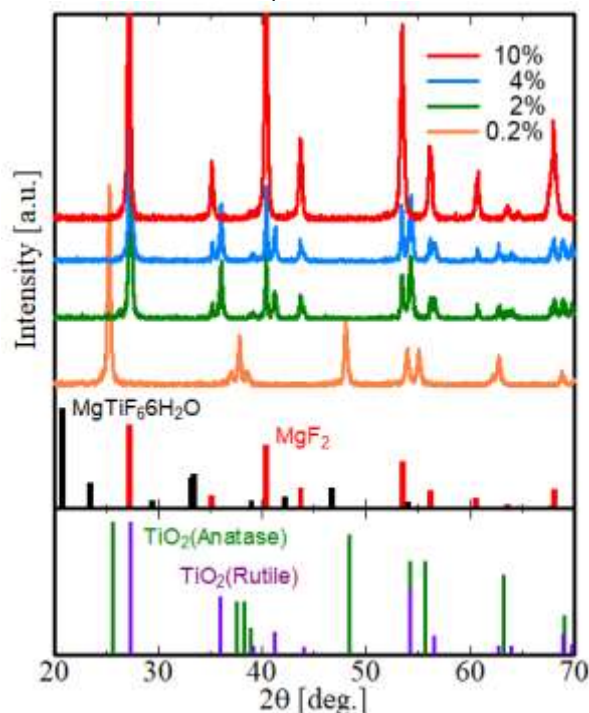


Fig.1 XRD patterns of MgTiOF:Mn phosphors.

From the results of elemental analysis by FE-SEM shown in Fig.2, it was confirmed that the proportions of Mg and F in the sample decreased and the proportions of Ti and O increased as the amount of HF added decreased.

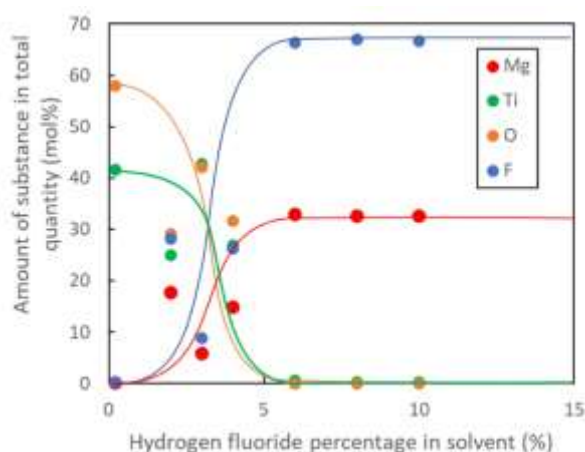


Fig.2 Multi-points analysis of Mg, Ti, O and F compounds comparing the effect of changing HF ratio in solvent.

Finally, Fig.3 shows the results of PL measurement under excitation light of 450 nm. For the reference, PL spectrum of $\text{Mg}_2\text{TiO}_4\text{:Mn}^{4+}$ is also shown in Fig.3. Red emission around 670 nm and 750 nm were obtained in all powders. In addition, a broad emission around 400 - 500 nm was observed in the powder with HF content of 0.2 %. According to the previous research, the emission at 670 nm is considered to be due to the formation of a crystal field close to the Mg_2TiO_4 phase. The emission around 750 nm is considered to be luminescence due to the formation of a crystal field close to the MgTiO_3 phase. The emission extending to the shorter wavelength seen in the sample with HF content of 0.2 % is considered to be luminescence due to Mn^{2+} .

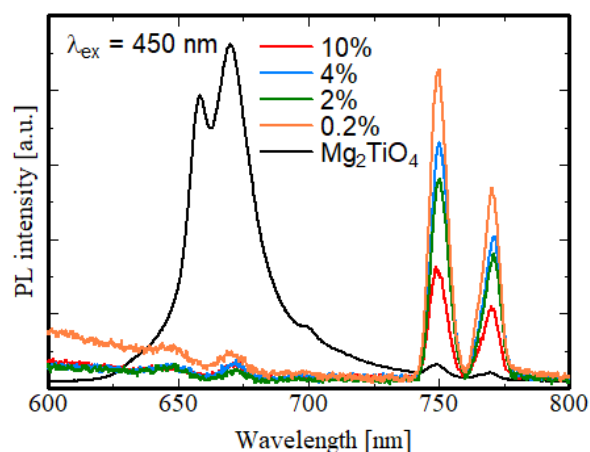


Fig.3 PL spectra of MgTiOF:Mn

4 Discussion

According to XRD, PL and FE-SEM measurements, the formation of Mg-based products was predominant due to the effect of fluorine in samples with HF content of 10% or more. Formation of a phase attributed to Ti was hardly obtained, and formation of Ti fluoride was not observed. It is thought that Ti hardly reacted with fluorine and was

removed by centrifugation because it was ionized. However, when the amount of HF to be added was 1 % or less, almost no effect of fluorine was observed, and Ti-based products precipitated as oxides. On the other hand, due to the suppression of the formation of Mg-based products, the obtained samples were only Ti-based. When the amount of HF was 1 - 10%, samples were obtained in which Mg was fluorinated and Ti was oxidized. In addition, it was confirmed that the formation ratio changes due to a subtle difference in concentration. Also, Mg is stable as a fluoride, and Ti is stable as an oxide. Therefore, it is considered that the MgTiOF -based phase containing both Mg and Ti elements is difficult to form.

Next, consider the substitution site of Mn, the luminescent center. Mn has a larger ionic radius than Mg. Therefore, it is considered that the possibility of substituting with Mg was low and substituting with Ti. From the results of Multi-points analysis, the ratio of F/Mg is almost 2 at high HF concentration. However, at lower concentration, the ratio of F/Mg became less than 2. Moreover, the ratio of O/Ti was much less than 2 in all powders. It indicates that Mg and Ti are also combined with O and F. Therefore, it is considered that Ti is not bound only to O, but that part of Ti binds to F, resulting in divalent substitution of Mn. TiO_2 (anatase) is mainly produced in the sample with HF content of 0.2 %. However, since HF is highly reactive, a small amount of fluoride of Ti was formed, and it is considered that emission of Mn^{2+} was confirmed. In addition, it is considered that the luminescence of Mn^{4+} was confirmed because a part of TiO_2 was replaced with Mn or a slight MgTiOF -based phase was formed. On the other hand, in the sample with HF content of 10 %, which is strongly affected by fluorine, MgF_2 is mainly produced, but a small amount of MgTiOF -based phase is formed, and it is considered that emission of Mn^{4+} was confirmed.

Finally, consider the formation of the luminescent phase. Production of a luminescent phase was not confirmed only by pressure synthesis. However, it is possible to adjust the elements to be deposited by adjusting the amount of HF to be added. Since Ti is stable as an oxide and Mg is stable as a fluoride, it is considered necessary to fabricate under higher temperature and pressure conditions than the current situation in order for the reaction to proceed.

5 Conclusions

It was confirmed that no luminescent phase was generated during the pressurization stage. This is because Mg is stable as a fluoride and Ti is stable as an oxide. Therefore, it is considered that the MgTiOF -based phase containing both Mg and Ti elements was difficult to generate. However, from the results of PL measurement, it was confirmed that Mn^{4+} doped in the formed phase emits light, so there is a possibility that a small amount of MgTiOF -based phase is formed. Precipitates can be controlled by adjusting the amount of HF added.

References

- [1] Karl A. Gschneidner, Jr, HANDBOOK ON THE PHYSICS AND CHEMISTRY OF RARE EARTHS VOLUME 3 (NORTH-HOLLAND PHYSICS 1979) p.147-151.
- [2] Shigeo Shioyama, William M. Yen, PHOSPHOR HANDBOOK, CRC Press LLC, p.834 (1999).
- [3] Shigeto Miyachi, Photosynthesis and Matter Production Utilization of Solar Energy by Plants in Japanese (Rikogakusya 1980) p.13-43.
- [4] Yutaka Yoshida, Dye-sensitized Solar Cells for Practical Use: Higher Efficiency, Lower Cost, and Higher Reliability in Japanese (NTS 2003.9.3) p.4-5.
- [5] Masayuki Endo, Naoki Uesugi, Hiroko Kominami, Kazuhiko Hara, Effect of High-Pressure Liquid Phase Synthesis of Deep Red Emitting $\text{Mg}_2\text{TiO}_4\text{:Mn}$, Proc. IDW'21, PHp1-4L pp331-333 (2021).
- [6] R. Vijayalakshmi, Synthesis and characterization of nano- TiO_2 via different methods, Scholars Research Library Archives of Applied Science Research 2012,4(2):pp.1183-1190 (2012).