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Effect of Al and Mg Codopants on Cathodoluminescence of ZnO:Tm Phosphor*

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The cathodoluminescence of ZnO:Tm has been investigated in powders prepared by baking in different forming atmosphere. The samples baked in argon atmosphere show the white emission, while the greenish-blue emission is obtained from the samples baked in reducing atmosphere. In addition, the effects of Al and Mg codopants on cathodoluminescence of ZnO:Tm phosphor powders have been investigated. As a result, the Al codopant is found to form $ZnAl_2O_4$, whereas the Mg codopant is found to increase the intensity of blue emission.

KEYWORDS: ZnO:Tm, Al, Mg, cathodoluminescence, FED, phosphor

INTRODUCTION

A wide variety of information displays have been developed. A field emission display (FED) is considered to be a candidate for the next generation of flat-panel displays. However, the tiny space of vacuum and the cathode structure of FED restrict the use of conventional sulfide phosphors for cathode-ray tube (CRT). The cathode tips of FED can be poisoned by the dissociated sulfur atoms when the sulfide phosphors such as ZnS:Cu or ZnS:Ag are used. The contamination of cathode tips lead to the degradation of display performance. The contamination of cathode tips can be minimized if the oxide-based phosphors are utilized.[1]

A ZnO:Zn phosphor powder has been utilized for vacuum fluorescent display (VFD) for many years because ZnO:Zn has low resistivity and high luminous efficiency at low voltage excitation. Then, ZnO is considered to be suitable for phosphor matrix used for FED. However, the preparation of rare earth activated ZnO phosphors is difficult because the ionic radius of rare earth ions is larger than that of Zn^{2+} ions.

Al ion has small ionic radius. Therefore, the Al codopant is considered to relax the lattice distortion caused by the difference of ionic radius between Zn^{2+} and Tm^{3+} when the Tm ions substitute the Zn ions. In this work, the effect of Al codopant on ZnO:Tm were investigated with use of cathodoluminescence (CL). Moreover, the synthesis of $Mg_xZn_{1-x}O$:Tm powders was attempted because the absorption band peaking around 3.4 eV of Tm^{3+} ions is in good agreement with the emission band of host matrix, and the CL of $Mg_xZn_{1-x}O$:Tm was also investigated.

EXPERIMENTAL

The ZnO:Tm phosphor powders were prepared by baking the mixture of ZnO and TmF_3 for 3 hours in argon (Ar) at 1000℃ or reducing atmosphere (H_2/N_2=5/95) at 1050℃. In the case of Al doping, Al metal powder was added to the mixture of ZnO and TmF_3. The Tm content in the starting mixed powder was varied from 0.1 to 3.0 at. %. The synthesis of $Mg_xZn_{1-x}O$:Tm powders was attempted by re-baking the mixture of ZnO:Tm, which is prepared by baking the mixture of ZnO and TmF_3 in Ar, and $MgCO_3 \cdot 5H_2O$ in reducing atmosphere. The CL spectra of samples were recorded under the condition of 2.5 keV excitaion at room temperature.

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RESULTS AND DISCUSSION

The ZnO:Tm phosphor powders prepared by baking in Ar atmosphere yield white emission. The CL spectra are shown in Fig. 1. The band edge emission of ZnO is observed at 390 nm. The broad band peaking around 550, 560 and 565 nm is thought to be due to the zinc vacancy (V_{Zn}) of ZnO.[2] The result is almost the same as that of photoluminescence obtained by excitation at 390 nm. No emission arising from Tm^{3+} could be observed.[3]

Figure 2 shows the CL spectra of ZnO:Tm phosphor powders baked in reducing atmosphere. In contrast to the powders baked in Ar atmosphere, the intensity of band edge emission at 390 nm is strongest at 1.0 at. % of Tm content. The broad band at 500 nm due to the oxygen vacancy (V_o)[4] of ZnO is similar to the V_{Zn} band in Fig. 1. The intensity of broad band emission is decreased with increasing the Tm content. At present, it is not determined whether the compensation of V_o due to the dissociated F atoms of TmF_3 or the contribution of Tm atoms leads to the quenching of V_o band. As a result, however, it is found that the emission color is changed from green to greenish blue with increasing the Tm content although the intensity of blue emission is very weak.

Figures 3 and 4 show the X-ray diffraction (XRD) patterns of ZnO:Tm baked in Ar and reducing atmosphere, respectively. The Tm_2O_3 pattern is recognized in both XRD patterns besides the ZnO pattern. The lattice constants a and c of ZnO:Tm do not change significantly with increasing the Tm content. Then, it is found that almost all of Tm atoms are segregated as Tm_2O_3 at the grain boundary or the surface of ZnO powder.

It is clear from the above results that Tm atoms are almost impossible to be incorporated into ZnO matrix by the conventional sintering method. In order to obtain a high intensity of blue emission, the substitutional solution of Tm atoms is needed.

Al has small ionic radius (r_{Al}=0.053 nm), while Tm has large ionic radius (r_{Tm}=0.102 nm). The mean radius between Al and Tm is almost equal to the ionic radius of Zn (r_{Zn}=0.074 nm). Al codoping was attempted because the Al codopant is considered to relax

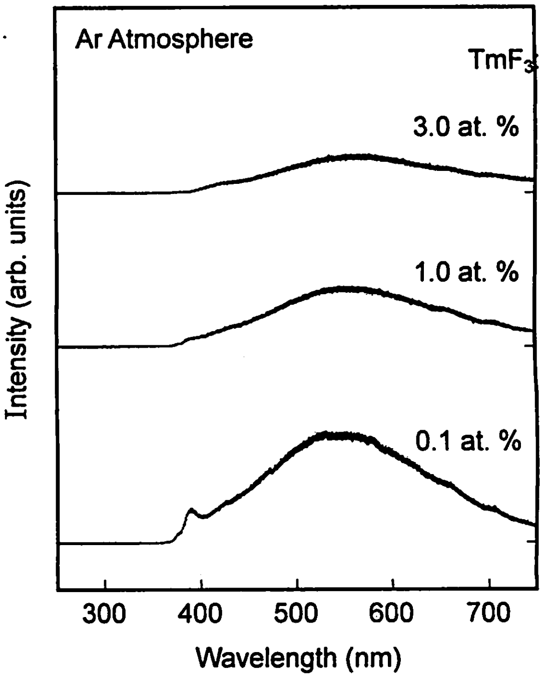

Fig. 1. CL spectra of ZnO:Tm baked in Ar atmosphere.

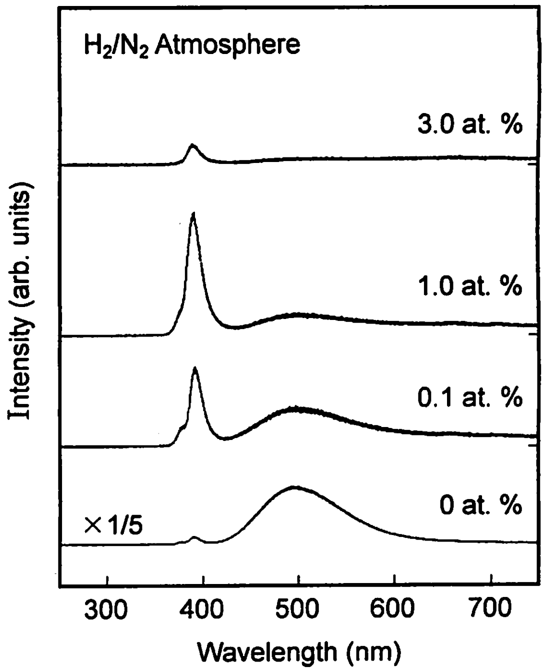

Fig. 2. CL spectra of ZnO:Tm baked in reducing atmosphere.

the lattice distortion caused by the difference of ionic radius between Zn^{2+} and Tm^{3+}. Figure 5 shows the CL spectra of ZnO:Tm baked in reducing atmosphere with and without of Al. Contrary to the expectation, no Tm^{3+} emission is observed in the CL spectra of ZnO:Tm with Al. Instead of the emission of Tm^{3+}, faint ultra violet (UV) emission is observed around 280 nm, as indicated by an arrow. The UV emission is considered to be due to $ZnAl_2O_4$.

In order to obtain the blue emission of Tm^{3+} ions, the relationship between the energy gap of host matrix and the excited energy level of Tm^{3+} ion is examined. Figure 6 shows the energy level of MgO, ZnO and Tm^{3+} ion, where that of MgO is the energy gap at the Γ point. The diagrams point out that only the $^1G_4 \rightarrow {}^3H_6$ transition can be expected, even if the Tm atoms are incorporated into ZnO matrix. However, the $^1G_4 \rightarrow {}^3H_6$ transition (at 485 nm) in Tm^{3+} ions is not observed in ZnO:Tm in contrast to the ZnS:Tm system[5] as shown in Figs.1, 2 and 5. The result is similar to that in the case of ZnO:Tm under UV (350

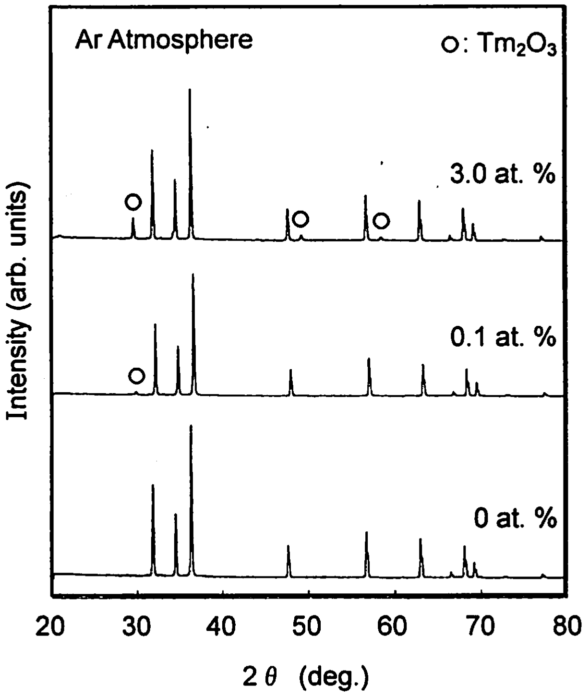

Fig. 3. XRD patterns of ZnO:Tm baked in Ar atmosphere.

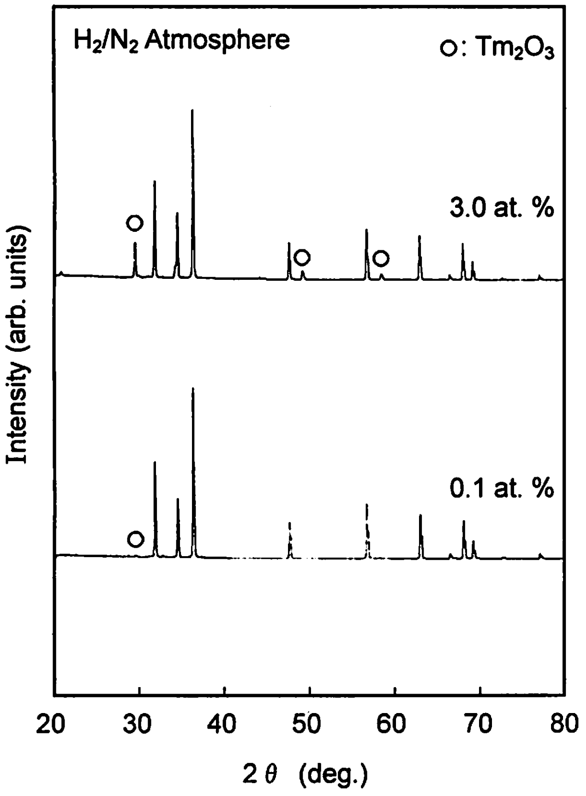

Fig. 4. XRD patterns of ZnO:Tm baked in reducing atmosphere.

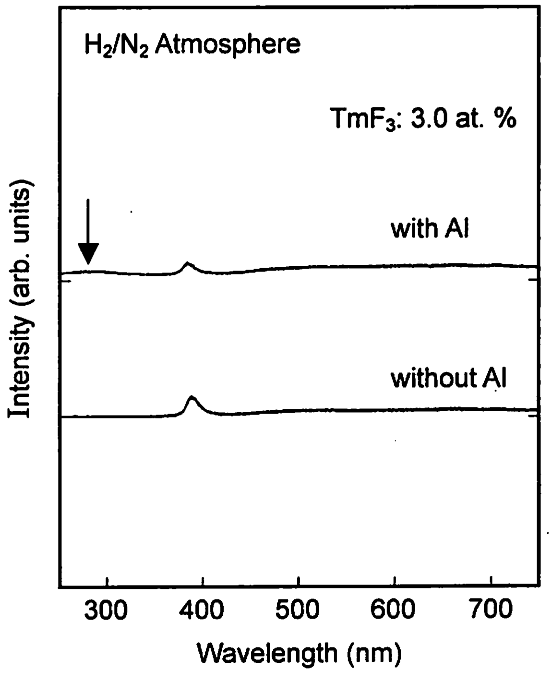

Fig. 5. CL spectra of ZnO:Tm baked in reducing atmosphere with and without Al.

- 385 nm) excitaion.[6] The excitation to $^1D_2$ or $^3P_0$ state which locates at higher energy level than that of $^1G_4$ state is attempted in order to increase the intensity of blue emission ($^1D_2 \rightarrow {}^3F(H)_4$; ~460 nm). The $^1D_2$ level is located at about 3.47 eV from the $^3H_6$ ground state.[6] Moreover, the band gap energy of $Mg_xZn_{1-x}O$ is in good agreement with the $^1D_2$ level at an appropriate mole fraction (x) of Mg. In addition to the agreement of $^1D_2$ energy level, the incorporation of Tm atoms into $Mg_xZn_{1-x}O$ solution alloy can be realized because the solution alloy is re-crystallized in an atomic scale. Therefore, the synthesis of $Mg_xZn_{1-x}O$:Tm was attempted in this work.

The $Mg_xZn_{1-x}O$:Tm powders were prepared by baking the mixture of $MgCO_3 \cdot 5H_2O$ and ZnO:Tm in reducing atmosphere for 3 hours at 1050℃, where the ZnO:Tm powders had been previously baked in Ar. Figure 7 shows the CL spectra of $Mg_{0.09}Zn_{0.91}O$:Tm. The $Mg_{0.09}Zn_{0.91}O$ without Tm presents the edge emission and a broad band which is thought to be due to the oxygen vacancy at 370 and 472 nm, respectively. The wavelength is shifted toward shorter region than that of

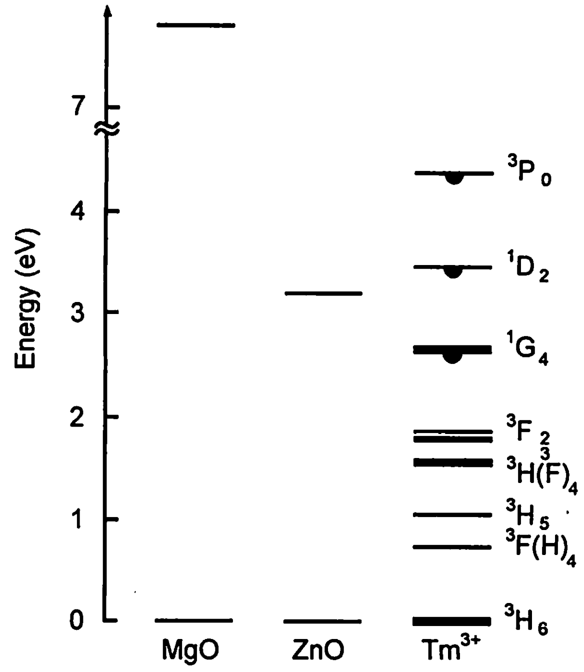

Fig. 6. Energy level of MgO, ZnO and Tm^{3+} ion.

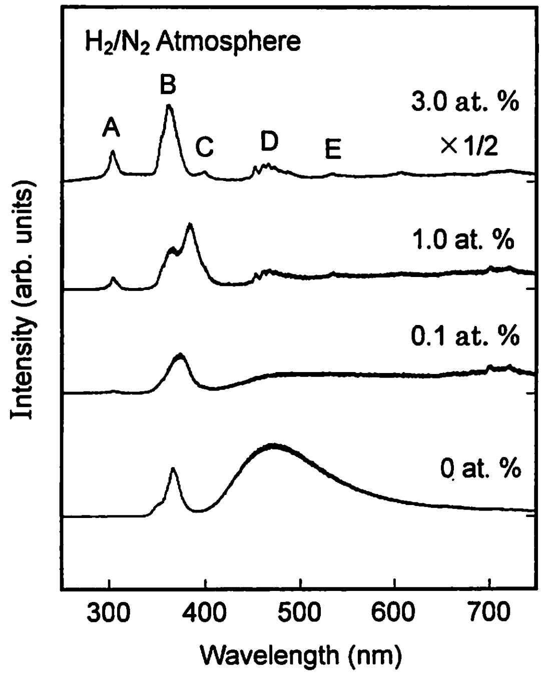

Fig. 7. CL spectra of $Mg_{0.09}Zn_{0.91}O$:Tm baked in reducing atmosphere.

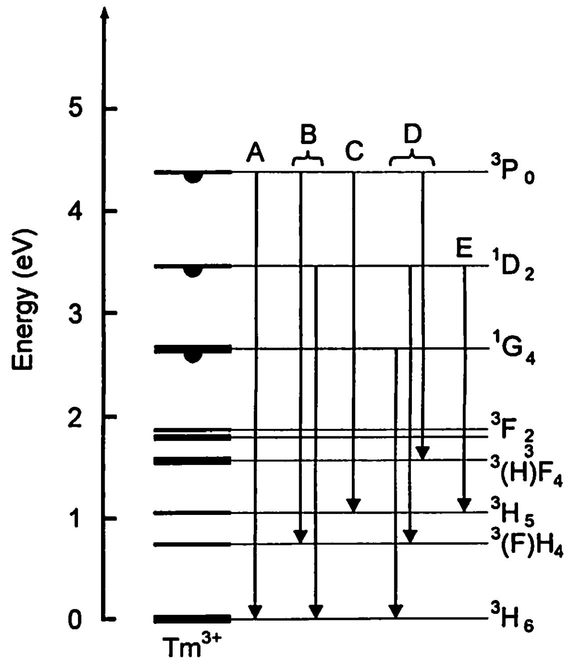

Fig. 8. Energy diagram of Tm^{3+} ion.

ZnO:Zn without Tm in Fig.2. When the Tm content is increased, the above intrinsic emission of $Mg_{0.09}Zn_{0.91}O$ is disappeared, and the emission considered to be due to the Tm^{3+} ions is appeared, as indicated by notations (A-E). These emissions are assigned as shown in Fig. 8. Especially, the emission due to $^1D_2 \rightarrow {}^3F(H)_4$ transition in Tm^{3+} ions is found to be observed around 450 - 480 nm. As a result, the intensity of blue emission is increased compared to that of ZnO:Tm baked in reducing atmosphere. This result suits the purpose of this work.

Figure 9 shows the XRD patterns of $Mg_{0.09}Zn_{0.91}O$:Tm baked in reducing atmosphere. The intensity of Tm_2O_3 is increased with increasing the Tm content. At 3 at. % of Tm content, the pattern of hexagonal structure is disappeared, and Tm_2O_3 and MgO patterns exist. It is concluded from the results that the emission of Tm^{3+} ions observed in Fig. 7 is not due to the $Mg_{0.09}Zn_{0.91}O$:Tm but segregated Tm_2O_3. Although the greenish-blue emission is obtained by baking the mixture of $MgCO_3 \cdot 5H_2O$ and ZnO:Tm, the prepared sample is not a simple solution alloys such as $Mg_xZn_{1-x}O$:Tm. Hereafter, the doping of Tm atoms into $Mg_xZn_{1-x}O$ matrix without the phase separation to the MgO and ZnO is required because $Mg_xZn_{1-x}O$ separates to MgO and ZnO with increasing the Tm content.

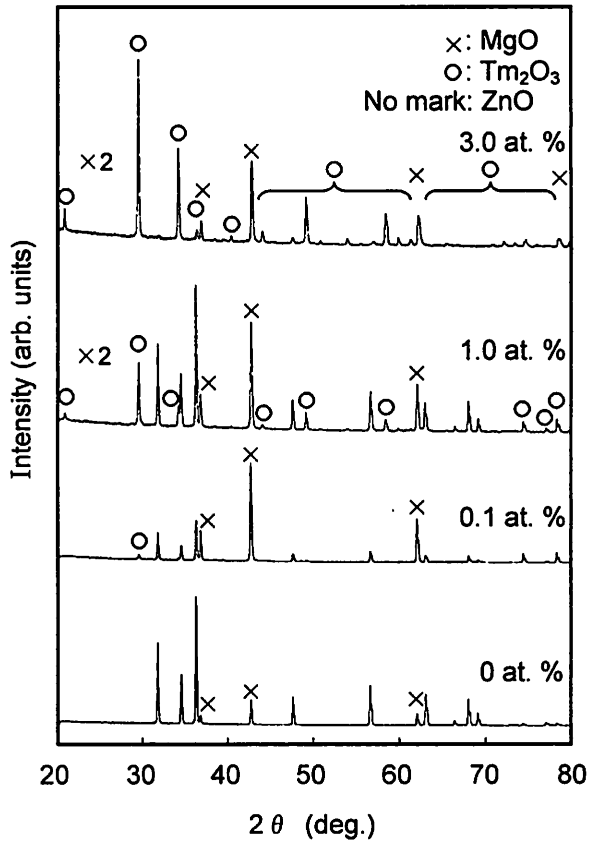

Fig. 9. XRD patterns of $Mg_xZn_{1-x}O$:Tm baked in reducing atmosphere.

CONCLUSION

The cathodoluminescence of ZnO:Tm was investigated. It has been found that the greenish-blue emission is obtained by baking the reducing atmosphere. The Al codoping to ZnO:Tm leads to product $ZnAl_2O_4$, while the intensity of blue emission has been found to be increased when the ZnO:Tm is re-baked with $MgCO_3 \cdot 5H_2O$ in reducing atmosphere.

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