Mn⁵⁺ activated M₂GeO₄(M = Ca, Sr, Ba) near-infrared phosphors

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ABSTRACT

 M_2 GeO₄: Mn^{5+} (M = Ca, Sr, Ba) phosphors have been synthesized by solid-state reaction method. The strongest PL intensity under 600 nm excitation is observed from the Ca₂GeO₄ host. Its PL integrated intensity is stronger by 6.7 times than that of the Ca₁₀(PO₄)₆(OH)₂: Mn^{5+} nanoparticle phosphor synthesized by liquid-phase reaction method.

1 INTRODUCTION

Recenly, a bioimaging technology as a medical diagnosis has received considerable attention. A fluorescent bioimaging is one of the in-vivo imaging. In the fluorescent bioimaging, phosphor particles as a biomarker are transported to the affected area with drug delivery system (DDS), and show optical image such as early diagnosis of cancer. Therefore, this technology is expected to solve the problems of MRI, CT scan, and X-ray diagnoses.

There are several requirements of phosphor for bioimaging. First, the particle size should be 100 nm or less to be applied to DDS. Since the phosphor should be efficiently excited from the outside of the body, the excitation and the bioimaging should be performed in the near-infrared region between from 650 nm to 1350 nm, so-called the "biological window" [1]. In addition, the phosphor material should be less-invasive.

We have investigated Mn⁵⁺ activated inorganic phosphors, which can be excited and emit in the "biological window". We have paid attention to Ca₁₀(PO₄)₆(OH)₂ (HAp) as a host material, which composes teeth and bones and has high biocompatibility. We have succeeded in synthesizing HAp:Mn⁵⁺ nanoparticles by the liquid phase synthesis method [2]. We also reported that the photoluminescense (PL) intensity is improved by about 22 times by annealing at 1300°C [3]. In the HAp:Mn5+ phosphor, Mn⁵⁺ substitutes for P⁵⁺. Very recently, it has been reported that Mn5+ also substitute for Si4+ [4]. In this study, to further improve the infrared emission intensity, a substitution at Ge4+ site has been attempted in consideration of the ionic radii. Mn5+ activated M2GeO4 (M = Ca, Sr, Ba) phosphors have been prepared and infrared photoluminescent properties has been investigated.

2 EXPERIMENT

 $M_2GeO_4:Mn^{5+}(M = Ca, Sr, Ba)$ phosphor samples were prepared by a conventional solid phase reaction method

with reference to the paper [4] regarding the preparation of Mn^{5+} activated M_2SiO_4 (M = Ca, Ba, Sr). The raw powder materials of MCO₃, MnCO₃, and GeO were mixed with a stoichiometric composition. The Mn concentration was 0.5 mol% for all samples. The mixture was once baked at 400°C for 3 h in air. After that, the firing was performed in air for 6h at 1400°C for the synthesis of Ca₂GeO₄ and Sr₂GeO₄. Only Ba₂GeO₄ sample was fired at 1200°C, because it melts at 1400°C. The X-ray diffraction (XRD) measurements were performed using a parallel-beam-type X-ray diffractometer (Rigaku RINT-TTR III). Photoluminescence (PL) spectra were measured in a near-infrared wavelength region using a Spectroscope (Fluorolog-NIR) at room temperature.

3 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the prepared $M_2GeO_4:Mn^{5+}$ (M = Ca, Sr, Ba) phosphor samples. The diffraction pattern from the inorganic crystal structure database (ICSD) of Ca₂GeO₄ (No.173459), Sr₂GeO₄ (No.56382), and the diffraction pattern of Ba₂GeO₄ of the PDF card (00-039-1257) are also shown for reference. The target crystal phases are confirmed in all samples. However, only the Ba₂GeO₄:Mn⁵⁺ sample has an unidentified peak due to impurity phase (designated by " \mathbf{V} "), which is considered to be formed due to the insufficient high firing temperature to crystallize Ba₂GeO₄.



Fig. 1 XRD patterns of prepared samples.

Figure 2 shows the PL spectra of the same samples. That of the HAp nano phosphor sample, which shows the most strongest near-infrared PL emission in previously prepared all nano and bulk phosphor samples, is also shown. The measurements were performed under a red light excitation at 600 nm. All phosphor samples show a near-infrared emission due to 3d² inner shell transition (¹E \rightarrow ³A₂) of Mn⁵⁺ centers. Other PL emission peaks were hardly observed even under UV and visible lights excitation. The fact suggests that Mn²⁺ and/or Mn⁴⁺ ions do not act as luminescent centers. The PL intensity of all germanate phosphors is much stronger than that of the HAp. Especially the peak intensity of the Ca₂GeO₄:Mn⁵⁺ is about 7.6 times compared to the HAp. It can be confirmed that the PL peak wavelength changes to longer wavelength in the order of atomic number of cation from small (Ca) to large (Ba). The results suggest that the crystal field around Mn5+ center is different in the germanate phosphors. According to the Tanabe-Sugano diagram of $3d^2$ ions [5], the energy level of ${}^{3}A_2$ slightly decreases with increasing the crystal fields. These facts imply that the crystal field in Ca₂GeO₄ is the strongest.

However, the details are still unclear.

The total emission intensity was estimated by integrating PL spectra in a wavelength region from 1000 to 1350 nm. The results of the germanate and silicate phosphors are summarized in Fig. 3. In all phosphors, the Ca₂GeO₄:Mn⁵⁺ has the strongest emission intensity. Its intensity is about 6.7 times that of the HAp nano phosphor, and is about 10.9 times than that of the Ca₂SiO₄:Mn⁵⁺ phosphor. Overall the intensity of the germanate phosphors is stronger than that of silicate phosphors. One can consider that Mn⁵⁺ tends to be easily incorporated into Ge⁴⁺ site compared to Si⁴⁺, since the ion radius of Mn⁵⁺ (0.47 Å) is closer to Ge⁴⁺ (0.53 Å) compared to Si⁴⁺ (0.40 Å) [6]. However, it is wonder why Mn⁴⁺ having the ion radius of 0.53 Å is not preferentially incorporated.



Fig. 2 PL spectra of prepared samples.

Moreover, a charge self-compensation might be takes place, and complex centers such as Mn^{5+} - oxygen vacancy might be formed, because we add no charge compensator for Mn^{5+} .

4 CONCLUSION

The preparation of Mn^{5+} activated M_2GeO_4 (M = Ca, Sr, Ba) phosphors was attempted by the solid-state reaction method in air. It was found that the near-infrared emission intensity of germanate phosphors is much higher than that of silicate and HAp phosphors.

Considering the ion radius of Mn^{5+} , Ge^{4+} is a suitable substitution site. The Ca₂GeO₄: Mn^{5+} phosphor shows the strongest emission, that is, the intensity is about 6.7 times that of the HAp nano phosphor, and is about 10.9 times than that of the Ca₂SiO₄: Mn^{5+} phosphor. It concludes that Ca₂GeO₄: Mn^{5+} is one of candidates near-infrared inorganic phosphors for in-vivo imaging.

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REFERENCES

- E.Hemmer et.al., Nanoscale Horiz., 1, 168-184 (2016).
- [2] W.Uehara et al., IEICE Technical Report, EID2016-43,117-120(2017).
- [3] R. Takeuchi et al., IEICE Technical Report, EID2018-13,91-96(2019).
- [4] Zhang, X. et al., L Mater Sci: Mater Electrons., 29, 6419-6427(2008).
- [5] H. Kamimura et al., Ligand field theory and its applications(1969).
- [6] J. E. Huheey, Inorganic Chemistry, 75 (1984).



Fig. 3 PL integrated intensity of the prepared Samples.