Investigation of the Fabrication Parameters Affecting the Cathodoluminescence Property of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ Green Phosphors

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We investigated systematically the effects of fabrication parameters on the luminescent property of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ phosphor, which emits a highly chromatic pure green light. The samples used were synthesized in the air at 1200 °C by a solid phase method using ZnO , $\alpha\text{-Al}_2\text{O}_3$, and MnCl_2 or MnCO_3 powders, followed by thermal treatment in a reducing atmosphere at temperatures (T_r) from 800 to 1200 °C. We confirmed that the cathodoluminescence (CL) property of the as-synthesized sample strongly depends on the molar ratio of Zn and Al atoms in the source ($R_{\text{Zn/Al}}$). Namely, intense CL was observed only from the samples synthesized from the source with $R_{\text{Zn/Al}} < 0.5$, indicating that the Zn-deficient conditions are favorable for Mn impurities to be incorporated into the Zn site of ZnAl_2O_4 . More importantly, it is suggested from the T_r dependence of CL that most of the Mn impurities in the samples synthesized under the Zn-deficient conditions are in the state of the divalent ions even without a reduction treatment.

1. Introduction

ZnAl₂O₄:Mn shows green luminescence with a peak at 510 nm, which is attributed to the ⁴T₁-⁶A₁ transition within the 3d orbital of a Mn²⁺ ion.¹⁾ This luminescence is very attractive owing to its high chromatic purity. The CIE chromaticity coordinates (x, y) of the emission color for ZnAl₂O₄:Mn are typically (0.15, 0.73), while those of ZnS:Cu,Al, which is commonly used as a green phosphor in cathode-ray tubes, are (0.29, 0.61).²⁾ In addition, owing to the high thermal stability of the host crystal,^{3,4)} ZnAl₂O₄:Mn is expected to be stable even under exposure to high-current electron beams in a vacuum, which often causes the degradation of phosphors.⁵⁾ These features lead us to expect the use of ZnAl₂O₄:Mn as a green phosphor not only for wide-color-gamut displays, but also for those operated by low-energy electron beams, such as a field emission display and a vacuum fluorescence display.²⁾

In recent years, various synthesis techniques, such as a solid phase method,^{6,7)} a hydrothermal method,⁸⁾ a spray pyrolysis method²⁾, and a combustion method,⁹⁾ have been studied for the preparation of the ZnAl₂O₄:Mn phosphor. It has also been reported that the thermal treatment in a reducing atmosphere after synthesis dramatically increases the luminescent efficiency of this phosphor.^{2,6,7)} These reports have described that such improvement is attributed to the increase in Mn²⁺ content, which results from the reduction of Mn³⁺ ions incorporated into the host crystal. On the other hand, we have found that intense cathodoluminescence (CL) is observed without a reduction treatment when the molar ratio of Zn and Al sources is properly selected in the synthesis of ZnAl₂O₄:Mn by a citric gel method.¹⁰⁾

In this study, in order to understand these factors further, we investigated systematically the effects of both the ratio of sources and the reduction condition on the CL property of ZnAl₂O₄:Mn for the samples prepared by solid phase synthesis. This

synthesis method is preferable for the purpose since it is based on a simple solid phase reaction compared with the other reactions. The situation of the Mn centers in the host crystal was also discussed on the basis of the relationship between the preparing conditions and the luminescent and structural properties.

2. Experimental Procedure

ZnAl₂O₄:Mn powders were synthesized by a solid phase method using ZnO (99.999 %) and α -Al₂O₃ (99.99 %) powders as host crystal sources, and MnCl₂ (99.9 %) or MnCO₃ (99.9 % up) powder as an impurity source. The amounts of ZnO and α -Al₂O₃ sources were determined so that the molar ratio of Zn and Al atoms ($R_{\text{Zn/Al}}$) could be varied from 0.35 to 0.55, where 0.50 corresponds to the stoichiometric ratio. The molar ratio of Mn and Al atoms was maintained for all the synthesis processes at 0.01, where the most intense CL was obtained for the synthesis using MnCl₂. For MnCO₃, CL with the same intensity level was observed at this source composition. These sources were mixed in pure water, dried at 140 °C for 12 h, and then subjected to grinding by mortar and pestle. The obtained mixed powder was put in an alumina crucible and thermally treated at 1200 °C for 3 h in the air by a muffle furnace.

The reduction treatment was conducted on the calcinated powder using doubled alumina crucibles. The as-synthesized sample was put in the inner crucible, and the space between the two crucibles was filled with grains of active charcoal. Finally, the crucibles with the nested structure were thermally treated by the furnace for 5 h in the air. The reduction temperature (T_r) was varied from 800 to 1200 °C. Scanning electron microscopy (SEM) observation showed that the as-synthesized samples consisted of particles with a size of about 300 nm. Additional particle growth was not observed for the powders after the reduction treatments. Typical SEM images are shown in Fig. 1.

The structural properties of the prepared powders were evaluated by x-ray diffraction (XRD) measurement using the $\text{CuK}\alpha$ lines. The luminescent properties of the powders were characterized by CL measurement at room temperature. The samples were put on an aluminum plate using an adhesive conductive carbon tape. The anode voltage was varied from 3 to 7 kV at a constant current density of $60 \mu\text{A}/\text{cm}^2$ in the measurement. However, any noticeable differences in the $R_{\text{Zn}/\text{Al}}$ and T_r dependences of CL were not observed in the region of anode voltage. In this paper, therefore, the data obtained at 5 kV are shown as typical results.

3. Results and Discussion

3.1 Dependence on the molar ratio of Zn and Al atoms in the source ($R_{\text{Zn}/\text{Al}}$)

Figure 2 shows the XRD patterns of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ samples synthesized from the source with $R_{\text{Zn}/\text{Al}}$ from 0.40 to 0.55 and MnCl_2 . The analysis indicates that the sample synthesized with $R_{\text{Zn}/\text{Al}}$ of 0.50 consists of only ZnAl_2O_4 particles. However, the weak diffraction peaks from $\alpha\text{-Al}_2\text{O}_3$ and ZnO were observed for the samples with $R_{\text{Zn}/\text{Al}}$ lower and higher than 0.50, respectively. This trend on the products in the samples well reflects the variation in $R_{\text{Zn}/\text{Al}}$ for the method in this study. The full width at half maximum (FWHM) of the XRD line from the (311) plane of ZnAl_2O_4 was almost constant within the experimental accuracy in the $R_{\text{Zn}/\text{Al}}$ region investigated in this study.

Figure 3 shows the CL spectra of the as-synthesized samples. As seen in the figure, the CL property depended strongly on $R_{\text{Zn}/\text{Al}}$. Namely, the samples synthesized with $R_{\text{Zn}/\text{Al}}$ lower than 0.50 exhibited an intense narrow-band emission with a peak wavelength of 510 nm, while those synthesized from the source with $R_{\text{Zn}/\text{Al}}$ of 0.50 or higher showed only a very weak luminescence. It should be noted that the highest CL intensity was observed for the sample with $R_{\text{Zn}/\text{Al}}$ of 0.45 but not for the sample with a

stoichiometric source ratio of 0.50. The luminance of the emission from the sample with $R_{\text{Zn/Al}}$ of 0.45 was 2520 cd/m². The integrated CL intensity is also plotted in Fig. 4 with those measured from the samples synthesized using MnCO₃, whose spectra were also characteristic of ZnAl₂O₄:Mn. It can be seen in this figure that the dependences observed for the two series of ZnAl₂O₄:Mn are similar. This result has confirmed that the effect of $R_{\text{Zn/Al}}$ on the CL property is essential for this phosphor material regardless of the type of Mn source used in synthesis. It should also be noted that the powder color varied, depending on $R_{\text{Zn/Al}}$. Namely, the samples were almost white with a tinge of very faint pink for the case of $R_{\text{Zn/Al}} \leq 0.45$, while those exhibiting weak CL were tinged with pale brown for the case of $R_{\text{Zn/Al}} \geq 0.50$. The observed variation in the powder color correlated well with CL intensities.

We should consider at least two effects for $R_{\text{Zn/Al}}$ as the factors relating to the CL intensity. One is the efficiency of the incorporation of a Mn²⁺ ion into the host crystal as a luminescent center. ZnAl₂O₄ is crystallized in the spinel structure with a chemical formula of AB₂O₄ that belongs to the space group Fd3m. In this structure, there are two cation sites. One is the A site for a divalent ion, which is tetrahedrally coordinated by four oxygen atoms. The other is the B site for a trivalent ion, which is octahedrally coordinated by six oxygen atoms.¹¹⁾ From the viewpoint of charge balance, a Mn²⁺ ion is assumed to occupy the A site in competition with Zn²⁺ ions when a ZnAl₂O₄:Mn crystal is formed. It has been shown by EPR measurement that Mn²⁺ ions occupy the Zn sites in ZnAl₂O₄.⁹⁾ Therefore, our systematic investigation of the dependence on $R_{\text{Zn/Al}}$ has confirmed that the Zn-deficient conditions promote the occupation of Zn sites in ZnAl₂O₄ by Mn²⁺ ions as luminescent centers. A similar result has also been reported for the ZnGa₂O₄:Mn thin-film phosphor, where the molar ratio of Zn and Ga atoms affects the luminescent properties, with strong green emission observed in the

Zn-deficient films.^{12,13)}

The other factor is the valence of Mn ions incorporated into the sample. It has been reported that the powder color of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ changes from brown to white in conjunction with the change in the valence of Mn ions from the trivalent state to the divalent state by a reduction treatment.^{2,6,7)} Therefore, the change in powder color observed in this study suggests that the ratio of the Mn^{2+} ion and the Mn^{3+} ion in the sample increased with decreasing $R_{\text{Zn/Al}}$. The valence of Mn ions will also be discussed in the next section.

3.2 Dependence on the reducing temperature (T_r)

The reduction treatment was carried out on the $\text{ZnAl}_2\text{O}_4\text{:Mn}$ powders synthesized from the source with $R_{\text{Zn/Al}}$ of 0.45 and 0.50, and MnCl_2 , which showed different CL properties, as described in the previous section. The powder color of both samples was changed to white completely by the treatment. We investigated the dependence of the luminescent and structural properties on T_r in order to elucidate the effect of the reduction treatment.

Figure 5 shows the XRD patterns of the $\text{ZnAl}_2\text{O}_4\text{:Mn}$ sample synthesized from the source with $R_{\text{Zn/Al}}$ of 0.50 and those after the reduction procedure at various T_r . As seen in the figure, the patterns, which consisted of the diffraction peaks corresponding to ZnAl_2O_4 , did not change markedly at T_r up to 900 °C. On the other hand, the peaks corresponding to the defective spinel structure, which is the Zn-deficient phase of ZnAl_2O_4 ,^{7,14)} appeared in the sample treated at 1000 °C and were dominant in the sample treated at 1100 °C. From the sample treated at 1200 °C, only a series of peaks from $\alpha\text{-Al}_2\text{O}_3$ were found. These results indicate that the elimination of Zn from the ZnAl_2O_4 crystal due to thermal decomposition is enhanced in the reducing atmosphere,

which is a trend similar to that reported by Matsui et al.⁷⁾

Figure 6 shows the CL spectra of the samples shown in Fig. 5. As mentioned in the previous section, the as-synthesized sample emitted only a very weak luminescence. The intensity was slightly increased by the treatment at 800 °C. The dramatic improvement in CL property was achieved for the samples treated at T_r from 900 to 1100 °C. No luminescence was observed from the sample treated at 1200 °C owing to the complete decomposition of ZnAl_2O_4 , as confirmed from the results of XRD measurement. The observed dependence of CL intensity on T_r is similar to the results reported for PL⁷⁾ and CL²⁾ properties, although the T_r region showing intense luminescence is different. In these previous reports, the improvement in CL property was attributed to the increase in the number of Mn^{2+} ions due to the reduction of Mn^{3+} ions in the host crystal. In addition, we have found that the FWHM of the CL band increased remarkably with increasing T_r from 900 to 1100 °C, while the intensity did not show any particular trend in this T_r region. The increase in FWHM for the samples treated at 1000 and 1100 °C is probably attributed to the mixing of the defective spinel structure, in which the ligand field around the Mn^{2+} center changes with the structural change from the spinel structure due to the reduction process, as shown in Fig. 5.

Figure 7 shows the XRD patterns of the $\text{ZnAl}_2\text{O}_4\text{:Mn}$ sample synthesized from the source with $R_{\text{Zn/Al}}$ of 0.45 and those treated at various T_r . As you can see in the figure, the patterns of the samples treated at T_r up to 900 °C are similar with the dominant ZnAl_2O_4 and weak $\alpha\text{-Al}_2\text{O}_3$ peaks. From the results shown in both Figs. 5 and 7, it is confirmed that ZnAl_2O_4 is stable at temperatures lower than 900 °C in the reducing atmosphere formed in this study. However, the decomposition proceeded in different manners depending on $R_{\text{Zn/Al}}$ at T_r higher than 1000 °C. Namely, ZnAl_2O_4 started to decompose directly to $\alpha\text{-Al}_2\text{O}_3$ at 1000 °C for $R_{\text{Zn/Al}}$ of 0.45, whereas the defective

spinel structure was preferably formed for $R_{\text{Zn/Al}}$ of 0.50. The origin of such a difference is not clear at the present stage. One of the possibilities is that the $\alpha\text{-Al}_2\text{O}_3$ fine particles remaining in the as-synthesized samples exhibit the catalytic effect promoting the decomposition of ZnAl_2O_4 to $\alpha\text{-Al}_2\text{O}_3$. However, further studies are required to elucidate the mechanism. The sample decomposed completely to $\alpha\text{-Al}_2\text{O}_3$ by the treatment at 1200 °C, as is the case for $R_{\text{Zn/Al}}$ of 0.50.

The dependence of CL property on T_r , shown in Fig. 8, was also different from that observed for $R_{\text{Zn/Al}}$ of 0.50. The as-synthesized sample and those treated at T_r up to 1000 °C exhibited the luminescence characteristic of $\text{ZnAl}_2\text{O}_4\text{:Mn}$. The CL intensity increased slightly by the treatment at 800 °C. However, in contrast to the case for $R_{\text{Zn/Al}}$ of 0.50, the intensity turned out to decrease at T_r higher than 900 °C. It should also be noted that the FWHM of the emission band almost kept the value observed for the as-synthesized sample in the T_r region up to 1000 °C. The sample treated at 1100 °C exhibited a weak and broad luminescence. The observed behavior of CL bandwidth is correlated well with the finding that the defective spinel structure appeared in the sample treated at 1100 °C. On the other hand, we believe that the decrease in CL intensity with increasing T_r from 800 to 1000 °C is probably due to the increase in the numbers of defects originating from the excessive elimination of Zn atoms from the host crystal, which is suggested by the appearance of $\alpha\text{-Al}_2\text{O}_3$ peaks in the XRD pattern. No luminescence was obtained from the sample treated at 1200 °C, reflecting the complete decomposition of the sample to $\alpha\text{-Al}_2\text{O}_3$.

3.3 Factors affecting the state of Mn impurities in $\text{ZnAl}_2\text{O}_4\text{:Mn}$ phosphor

The T_r dependence of CL intensity is summarized in Fig. 9. This data has revealed that the reduction treatment is effective in increasing the CL efficiency, although its

effect strongly depends on the $\text{ZnAl}_2\text{O}_4\text{:Mn}$ sample subjected to it. For the sample synthesized from the source with $R_{\text{Zn/Al}}$ of 0.50, the effect was pronounced at T_r ranging from 900 to 1100 °C. This dependence indicates that most of the Mn impurities are in the trivalent state in the as-synthesized sample, and then, their state is changed to the divalent state by the reduction treatment, as already reported by the other groups.^{2,6,7)} In contrast, for the case of $R_{\text{Zn/Al}} = 0.45$, the maximum CL intensity was observed at a lower T_r of 800 °C, and the increment in CL intensity from that observed for the sample before the treatment was limited. It should be noted that the improved CL intensities after the reduction treatment were not markedly different for both the cases of $R_{\text{Zn/Al}} = 0.45$ and 0.50. Therefore, the dependence observed for the case of $R_{\text{Zn/Al}} = 0.45$ suggests that most of the Mn impurities are in the divalent state even in the as-synthesized sample. These explanations are consistent with the powder color of the sample at each stage.

It is noteworthy that Mn ions are preferably in the divalent state in ZnAl_2O_4 calcinated under the Zn-deficient conditions in the air. This can explain why we assume that the lattice site occupied by a Mn ion is more effective for determining its valence than the ambience during thermal treatment. The Zn-deficient conditions formed during the reduction treatment may also promote the relocation of Mn ions from the Al site to the Zn site, changing the valence from Mn^{3+} to Mn^{2+} . To further pursue this subject, however, we should study in detail the situation of Mn atoms that exist in the sample but show no emission, including the valence and the site in a crystal. We believe that these investigations lead to the improvement in the luminescent property of this phosphor. In fact, the luminance achieved for the samples synthesized in this study is still insufficient for practical use, although it was improved compared with the value previously reported.²⁾

In terms of the application of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ phosphors for wide color-gamut displays, the emission with a high chromatic purity is necessary. In this sense, it is important to carefully control the molar ratio of the sources at an appropriate value since the emission band is broadened by the reduction treatment depending on $R_{\text{Zn/Al}}$. We have shown that the intensity can be increased by the thermal treatment while keeping a narrow emission band for the sample with $R_{\text{Zn/Al}}$ of 0.50 under the treatment conditions in this study.

4. Conclusions

We investigated systematically the effects of fabrication parameters on the CL property of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ phosphor using the samples synthesized by a solid phase method and those thermally treated in a reducing atmosphere after synthesis. We confirmed in this study that $R_{\text{Zn/Al}}$ is one of the important parameters that affect the luminescent property of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ phosphor. The dependence of CL intensity on $R_{\text{Zn/Al}}$ suggested that the Zn-deficient conditions are favorable for Mn atoms to be incorporated into the Zn site of ZnAl_2O_4 as a luminescent center during calcination. The reduction treatment increased the CL intensity, as reported by the other groups.^{2,6,7)} However, we found that the T_r appropriate for improving the CL property depends on $R_{\text{Zn/Al}}$ for the samples subjected to the reduction treatment. These results suggested that most of the Mn ions can be in the divalent state in ZnAl_2O_4 calcinated even in the air if $R_{\text{Zn/Al}}$ is properly selected in the region less than 0.5.

References

- 1) D. T. Palumbo and J. J. Brown, Jr.: J. Electrochem. Soc. **117** (1970) 1184.
- 2) Z. Lou and J. Hao: Appl. Phys. A **80** (2005) 151.
- 3) R. Roesky, J. Weiguny, H. Bestgen, and U. Dingerdissen: Appl. Catal. A **176** (1999) 213.
- 4) X. Duan, D. Yuan, X. Wang, and H. Xu: J. Sol-Gel Sci. Technol. **35** (2005) 221.
- 5) S. Itoh, H. Toki, Y. Sato, K. Morimoto, and T. Kishino: J. Electrochem. Soc. **138** (1991) 1509.
- 6) H. Matsui, C. N. Xu, and H. Tateyama: Appl. Phys. Lett. **78** (2001) 1068.
- 7) H. Matsui, C. N. Xu, Y. Liu, and H. Tateyama: Phys. Rev. B **69** (2004) 235109.
- 8) L. Mu, J. Wan, Z. Wang, Y. Gao, and Y. Qian: J. Nanosci. Nanotechnol. **6** (2006) 863.
- 9) V. Singh, R. P. S. Chakradhar, J. L. Rao, and D. K. Kim: J. Lumin. **128** (2008) 394.
- 10) T. Nagura, H. Kominami, Y. Nakanishi, and K. Hara: Proc. Int. Display Workshops, 2007, p. 1009.
- 11) A. Seko, K. Yuge, F. Oba, A. Kuwabara, and I. Tanaka: Phys. Rev. B **73** (2006) 184117.
- 12) T. Minami, T. Maeno, Y. Kuroi, and S. Takata: Jpn. J. Appl. Phys. **34** (1995) L684.
- 13) Y. E. Lee, D. P. Norton, and J. D. Budai: Appl. Phys. Lett. **74** (1999) 3155.
- 14) K. Shirasuka, G. Yamaguchi, and Y. Miyachi: Yogyo Kyokaishi **84** (1976) 14 [in Japanese].

Figure captions

Fig. 1 SEM photographs of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ powders synthesized from the sources with $R_{\text{Zn/Al}}$ of 0.45 and MnCl_2 : (a) as-synthesized sample and (b) that after the reduction treatment at 1100 °C. The marker represents 1 μm .

Fig. 2. XRD patterns of $\text{ZnAl}_2\text{O}_4\text{:Mn}$ powders synthesized from the sources with $R_{\text{Zn/Al}}$ of (a) 0.40, (b) 0.45, (c) 0.50, and (d) 0.55. MnCl_2 was used for the synthesis.

Fig. 3. CL spectra of the samples shown in Fig. 2.

Fig. 4. Integrated CL intensities of the samples synthesized using MnCl_2 ($\square$) and MnCO_3 ($\circ$) as a function of $R_{\text{Zn/Al}}$.

Fig. 5. XRD patterns of (a) the $\text{ZnAl}_2\text{O}_4\text{:Mn}$ powder synthesized from the source with $R_{\text{Zn/Al}}$ of 0.50 and those after the thermal treatment in the reducing atmosphere at various T_r of (b) 800, (c) 900, (d) 1000, (e) 1100, and (f) 1200 °C.

Fig. 6. CL spectra of the samples shown in Fig. 5.

Fig. 7. XRD patterns of (a) the $\text{ZnAl}_2\text{O}_4\text{:Mn}$ powder synthesized from the source with the $R_{\text{Zn/Al}}$ of 0.45, and those after the thermal treatment in the reducing atmosphere at various T_r of (b) 800, (c) 900, (d) 1000, (e) 1100, and (f) 1200 °C.

Fig. 8. CL spectra of the samples shown in Fig. 7.

Fig. 9. Dependence of the integrated CL intensities of the samples shown in Figs. 6 and 8 on T_r . The symbols $\square$ and $\circ$ show the data for the samples synthesized from the sources with $R_{\text{Zn/Al}}$ of 0.45 and 0.50, respectively.

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