# 微米級鍺酸鹽與奈米級鎵酸鹽螢光體之製備與發光特性之研究

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## 摘要

$Zn_2GeO_4:Mn^{2+}$系列螢光體，在交流薄膜電激發光元件、場發射與電漿平面顯示器被認為極具應用潛力，而奈米 $ZnGa_2O_4: Mn^{2+}$螢光體在高解析顯示元件亦被認為具有提升解析度的特性。本研究分別利用固態法與熱溶劑法合成微米級 $Zn_2GeO_4:xMn^{2+}$ (x = 0.1-6.0%)及 $Zn_2(Ge_{1-y}Si_y)O_4:1\%Mn^{2+}$ ($0 \leq y \leq 1$) 兩系列螢光體與奈米級 $ZnGa_2O_4:xMn^{2+}$螢光體，並深入探討其化學組成、自身活化發光與 $Mn^{2+}$發光特性、瞬態衰減與微米級螢光體微結構之相互關係。

在 $Zn_2GeO_4:xMn^{2+}$系列螢光體中，隨 $Mn^{2+}$摻雜量增加，$Zn_2GeO_4:xMn^{2+}$的螢光衰減期變短，此可能與高含量 $Mn^{2+}$摻雜的樣品中 $Mn^{2+}$-$Mn^{2+}$對形成有關；另一方面，其光致發光(PL)光譜中 $Mn^{2+}$放射峰波長由 527 nm 偏移至 534 nm，呈現紅位移。瞬態衰減量測結果顯示：自身活化發光與 $Mn^{2+}$發光分別在奈秒與微秒時間範圍。

本研究亦探討 Si 的摻雜對 $Zn_2(Ge_{1-y}Si_y)O_4:1\%Mn^{2+}$螢光體的發光特性、螢光衰減期與表面微結構分析之效應。研究結果發現：隨 $Mn^{2+}$

摻雜量增加，$Zn_2GeO_4:xMn^{2+}$的螢光衰減期變短，且其光致發光(PL)光譜 $Mn^{2+}$放射峰波長呈現紅位移；而隨 Si 的取代量增加，$Zn_2(Ge_{1-x}Si_x)O_4:xMn^{2+}$的螢光衰減期無顯著改變，但其 PL 光譜 $Mn^{2+}$放射峰波長則呈現藍位移。

最後本論文亦探討以高壓熱溶劑法，於 180-220℃所合成奈 $ZnGa_2O_4:xMn^{2+}$之合成化學、發光特性與發光機制，並藉製程條件調變，以探討其與奈米螢光體發光特性與微結構的關係。以乙二胺、甲醇或甲醇/乙二胺為溶劑，均可成功合成奈米 $ZnGa_2O_4:xMn^{2+}$，當以甲醇/乙二胺為溶劑時，可明顯看出相對於塊材，其 PL 光譜呈現藍位移現象，此可能與其材料尺寸有密切關係。

## Abstract

This research is attempted to investigate the synthesis and luminescent properties of phosphors with compositions of (a) $Zn_2GeO_4$:x$Mn^{2+}$ (x = 0.1-6.0%), (b) $Zn_2(Ge_{1-y}Si_y)O_4$:1%$Mn^{2+}$ ($0 \leq y \leq 1$) and (c) $ZnGa_2O_4$:$Mn^{2+}$ nanophosphor that have been proposed to show potential applications in field emission displays, plasma display panels and, potentially, for high resolution displays. We have investigated the synthesis, luminescence and time-resolved decay spectra for $Zn_2GeO_4$:xMn phosphors doped with different contents of $Mn^{2+}$ as an activator. The microstructure of $Zn_2GeO_4$:*x*Mn samples is highly dependent of synthetic conditions. The observed red shift in $\lambda_{em}$ with increasing $Mn^{2+}$ content from 527 to 534 nm has been investigated and rationalized by the presence of a weak crystal field due to the substitution of $Zn^{2+}$ by $Mn^{2+}$, which leads to a distorted tetrahedral lattice site. The CIE chromaticity coordinates were found to shift slightly with variation of doped $Mn^{2+}$ content. The time-resolved fluorescence decay of $Zn_2GeO_4$:*x*Mn has also been investigated. Interestingly, the shortening of fluorescence decay lifetime with increasing $Mn^{2+}$ dopant concentration has been rationalized by the alteration of transition probability as a consequence of magnetic interaction between $Mn^{2+}$-$Mn^{2+}$ pairs in the host lattice.

The effect of Si-substitution on the luminescence properties as well as the microstructures of $Zn_2(Ge_{1-y}Si_y)O_4$:*x*$Mn^{2+}$ ($0 \leq y \leq 1$) has also been investigated. The emission of $Mn^{2+}$ attributed to $^4T_1 \rightarrow {}^6A_1$ transition

was found to exhibit blue shift with increasing doped Si content, which is presumably related with the systematic broadening of gap energy of the $Zn_2(Ge_{1-y}Si_y)O_4$ host.

We have also investigated the luminescence of the $ZnGa_2O_4:Mn^{2+}$ nanophosphors synthesized by a solvothermal route by reacting composing metal nitrates in solutions of methanol, ethylenediamine or a mixture of the two at 180- 220℃. As indicated by TEM and SEM micrographs, the microstructure of nano-$ZnGa_2O_4:Mn^{2+}$ was found to be highly dependent of the solvents used. The photoluminescence spectra of nano-$ZnGa_2O_4:Mn^{2+}$ synthesized in solvent of methanol/ ethylenediamine were observed to exhibit a blue shift relative to those of bulk samples.