Red phosphorescence properties of Mn ions in MgO–GeO₂ compounds

Mineto Iwasaki, Duk Nam Kim, Keiko Tanaka, Takahiro Murata, Kenji Morinaga

Department of Applied Science for Electronics and Materials, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakouen, Kasuga-shi, Fukuoka 816-8580, Japan

Fukuoka Industry, Science and Technology Foundation, 1-1-1 Tenjin, Fukuoka 810-0001, Japan

Department of Engineering Sciences for Electronics and Materials, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakouen, Kasuga-shi, Fukuoka 816-8580, Japan

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Abstract

Red phosphorescence properties on Mn ions doped MgO–GeO₂ compounds, Mg₄GeO₆, Mg₂GeO₄, and MgGeO₃, were investigated. The red phosphorescence was observed in MgGeO₃:Mn²⁺. The red phosphorescence intensity of MgGeO₃:Mn²⁺ increased with adding the MgF₂ and Yb₂O₃. The red phosphorescence duration time of sample with a batch composition of 44 mol%-MgO, 6 mol%-MgF₂, 50 mol%-GeO₂, 0.1 mol%-MnO, and 0.05 mol%-Yb₂O₃ is approximately 30 min. The mechanism of red phosphorescence in MgGeO₃:Mn²⁺ is discussed in terms of the relationship between valency state of manganese ions and point defects in matrix compound.

Keywords: Red-emitting phosphor; Phosphorescence; Manganese ions; Germanate compounds; Point defect; Photo-oxidation

1. Introduction

Phosphorescence is the phenomenon that luminescence can still be observed for a long time after the interruption of the excitation. Recently, SrAl₂O₄:Eu²⁺·Dy³⁺ as a long phosphorescent phosphor was developed [1]. SrAl₂O₄:Eu²⁺·Dy³⁺ emits green phosphorescence with a long duration time. The color of phosphorescence can be changed from green to violet with the matrix compositions and rare earth ions. Since SrAl₂O₄:Eu²⁺·Dy³⁺ was developed, the phosphorescence mechanism of SrAl₂O₄:Eu²⁺·Dy³⁺ [2,3] and new long phosphorescent phosphors [4–6] have been researched.

Long phosphorescent phosphors store energy of excitation light such as sun and fluorescent lamp and emit visible light for a long time after cessation of excitation. Therefore, long phosphorescent phosphors would be utilized for energy conservation products such as white-emitting lamp and multi color signboard. Blue-, green-, and red-emitting phosphorescent oxide phosphor has not been developed, to our knowledge.

The purpose of this work is to develop red-emitting phosphorescent phosphors based on Mn ions doped oxide compounds. As a result, Mn²⁺ doped MgGeO₃ exhibits red phosphorescence. The mechanism of red phosphorescence is discussed in terms of photo-oxidation of Mn²⁺ ions and point defects in MgGeO₃ matrix.

2. Experimental procedure

Mn ions doped MgO–GeO₂ compounds were prepared by a conventional solid-state reaction. There are three compounds in MgO–GeO₂ system [7]: Mg₄GeO₆, Mg₂GeO₄, and MgGeO₃ were used for matrix. Mn ions were added in the form of MnCO₃. MgF₂ and rare earth oxides were also added to serve as a flux and co-activator. Commercially available high purity reagents (99.9–99.999%) of MgO, GeO₂, MnCO₃, MgF₂, and rare earth oxides were used for the production of the samples. Each reagent was weighed totally 5 g including 0.1 mol% MnCO₃ and mixed using an alumina mortar and pestle. Mixed batches were fired in platinum crucible at 1673 K for 1 h in air. Fired specimens were ground using an alumina
mortar and pestle and sieved to classify the powder size from 53 to 38 μm for fluorescence and phosphorescence measurements.

Fluorescence and phosphorescence decay curves were measured at room temperature using a fluorescence spectrophotometer (Model F-4500, Hitachi, Tokyo, Japan) in the range of 600–750 nm. Excitation sources were a xenon short arc lamp (150 W, Model UXL-157, Ushio, Tokyo, Japan) and a black fluorescent lamp (15 W, FL15BLB, Toshiba, Tokyo, Japan) for fluorescence and phosphorescence measurements, respectively. Crystalline phases were characterized by X-ray diffraction analysis using a diffractometer (Cu Kα, 35 kV, 15 mA, Model RINT-2100, Rigaku, Tokyo, Japan).

3. Results

3.1. Compositional dependence of fluorescence and phosphorescence properties of Mn ions doped MgO–GeO2 compounds

Compositional dependence of fluorescence and phosphorescence properties of Mn ions in Mg4GeO6, Mg2GeO4, and MgGeO3 were investigated. Fig. 1 shows the fluorescence spectra of Mn ions in Mg4GeO6, Mg2GeO4, and MgGeO3 with excitation at 254 nm. The fluorescence spectrum of Mn ions in Mg4GeO6 exhibits narrow band between 600 and 700 nm with four sharp peaks occurring at about 625, 630, 655, and 660 nm due to the 2E → 3A2 transition of Mn4⁺ [8]. The fluorescence spectra of Mn ions in Mg2GeO4 and MgGeO3 have broad bands located at around 640 and 670 nm due to the 4T1 → 6A1 transition of Mn2⁺ [9,10]. Because of the similarity in fluorescence spectral profiles, we assigned the origin of the fluorescence bands in the Mg4GeO6 to Mn4⁺, and in the Mg2GeO4 and MgGeO3 to Mn2⁺.

Fig. 2 shows the phosphorescence spectra of Mg4GeO6:Mn4⁺, Mg2GeO4:Mn2⁺, and MgGeO3:Mn2⁺. The samples were irradiated with a black fluorescent lamp for 1 min and measured the spectra 10 s after the irradiation had been stopped at room temperature. The phosphorescence of Mg4GeO6:Mn4⁺ could not be observed. The phosphorescence spectra of Mg2GeO4:Mn2⁺ and MgGeO3:Mn2⁺ exhibit similar their fluorescence spectral profiles. MgGeO3: Mn2⁺ indicates the highest phosphorescence intensity in three compositions. Therefore, the purpose of following experiment is to improve the phosphorescence properties of MgGeO3:Mn2⁺.

3.2. Effect of MgF2 on the phosphorescence properties of MgGeO3:Mn2⁺

Effect of MgF2 on the phosphorescence properties of MgGeO3:Mn2⁺ was investigated because Thorington [8] reported that the fluorescence intensity of Mg4GeO6:Mn4⁺ red-emitting phosphor increased with adding the MgF2. MgF2 were added to replace with MgO. Fig. 3 shows the relationship between the initial phosphorescence intensity at peak wavelength of 670 nm, which measured 10 s after the irradiation with a black fluorescent lamp was stopped, and MgF2 content. The initial phosphorescence intensities were measured five times in each sample. The average values were plotted, and maximum and minimum values were measured.
indicated by the error bars in Fig. 3. The initial phosphorescence intensity increased with adding the MgF2. The initial phosphorescence intensity of MgGeO3: Mn2+ with 6 mol% MgF2 (MgGeO2.88F0.24) was approximately 65 times longer than that of MgGeO3:Mn2+.  

3.3. Effect of rare earth ions on the phosphorescence properties of MgGeO2.88F0.24:Mn2+ 

Commercially available green-emitting long phosphorescent phosphor of SrAl2O4:Eu2+ was codoped with Dy3+ in order to increase the phosphorescence intensity [1,2]. The effect of rare earth ions on the phosphorescence properties of MgGeO2.88F0.24: Mn2+ was investigated. Fig. 4 shows the relationship between the initial phosphorescence intensity and addition of rare earth ions. The samples were doped with 0.05 mol% of rare-earth oxides as RE2O3, where RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb. The initial phosphorescence intensity of Yb3+ doped MgGeO2.88F0.24:Mn2+ increased approximately three times longer than that of non-doped MgGeO2.88F0.24:Mn2+ sample. On the other hand, the initial phosphorescence intensities of the other rare earth ions doped samples became a one-tenth compared with non-doped MgGeO2.88F0.24:Mn2+ sample.

3.4. Red phosphorescence duration time of MgGeO2.88F0.24:Mn2+, Yb3+ 

The red phosphorescence duration time of MgGeO2.88F0.24:Mn2+, Yb3+ that shows the highest initial phosphorescence intensity in this study was investigated. Fig. 5 shows the phosphorescence decay of MgGeO2.88F0.24:Mn2+, Yb3+ after cessation of excitation with the black fluorescent lamp that had been irradiated for 1 min. The minimum intensity of red phosphorescence, which detected by the naked eye in the dark room, is located at value of 100 (a.u.) with dotted line in Fig. 5. The duration time is defined by a point of intersection of a decay curve and the dotted line in Fig. 5.

4. Discussion 

The red phosphorescence was observed in the MgGeO3: Mn2+. Moreover, the initial phosphorescence intensity of MgGeO3:Mn2+ increased with adding the MgF2 and Yb2O3. The mechanism of red phosphorescence is discussed in terms of valency state of manganese ions and defects in matrix compounds.

In general, the mechanism of phosphorescence was considered that the thermal stimulated recombination of holes and electrons at traps that leave holes or electrons in a long-lived excited state at room temperature [11]. Matsu- zawa et al. [2] suggested the phosphorescence mechanism in SrAl2O4:Eu2+, Dy3+. According to their mechanism, Dy3+ traps the hole that is formed by photo-ionization of Eu2+ → Eu+ with UV irradiation. However, as Qiu et al. [3,12] pointed out, no evidence was observed for the conversion of Eu2+ to Eu+ and Dy3+ to Dy4+ in the SrAl2O4:Eu2+, Dy3+ before and after X-ray irradiation on the basis of X-ray absorption measurement. Taking into account the ionization potential of Eu ion [13], it is difficult to consider the formation of monovalent europium ions. Thus, the phosphorescence mechanism of SrAl2O4:Eu2+, Dy3+ needs further consideration.

Qiu et al. [3,12] and Hosono et al. [5,14] proposed the mechanism of phosphorescence that point defects in a matrix act as a trapping center of electron, which is formed by UV irradiation. Hosono et al. [5,14] found that Tb3+ doped calcium aluminate glass melted under a strongly reducing atmosphere shows the green phosphorescence. They concluded the phosphorescence mechanism that the oxygen vacancy surrounded by Ca2+ ions in the matrix glass acts as a trapped center of electron, which is formed by UV irradiation due to the photo-oxidation of Tb3+ → Tb4+.
According to this mechanism, phosphorescence phosphors need photo-oxidizable activator ions and oxygen vacancies in matrix. Therefore, we shall focus on the valency state of Mn ions and the oxygen vacancies in matrixes affecting the phosphorescence in Mn ions doped MgO–GeO$_2$ compounds.

We will begin discussing valency states of manganese ions as an activator. Divalent manganese ions were formed in the Mg$_2$GeO$_4$ and MgGeO$_3$ compounds. In general, the concentration of Mn$^{2+}$ increases with decreasing matrix basicity [15]. The concentration of Mn$^{3+}$ in the MgGeO$_3$ compound would be higher than that in the Mg$_2$GeO$_4$ compound because of the lower matrix basicity. It was suggested that Mn$^{2+}$ ions formed Mn$^{3+}$ ions and electrons due to the photo-oxidation by UV irradiation in the literature [10]. Thus MgGeO$_3$;Mn$^{2+}$ would generate more excited electrons by UV irradiation because of a large amount of Mn$^{2+}$ ions, compared with Mg$_2$GeO$_4$;Mn$^{2+}$. On the other hand, tetravalent manganese ion was observed only in the Mg$_2$GeO$_4$ compound. Higher valency state of Mn$^{4+}$ would be easily formed by higher basicity of the matrix in which MgO content is larger than the other matrix compounds. Mn$^{4+}$ has the charge transition transition corresponding to the variation of Mn$^{4+} \rightarrow$ Mn$^{3+}$ in the UV region [16] so that Mn$^{3+}$ would not be able to generate the excited electrons by UV irradiation.

Next we will discuss about oxygen vacancies in MgO–GeO$_2$ compounds. It is well-known that as-quenched UV irradiation. The concentration of Mn$^{2+}$ would increase with decreasing matrix basicity [15]. The concentration of Mn$^{3+}$ in the MgGeO$_3$ compound would be higher than that in the Mg$_2$GeO$_4$ compound because of the lower matrix basicity. It was suggested that Mn$^{2+}$ ions formed Mn$^{3+}$ ions and electrons due to the photo-oxidation by UV irradiation in the literature [10]. Thus MgGeO$_3$;Mn$^{2+}$ would generate more excited electrons by UV irradiation because of a large amount of Mn$^{2+}$ ions, compared with Mg$_2$GeO$_4$;Mn$^{2+}$. On the other hand, tetravalent manganese ion was observed only in the Mg$_2$GeO$_4$ compound. Higher valency state of Mn$^{4+}$ would be easily formed by higher basicity of the matrix in which MgO content is larger than the other matrix compounds. Mn$^{4+}$ has the charge transition transition corresponding to the variation of Mn$^{4+} \rightarrow$ Mn$^{3+}$ in the UV region [16] so that Mn$^{3+}$ would not be able to generate the excited electrons by UV irradiation.

Next we will discuss about oxygen vacancies in MgO–GeO$_2$ compounds. It is well-known that as-quenched MgO–GeO$_2$ compounds. It is well-known that as-quenched GeO$_2$ glass melted in air has point defects, connected to partially reduced Ge species, the so-called oxygen-deficiency centers (ODCs), i.e. oxygen vacancies associated with Ge$^{4+}$ ions, Ge E$^*$ center, and Ge–Ge homobond [17,18]. Because the standard free energy of formation, $\Delta G$, of GeO$_2$ is larger than that of GeO above 1500 K [19], a part of GeO$_2$ can decompose into GeO and O$_2$: GeO$_2$ $\rightarrow$ GeO + 1/2O$_2$ when GeO$_2$ is melted above 1500 K. The thermodynamic stability of GeO brings the driving force for the formation of oxygen-deficiency centers [17–20]. Because all samples were fired at 1673 K, it is assumed that oxygen vacancies associated with Ge$^{4+}$ ions would be form and act as electron trap centers in the MgO–GeO$_2$ compounds. The formation of oxygen vacancies based on the reaction of GeO$_2$ $\rightarrow$ GeO + 1/2O$_2$ is influence by the matrix basicity. The concentration of oxygen vacancies would be increases with decreasing matrix basicity because the formation of GeO is inhibits by higher basicity. Therefore, MgGeO$_3$: Mn$^{2+}$ would have a large amount of oxygen vacancies as electron trap centers because of the lowest basicity of matrix compared with the other MgO–GeO$_2$ compounds. On the other hand, few oxygen vacancies would be formed in the Mg$_2$GeO$_4$:Mn$^{4+}$ due to higher basicity of matrix.

The consideration about the valency state of Mn ions and the oxygen vacancies associated with Ge$^{4+}$ ions in matrixes affecting the phosphorescence is consistent with the experimental observation that the phosphorescence intensities increase with decreasing MgO content in the Mn ions doped MgO–GeO$_2$ compounds as shown in Fig. 2. That is, MgGeO$_3$:Mn$^{2+}$ shows higher phosphorescence intensity because higher concentration of both Mn$^{2+}$ ions, which would generate electrons due to the photo-oxidation by UV irradiation, and oxygen vacancies associated with Ge$^{4+}$ ions, which would act as electron trap centers, were formed due to lower matrix basicity. On the other hand, Mg$_2$GeO$_4$:Mn$^{4+}$ does not show any phosphorescence because few Mn$^{2+}$ ions and oxygen vacancies would be formed due to higher matrix basicity.

Fig. 6 schematically shows the red phosphorescence mechanism of MgGeO$_3$:Mn$^{2+}$ based on the mechanism proposed by Hosono et al. [5,14]. The photo-oxidized reaction of Mn$^{2+}$ ions in MgGeO$_3$ compound would occur with UV irradiation, so that the photo-oxidized Mn$^{2+}$ ions, (Mn$^{2+}$)$^+$, and the excited electrons, e$^-$, would be generated:

$$\text{Mn}^{2+} + h\nu(A=256 \text{ nm}) \rightarrow (\text{Mn}^{2+})^+ + e^-.$$  \hspace{1cm} (1)

The e$^-$ would be trapped on oxygen vacancies associated with Ge$^{4+}$ ions VO:

$$e^- + \text{VO} \rightarrow \text{F}^+ \text{ center.}$$  \hspace{1cm} (2)

MgGeO$_3$:Mn$^{2+}$ would be able to store the energy of excitation light based on Eqs. (1) and (2) during UV irradiation.

After cessation of UV irradiation, trapped e$^-$ would be exited thermally and released from VO at room temperature because the trapped energy level would be relatively lower:

$$\text{F}^+ \text{ center \hspace{0.5cm} } h\nu(T \sim 300 \text{ K}) \rightarrow e^- + \text{VO}.$$

(3)

The released e$^-$ would recombine with (Mn$^{2+}$)$^+$ to produce the excited state of Mn$^{2+}$ ions, Mn$^{2+}$$. Finally, the Mn$^{2+}$$^*$ decay radiatively into the ground state with the red phosphorescence due to the $^3\text{T}_1 \rightarrow ^6\text{A}_1$ transition:

$$e^- + (\text{Mn}^{2+})^+ \rightarrow \text{Mn}^{2+} + h\nu(A=670 \text{ nm}) \rightarrow \text{Mn}^{2+}.$$  \hspace{1cm} (4)

In this manner, MgGeO$_3$:Mn$^{2+}$ would be able to emit the red phosphorescence for a long time because excited...
electrons are released slowly from the oxygen vacancies at the room temperature.

Next, the effect of MgF$_2$ on the red phosphorescence intensity MgGeO$_3$:Mn$^{2+}$ sample is discussed. The red phosphorescence intensity of MgGeO$_3$:Mn$^{2+}$ containing MgF$_2$ is higher than that of MgGeO$_3$:Mn$^{2+}$ without MgF$_2$. No XRD pattern corresponding any fluoride compounds was observed in the MgGeO$_3$:Mn$^{2+}$ containing MgF$_2$ sample. The XRD pattern of sample containing MgF$_2$ was similar to that of MgGeO$_3$ compound. Fluorine would be vaporized as HF based on the reaction of MgF$_2$ with moisture in air [21,22]:

$$\text{MgF}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HF}. \quad (5)$$

It is hypothesis that MgF$_2$ could act as a catalyst to accelerate the formation of GeO based on Eq. (5); as a result, the red phosphorescence intensity of MgGeO$_3$:Mn$^{2+}$ improves because of increasing the concentration of oxygen vacancies associated with Ge$^{4+}$ ions.

Finally, we mention effect of rare earth ions on the red phosphorescence intensity in the MgGeO$_3$:Mn$^{2+}$ sample. The trivalent rare earth ions in matrixes exhibit various absorption and emission bands in the range of UV to IR on the basis of the transition between the 4f configurations. Except for Yb$^{3+}$, it is estimated that addition of rare earth ions would give rise to the energy transfer between Mn$^{2+}$ and rare earth ions; as a result, the red phosphorescence intensities of MgGeO$_3$:Mn$^{2+}$ containing rare earth ions are inferior to the MgGeO$_3$:Mn$^{2+}$ without any rare earth ions. On the other hand, Yb$^{3+}$ shows the only absorption and emission spectra around 1000 nm based on the $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$ transitions. It seems reasonable to suppose that Yb$^{3+}$ does not hinder the photo-oxidation of Mn$^{2+}$ by UV excitation and red phosphorescence of the $^{4}T_{1} \rightarrow ^{6}A_{1}$ transition of Mn$^{2+}$. Furthermore the ytterbium ion trends to be divalent state similar to the europium ion [23], so that Yb$^{3+}$ ions could trap the excited electrons, which would be generated by the photo-oxidation of Mn$^{2+}$ by UV irradiation. Therefore it supports the hypothesis that Yb$^{3+}$ could act as the electron-trapped center because of simple energy level of 4f electrons and stability of divalent state.

As mentioned above, the long lasting red phosphorescence mechanism in the MgGeO$_3$:Mn$^{2+}$ containing the MgF$_2$ and Yb$_2$O$_3$ was discussed in terms of valency state of Mn ions and oxygen vacancies associated with Ge$^{4+}$ ions. However, there is room for further investigation concerning the electron paramagnetic resonance measurements of valency state of Mn ions and point defects in matrix compounds before and after irradiation of UV in order to reveal the detailed mechanism.

5. Conclusion

Red phosphorescence properties on Mn ions doped MgO–GeO$_2$ compounds, Mg$_4$GeO$_6$, Mg$_2$GeO$_4$, and MgGeO$_3$, were investigated. The red phosphorescence was observed in MgGeO$_3$:Mn$^{2+}$. The mechanism of red phosphorescence in MgGeO$_3$:Mn$^{2+}$ is discussed in terms of the relationship between valency state of manganese ions and point defects in matrix compound. MgGeO$_3$:Mn$^{2+}$ shows higher phosphorescence intensity because higher concentration of both Mn$^{2+}$ ions, which would generate electrons due to the photo-oxidation by UV irradiation, and oxygen vacancies associated with Ge$^{4+}$ ions, which would act as electron trap centers, were formed due to lower matrix basicity.

The red phosphorescence intensity of MgGeO$_3$:Mn$^{2+}$ increased with adding the MgF$_2$ and Yb$_2$O$_3$. MgF$_2$ and Yb$_2$O$_3$ would be able to act as a catalyst to accelerate the formation of oxygen vacancies associated with Ge$^{4+}$ ions and an electron-trapped center, respectively. The red phosphorescence duration time of sample with a batch composition of 44 mol\%-MgO, 6 mol\%-MgF$_2$, 50 mol\%-GeO$_2$, 0.1 mol\%-MnO, and 0.05 mol\%-Yb$_2$O$_3$ is approximately 30 min.

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