

Effect of Co-dopant (Cr, Ti) in $\text{Zn}_2\text{SiO}_4\text{:Mn}$ Green Phosphors by Sol-Gel technique.

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Abstract

The main objective of this investigation is to improve the photoluminescent of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors prepared by the sol-gel technique. We try to use adding a new co-dopant such as Cr and Ti. The calcination temperature of sol-gel technique (1100 °C) was lower than that of the solid state reaction (1300 °C). Under 147nm excitation, the maximum emission intensity was obtained when the concentration of Cr and Ti was 0.1mol% with respect to $\text{Zn}_2\text{SiO}_4\text{:Mn}$. In order to study the effect of co-dopant, the content of Mn and the ratio of water to TEOS were fixed at 2mol% and 36:1, respectively.

1. Introduction

$\text{Zn}_2\text{SiO}_4\text{:Mn}$ has been widely used as a green emitting phosphor in display industry because of its high luminous efficiency. More recently this phosphor has been used in the Plasma Display Panels (PDP).

The photoluminescence process of this material has been characterized by the transition of $3d^5$ electrons in the manganese ion acting as activating center in this willemite structure. In particular, the transition from the lowest excited state to the ground state, i.e., ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ transition is directly responsible for the green light emission. [1,2]

Zinc orthosilicate having the formula of Zn_2SiO_4 has a willemite structure. The willemite lattice has two inequivalent Zn^{2+} sites. They are surrounded by oxygen ions in a slightly distorted tetrahedral configuration. The substitution of Zn^{2+} sites by Mn^{2+} ions results in excellent green light emission. There are several ways of enhancing the performance of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors. Co-doping is one of the most efficient approaches for goal of this work. The co-dopant are classified in two categories. First, some alkali earth and transition metals can be candidate for the replacement of Zn ions, and the other elements that can substitute for Si ion site, have been known as good co-dopants. In this regard, the element tested in the present investigation, only the co-doping effect of Cr and Ti are dealt with.

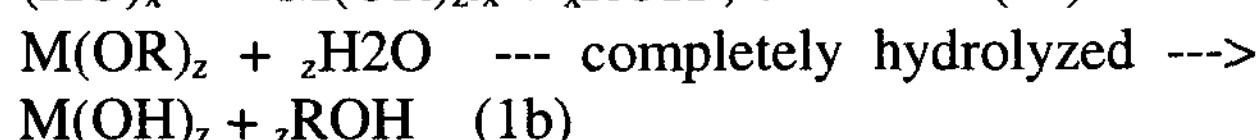
The decay time of the $\text{Zn}_2\text{SiO}_4\text{:Mn}$ has to be shorter

than few millisecond. Effectively, if the decay time is too short ($<0.1\text{ms}$), a flicker effect appears and if it is too long ($>10\text{ms}$) the images would be memory effect becomes a problem. Moreover, as the sensitivity of the human eye for video images is around 5ms, it is necessary to use phosphors having a decay time around 1 to 5ms. [3]

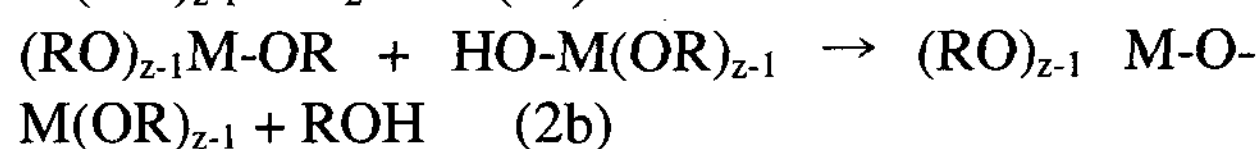
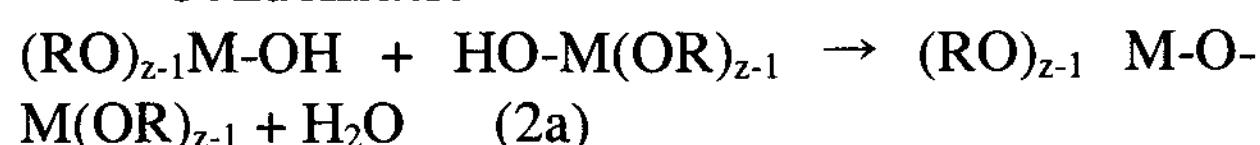
In general, it is possible to reduce the decay time of a phosphor by increasing the dopant content. However, because of the accompanying energy transfer, nonradiative de-excitation process will increase and the phosphor efficiency will decrease due to concentration quenching effect. [4]

The calcination temperature of sol-gel technique (1100 °C) is lower than that of the solid state reaction (1300 °C). The sol-gel process is considered as an effective route to prepare active materials with high specific surface areas and homogeneity. [5,6] It involves two major reactions: hydrolysis (Eqs. (1a) and (1b)) and condensation (Eqs. 2(a) and (2b)) [7]

<Hydrolysis>



<Condensation>



(R: alkyl group, M: metallic cations, z: valance of cations)

The above reactions can be controlled by adjusting the process parameters such as $\text{H}_2\text{O}/\text{M(OR)}_x$ molar ratio, pH conditions, reaction temperatures, acid or basic catalysts used and the precursor type. [8-11] In the preparation homogeneous multicomponent gels, comparable rates of hydrolysis and condensation are required during reaction. [12] It was attempted to prepare $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors by the sol-gel technique and their luminescent properties were compared with the commercial one. Under 147nm excitation, the maximum emission intensity was obtained when the concentration of each Cr and Ti was 0.1mol% with respect to

$\text{Zn}_2\text{SiO}_4\text{:Mn}$ wherein the content of Mn was fixed as 2mol% and the ratio of water to TEOS was fixed as 36:1.

2. Experimental

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), TEOS (Tetraethylorthosilicate), Chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) or Titanium iso-propoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$) were used as the starting materials and ethanol (EtOH) was adopted as solvent. Fig.1 shows the experimental procedures used to prepare the $\text{Zn}_2\text{SiO}_4\text{:Mn}$, M (M: Cr, Ti) phosphors. When Cr was co-doping, TEOS and Zn, Mn, Cr was dissolved into a solution of ethanol and distilled water. In case of Ti was added as co-dopant, TEOS and $\text{Ti}(\text{OC}_3\text{H}_7)_4$ were dissolved in half of required ethanol. In order to mix the reactants more thoroughly, distilled water was dissolved in the other half of ethanol before adding to the alcoholic solution of alkoxides. The hydrolysis and condensation reactions carried out at 65°C in the water bath. The resultant wet gels were dried at 80°C and 120°C for 24hr in a oven. First, the mixture phosphor powder was fired at 800°C and then, this powder was calcinated at 1100°C. The reduction process at 900°C (Ti) and 1000°C (Cr) by introducing the gas mixture of nitrogen and a small amount of hydrogen (5%) in a furnace. Crystalline phase and phase change of phosphors prepared were characterized by powder X-ray diffraction (XRD) using a Rigaku DMAX-33 X-ray diffractometer with Cu-K α radiation. The morphology of the phosphor particle was observed by field emission scanning electron microscopy (FE-SEM) using a Philips XL-30S. Photoluminescence measuring system was set up in order to achieve VUV excitation, which includes D2 lamp. All the emission spectra were obtained under the excitation of 147nm, so that the PL characteristics in the similar environment to the actual PDP application could be investigated. The decay curves were measured using Xenon flash lamp, preamplifier, and oscilloscope.

3. Results and Discussions

The main objective of the present investigation is to improve the photoluminescent performance of existing $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors by adding a co-dopant. Several candidates have been adopted as co-dopants for this purpose. Some of them give an advantageous influence on either the emission intensity or the decay behavior, whereas some of them deteriorate these properties. Of the co-doping

elements considered, consideration of only two elements (such as Ti and Cr), which are known as a substituent for zinc site, is taken into account in the present investigation based on the fact that these elements have favorable influences on the photoluminescence process.

$\text{Zn}_2\text{SiO}_4\text{:Mn}$ green phosphor by sol-gel technique have the highest photoluminescent when the content of Mn was 2mol%. Thus, in order to studied the co-doping effect of Ti and Cr, the content of Mn and the ratio of water TEOS were fixed at 2mol% and 36:1, respectively.

Fig.2 (a) and (b) show, respectively, the emission spectra and the normalized decay curves of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors as a function of Cr concentration. As can be seen in Fig.2 (a) the 0.1mol% Cr co-doped powder proved to provide a best combination of luminance and while the emission intensity decreases with increase Cr content, the decay time are improved by the introduction of Cr.

The emission intensity of powder that dried at 80°C better than at 120°C. The emission intensity of dried at 80°C powder were extremely decrease with increase Cr content and dried at 120°C powder were slowly decrease. Cr was intruded for the purpose of shortening the decay time. There is considerable spectral overlap between this broad absorption band and the green emission band of Mn ions, which covers the range between 480 and 560nm. Such an overlap reflects an energy transfer from Cr^{4+} ions to Mn^{2+} ions to a certain extent.[13] As a result, the emission should also be shortend by the presence of nonradiative energy transfer, since the energy transfer process shortens the lifetime of the excited state of Mn ions.[13] Fig. 3. shows XRD patterns of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ powder obtained by the sol-gel technique at various Cr concentrations. JCPDS card (08-492) of Zn_2SiO_4 is shown as reference. It is obvious that the single phase of zinc orthosilicate was formed by firing at 1100°C

The SEM photographs of the Cr co-doped $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor prepared by sol-gel technique as well as the commercial phosphor by solid state reaction was expressed in Fig. 4. The phosphor particles synthesized appear particle size under 1 μm to be dispersed and spherical shape. Whereas the commercial ones show irregular and large particle size.

The emission intensity and decay time of Ti co-doped $\text{Zn}_2\text{SiO}_4\text{:Mn}$ as a function of Ti content and it is shown in Fig.5 (a) and (b). It is possible to reduce extremely the emission intensity of a phosphor when the concentration of Ti was 2.0mol% due to

the well-known concentration quenching effect. The concentration quenching behaviors may be due to the cross relaxation or energy migration to quenching centers where the excitation energy is lost nonradiatively. Our sample exhibit higher emission intensity by about 15% located at 525nm than the commercial ones while there is a need to improve decay properties. Fig.6 shows the X-ray diffraction (XRD) patterns of the Ti co-doped $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor particle synthesized by the sol-gel technique fired at 1100°C . It appears from their XRD pattern that 2.0mol% Ti co-doped $\text{Zn}_2\text{SiO}_4\text{:Mn}$ particle were not well crystallized. This sample is believed to be caused by the luminescent killer. All the XRD peaks except for 2.0mol% Ti co-doped in Fig.6 match very well with the standard values from the JCPDS data card number 08-492 which can be assigned to willemite structure.

The morphology of the Ti co-doped powder by sol-gel technique are represented in Fig.7. Our phosphor particles appear particle size of under $1\ \mu\text{m}$ to be dispersed and spherical shape, whereas the Fig.7 (d) show shapeless and large agglomerated, between $10\sim 20\ \mu\text{m}$, are present, and they are constituted by a great number of irregular grains. These agglomerates will be too large for a good deposition of the phosphors on the glass panel. Effectively, when phosphors are used in plasma panels, the optimum mean grain size is around 6 to $8\ \mu\text{m}$. [3]

4. Conclusions

In this investigation, $\text{Zn}_2\text{SiO}_4\text{:Mn}$ green phosphor preparation was designed by the sol-gel technique. The calcination temperature of sol-gel technique (1100°C) was lower than that of the solid state reaction (1300°C). In order to improve the photoluminescent properties, co-dopants such as Cr and Ti were incorporated into $\text{Zn}_2\text{SiO}_4\text{:Mn}$ green phosphors. As a result of, Both the Cr and Ti ions are proved to be favorable co-dopants for enhancing the emission intensity and for shortening the decay time, respectively.

Especially, when the concentration of Ti was 2.0mol%, it shows the concentration quenching.

5. References

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Figure

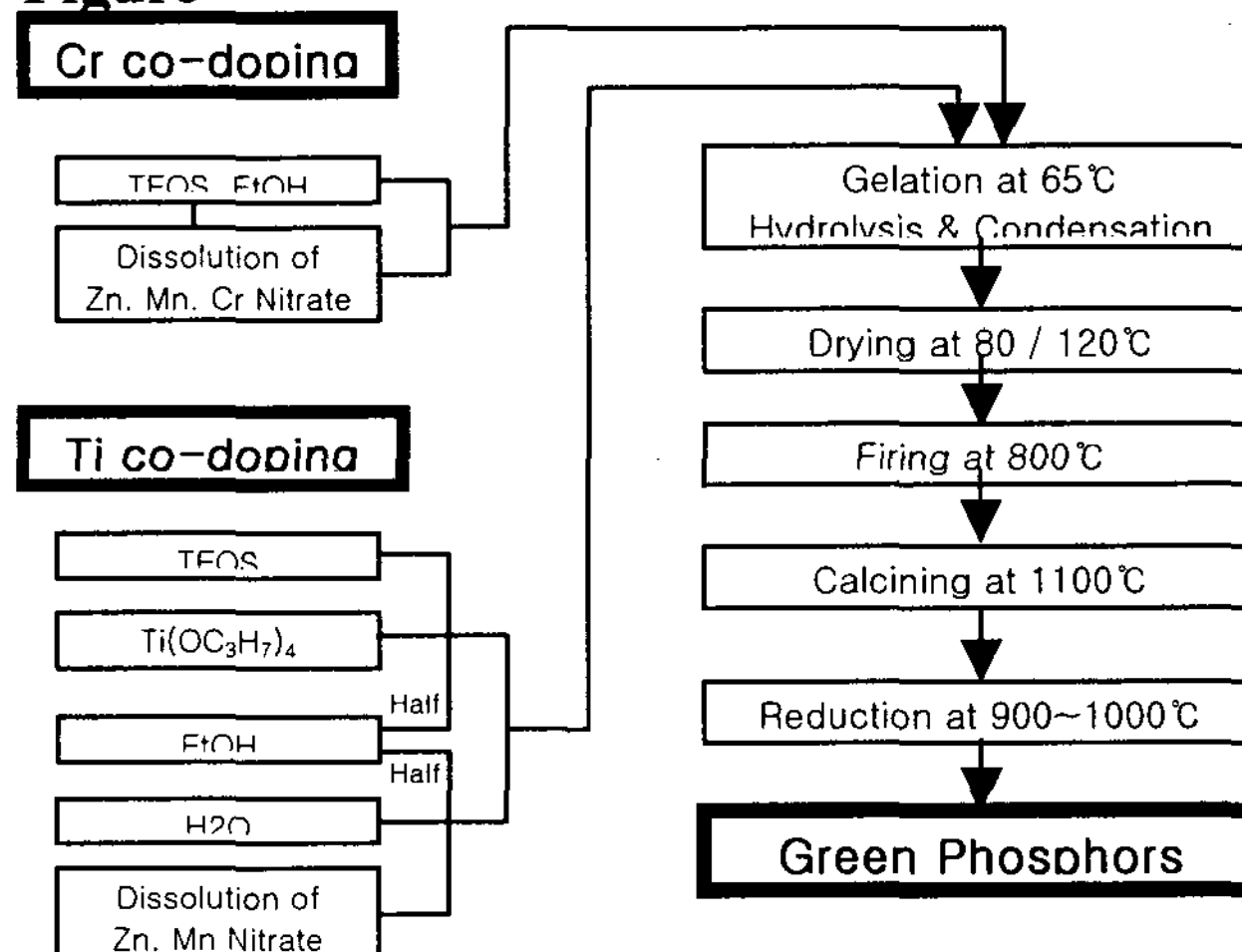
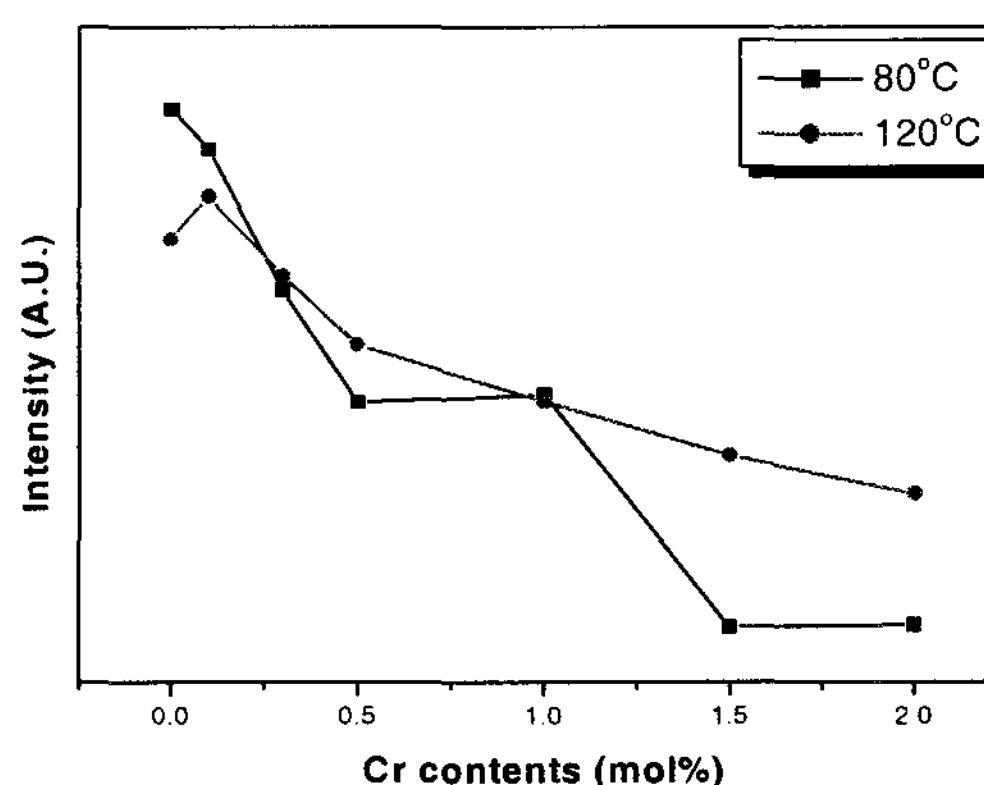


Fig. 1. Experimental procedures for preparing the $\text{Zn}_2\text{SiO}_4\text{:Mn}$, M (M=Cr, Ti) phosphors by using sol-gel method.



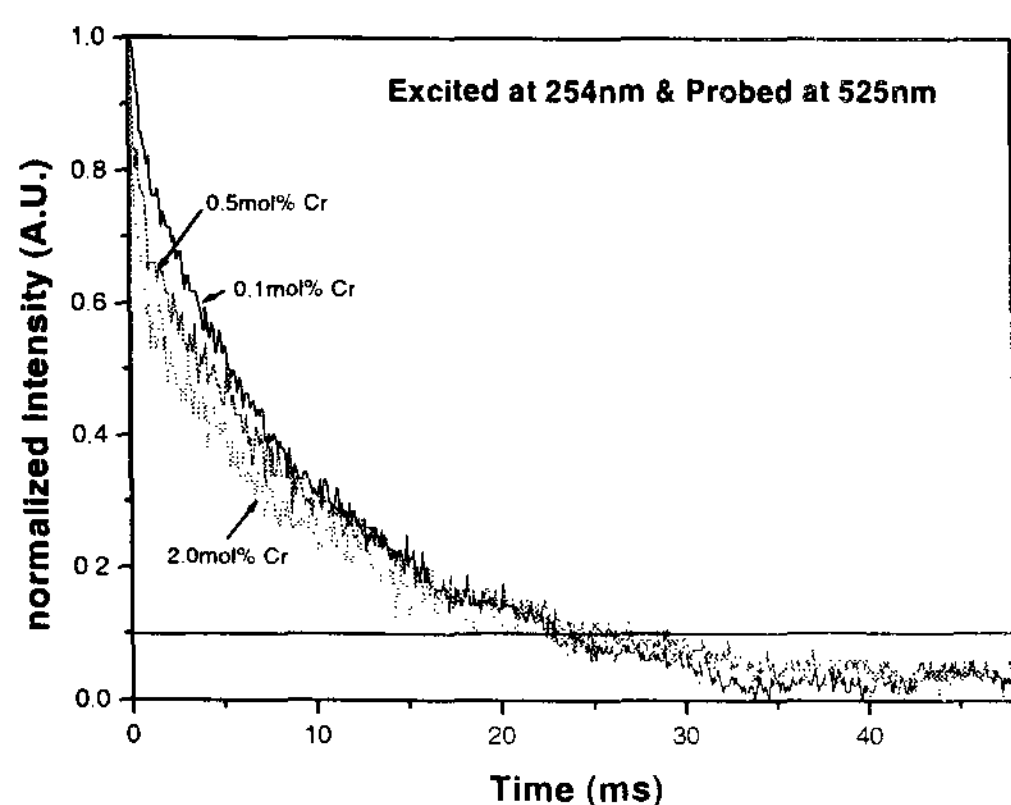


Fig. 2. (a, top) Emission peak intensities and (b, bottom) decay curves of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors for various Cr co-doping concentrations under the excitation light wavelength of 147nm.

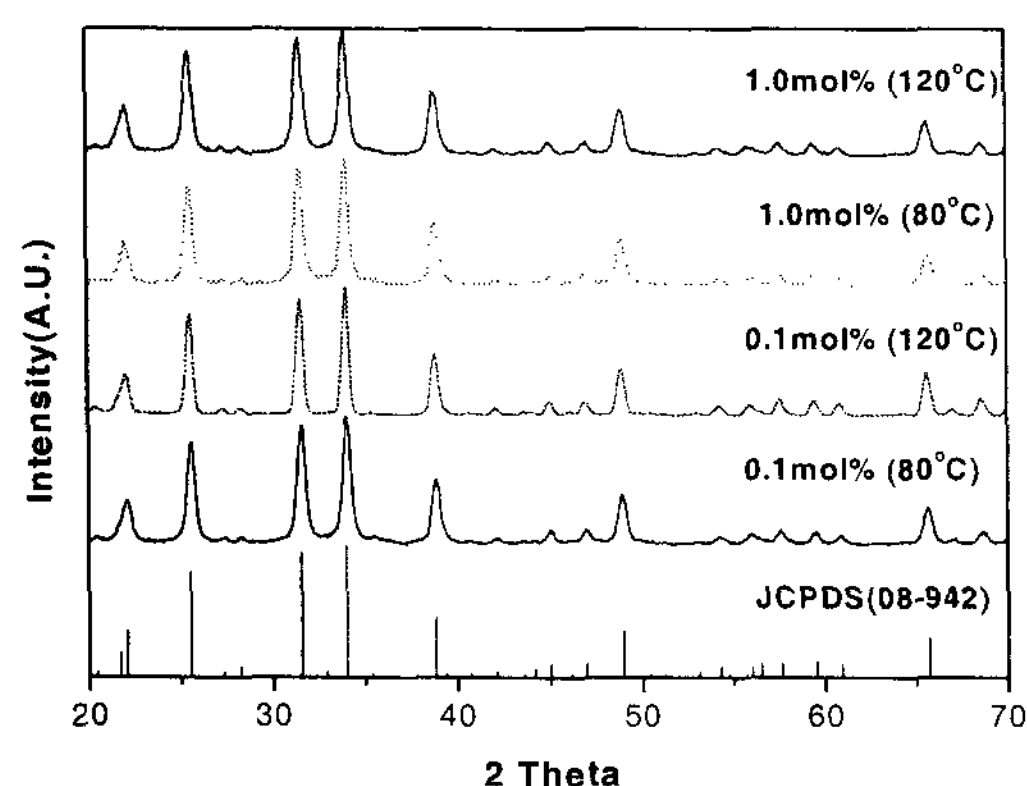


Fig. 3. X-ray diffraction patterns of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors in various Cr co-doping concentrations and drying temperatures (fired at 1100°C for 4hr).

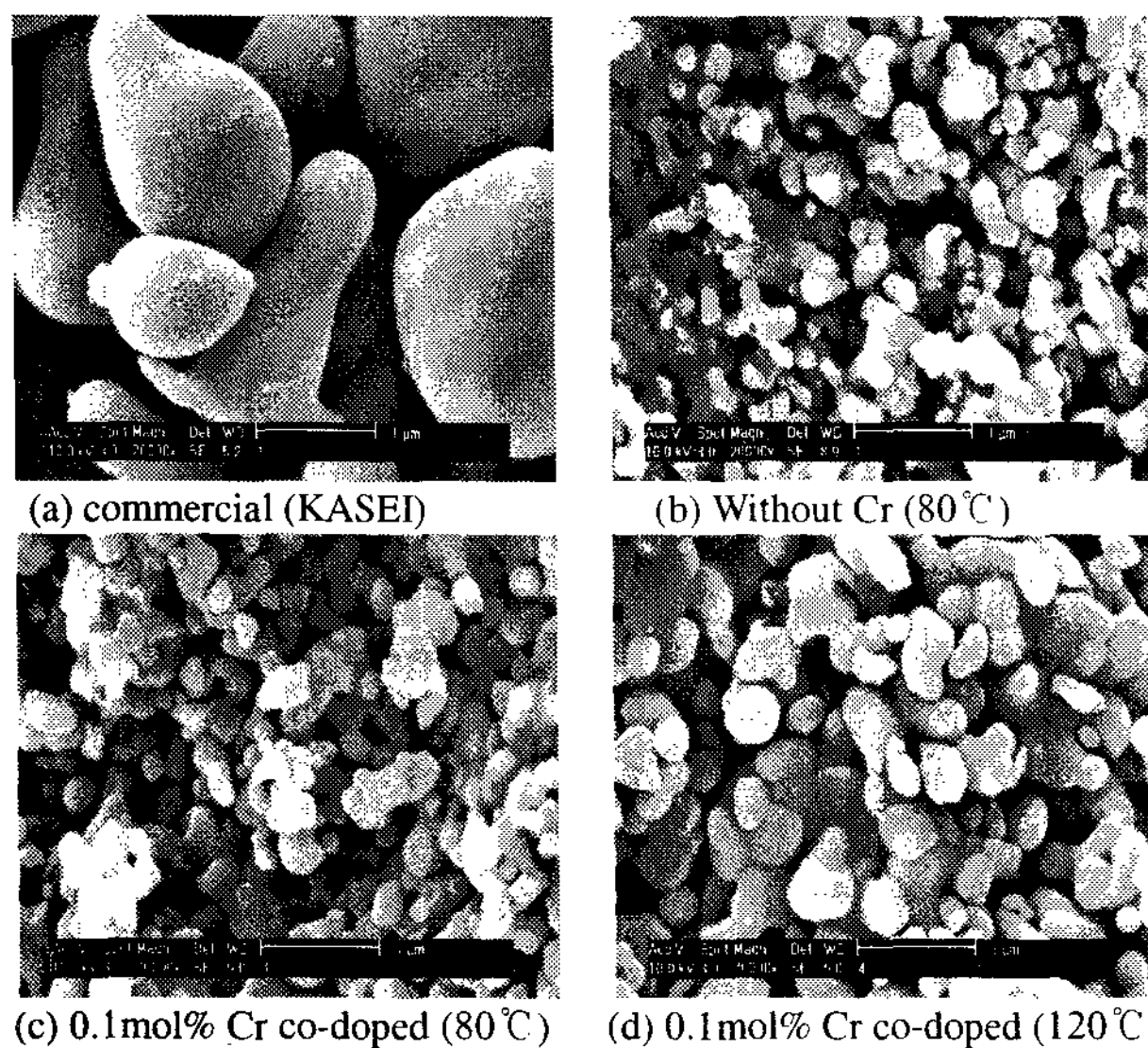


Fig. 4. SEM photographs of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors in various Cr co-doping concentrations compared with commercial and drying temperatures. (fired at 1100°C for 4hr)

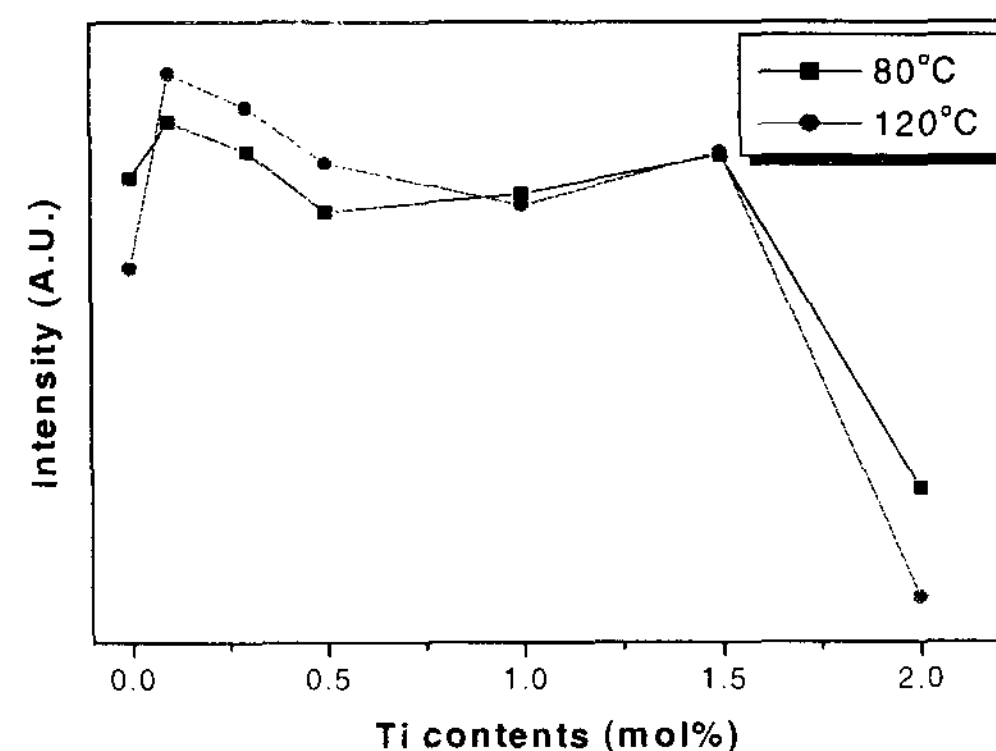


Fig. 5. (a, top) Emission peak intensities and (b, bottom) decay curves of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors for various Ti co-doping concentrations under the excitation light wavelength.

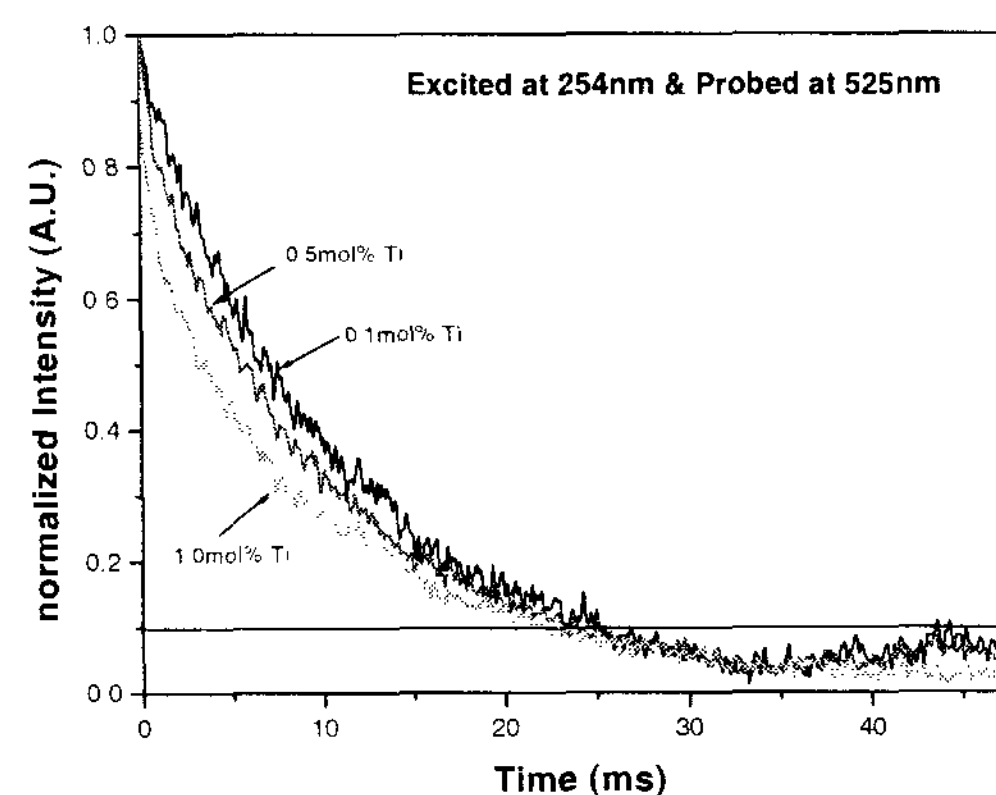
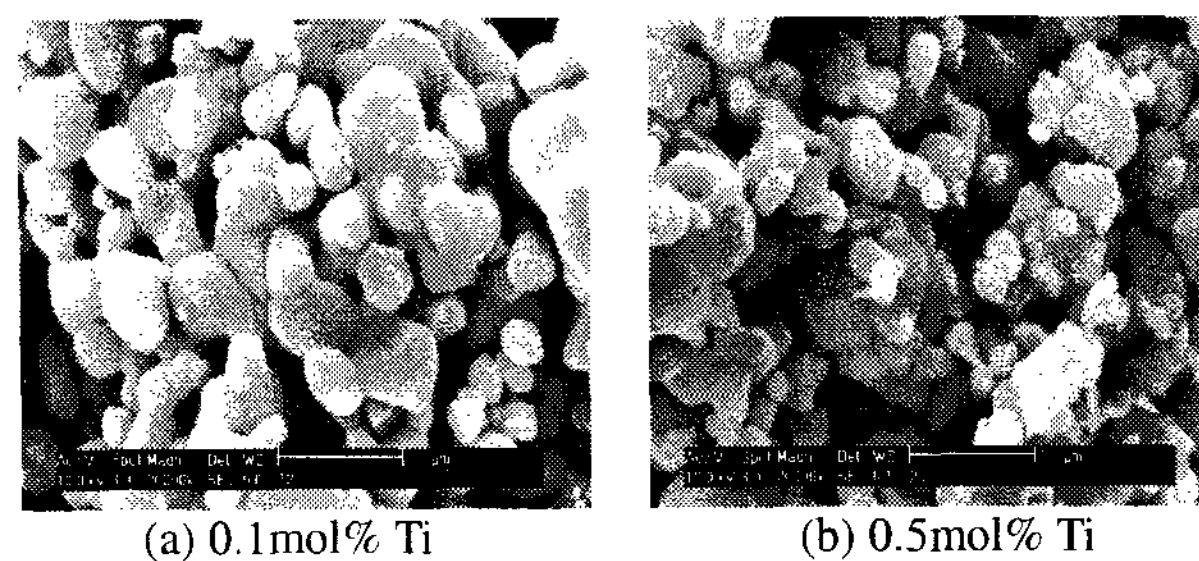
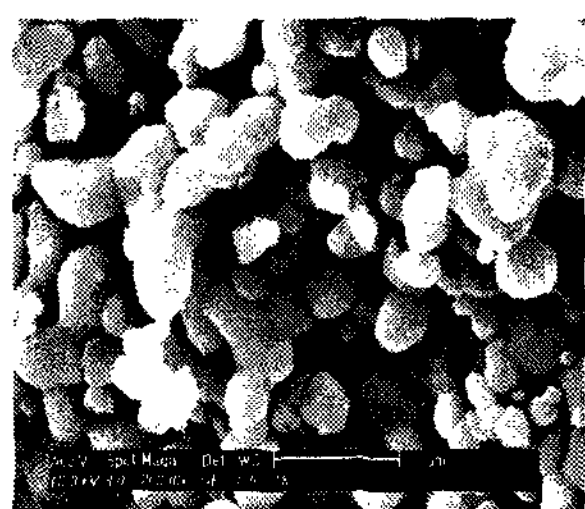
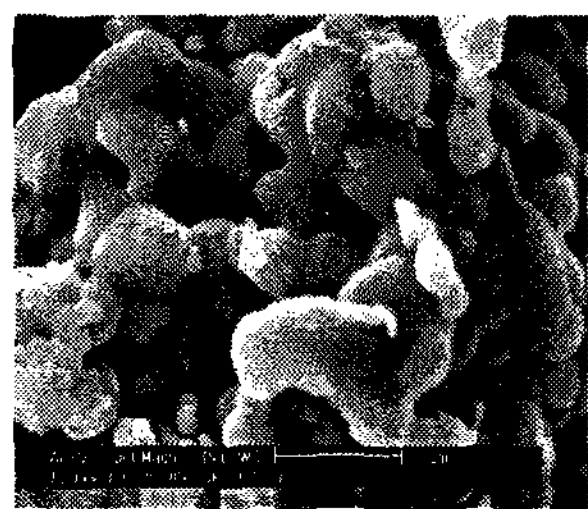


Fig. 6. X-ray diffraction patterns of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors in various Ti co-doping concentrations. (fired at 1100°C for 4hr)





(c) 1.5mol% Ti



(d) 2.0mol% Ti

Fig. 7. SEM photographs of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors in various Ti co-doping concentrations and drying temperature at 120 °C. (fired at 1100 °C for 4hr)