Influence of Cr and Mn co-doping on the microstructure and optical properties of spinel structured Zn_{0.95-x}Cr_{0.05}Mn_xAl_2O_4 nanoparticles

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Cr and Mn co-doped Zn_{0.95-x}Cr_{0.05}Mn_xAl_2O_4 nanoparticles with different contents of Mn were synthesized via simple hydrothermal route and heat treatment technology. The influences of Cr and Mn doping on the microstructure, morphology, binding energy and optical property of the as-synthesized samples were characterized. X-ray diffraction confirm that Zn_{0.95-x}Cr_{0.05}Mn_xAl_2O_4 nanoparticles exhibit cubic spinel structure, the average crystallite size decrease and the lattice parameter increase with the increase of Mn doping concentration. X-ray energy dispersive spectroscopy and X-ray photoemission spectroscopy demonstrate Cr and Mn ions are successfully substituted for the lattice site of Zn^{2+}, enter ZnAl_2O_4 matrix and mainly occupy the tetrahedral sites of the doped samples. Scanning electron microscopy and high-resolution transmission electron microscopy show the morphology of the samples are irregular spherical or ellipsoid particles with small particle size and good dispersion. Ultraviolet–visible spectra indicate co-doped samples possess strong visible light absorption ability, and the band gap decrease as Mn ions concentration increase and occur red shift. Photoluminescence spectra show the intensity decrease and occur luminescence quenching phenomenon for doped samples. The intensity of Fourier transform infrared spectroscopy for doped samples decrease slowly and occur red shift.

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1. Introduction

In recent years, spinel structure mix-metal-oxides nanomaterials have received remarkable attention due to its unique crystal structure and interesting characteristics of high chemical and thermal stability, high mechanical strength, low surface acidity, good cationic dispersion, excellent optical and dielectric properties.¹⁻⁴ ZnAl_2O_4 as a type of aluminates with spinel structure, the chemical formula generally have expressed as AB_2O_4, where A represents divalent metal cation, occupies the tetrahedral position, the tetrahedral gap formed by four oxygen ions, while B represents trivalent cation, occupies the octahedral position, and the octahedral void formed by six oxygen ions.¹⁻⁸ ZnAl_2O_4 has been widely used in many fields, such as magnetic storage devices, catalysts, photosynthesis enhancement, high-temperature ceramics, laser and fluorescent substrate materials, sensing and dielectric materials,⁵⁻¹⁸ etc. various methods have been adopted to adjust the microstructure and band structure of spinel structure mix-metal-oxides to further improve its practical application, such as the exposure of facet ion doping,¹⁴,¹⁵ noble metal loading,⁵⁻⁷ and heterostructure construction.¹⁹⁻²¹ The microstructure and band structure of spinel structure mix-metal-oxides can be adjusted by doping transition metal ion. The hole or electron carrier acts as the receptor or donor, the electrical, magnetic and optical properties of the new semiconductor materials are effectively controlled by adjusting the type and concentration of the carrier.²²⁻²⁶ Many investigations have been studied on the Preparation and characterization of spinel structure metal oxides doped with transition metal ions, and the physical properties of transition metal ions doped metal oxides depend largely on their synthesis route, annealing temperature and impurity content.²⁷⁻³¹ Basavaraju et al. found that Cr^{3+} doped spinel compounds AB_2O_4 with A = Zn, Mg and B = Ga, Al exhibit a long, near infrared persistent luminescence when excited with UV or X-rays.³⁰ Huang et al. synthesized Zn_{1-x}Mn_xAl_2O_4 (x = 0, 0.10, 0.20, 0.30 and 0.40) nanoparticles by hydrothermal method, found the average crystal size decreases, the lattice parameters increase and the band gap of doped samples decreases with the increase of Mn doping concentration.³¹ Unfortunately, to the best of our knowledge, up to now, most of the studies focused on the physical properties of single transition metal ion doped metal oxide semiconductor, there are few studies on the effects of Cr and Mn
co-doping on the microstructure and optical properties of spinel structure ZnAl2O4 nanoparticles. Therefore, the main purpose of this study is to study the effect of Cr and Mn co-doping on microstructure and optical property.

In this paper, Cr and Mn co-doped Zn0.95-xCr0.05MnxAl2O4 (x = 0.01, 0.03, 0.05 and 0.07) nanoparticles are synthesized by hydrothermal method and heat treatment technology, and the effects of Cr and Mn doping content on the microstructure, morphology, binding energy and optical property of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray energy dispersive spectroscopy (XEDS), X-ray photoemission spectroscopy (XPS), ultraviolet-visible (UV-Vis) spectroscopy, photoluminescence spectra (PL) and fourier transform infrared spectroscopy (FT-IR).

2. Experimental

2.1 Preparation of Zn0.95-xCr0.05MnxAl2O4 nanoparticles

Pure ZnAl2O4 and doped Zn0.95-xCr0.05MnxAl2O4 nanoparticles with different amount of dopant was fabricated via an efficient hydrothermal method and heat treatment technology. The raw materials used in this experiment are analytical grade and need not be further purified. The typical synthesis process of Zn0.95-xCr0.05MnxAl2O4 nanoparticles is as follows: according to the chemical formula Zn0.95-xCr0.05MnxAl2O4 (x = 0.01, 0.03, 0.05 and 0.07) and the molar ratio of metal cations Zn:Cr:Mn:Al were kept at (0.95-x):0.05:x:2, weighed stoichiometric amounts of Zn(NO3)2·6H2O, Al(NO3)3·9H2O, CrCl3·6H2O and Mn (CH3COO)2·4H2O used as precursors, the Zn2+, Cr3+, Mn2+ and Al3+ cations respectively dissolved in distilled water and added into a 100 mL glass container by continuous stirring to obtain mixed metal salt solution. Firstly, the pH value of above mixed solution was adjusted to 12 by dropping NaOH solution with constant stirring. Then a certain amount of CTAB was slowly added to the above suspension and magnetic stirring for 30 min. Subsequently, the mixture was transferred and sealed in 100 ml Teflon-lined autoclave, and hydrothermally treated at 200℃ for 24h. Then the acquired sample was cooled down to the environment temperature naturally. The obtained precipitates were collected by centrifugation, washed by distilled water and absoluted alcohol for several times to remove ionic impurities, respectively. Finally, the precursor was thermally treated kept at 700℃ for 6 h in a muffle furnace to remove moisture and obtained Zn0.95-xCr0.05MnxAl2O4 sample.

2.2 Characterization

The crystal structure was performed via an X-ray powder diffraction (Rigaku Corporation, Japan, D/Max-2400) with monochromatized Cu Kα radiation (λ = 0.15406 nm) at 40 kV and 80 mA. The morphology and microstructure of the products were observed by SEM (JEOL JSM-6701F) and HRTEM (JEM-2010). The chemical composition analysis of the products was measured by XEDS.

The bandgap energy of the as-prepared samples was characterized by UV-Vis spectrophotometer (PERSEE TU-1901) with an integrating sphere attachment. The surface chemical composition and chemical state of elements were studied by XPS (PHI-5702). The photoluminescence spectra (PL) were recorded by PerkinElmer spectrophotometer (LS-55) with an excitation wavelength of 320 nm. FT-IR analysis were performed by Nexus 670 FT-IR Spectrometer in the range of 4000–375 cm⁻¹ with the KBr pellet method.

3. Results and discussion

3.1 Structural characterization

Cubic spinel structure ZnAl2O4 belongs to Fd3m space group with unit cell parameters a = b = c = 0.8048 nm, V = 0.52478 nm³ and Z = 8, and the chemical formula generally is expressed as AB2O4, where A (yellow structure in Fig. 1) represents the tetrahedral position occupied by divalent metal cations, and the tetrahedral gap formed by four oxygen ions, and B (purple structure in Fig. 1) position represents the octahedral position occupied by the trivalent metal cations, and the octahedral void formed by six oxygen ions.³²⁻⁴ The crystal structure of ZnAl2O4 is presented in Fig. 1. It can be observed that cubic spinel structure ZnAl2O4 unit cell contains 56 ions, including 8 Zn ions, 16 Al ions and 32 oxygen ions, and the general formula is X₈Y₁₆O₃₂, equivalent to eight AB₂O₄ stacked together.

Figure 2 displays the XRD patterns of pure ZnAl2O4 and Zn0.95-xCr0.05MnxAl2O4 (x = 0.01, 0.03, 0.05 and 0.07) samples, which confirm the same structure of pure Cr and Mn co-doped samples, the integration of Cr and Mn dopant into the lattice of ZnAl2O4 without change (changing) the structure of ZnAl2O4. Although with different Mn, all the five samples display similar characteristic peaks at 2θ = 31.5, 36.8, 44.9, 47.3, 56.2, 58.1, 65.3, 73.6 and 77.3°, which are well indexed to the (220), (311), (400), (331), (422), (511), (440), (620) and (533) crystal planes of single-phase ZnAl2O4 cubic spinel structure, respectively, and consistent with the standard spectrum JCPDS Card No. 05-0669. In addition, for the doped samples, there are no extra diffraction peaks of other impurities related to Cr or Mn related oxides or clusters are detected within the detection limit of XRD, ZnAl2O4 is the only phase detected for all the samples. These results indicates that all Cr and Mn ions successfully occupied the lattice
sites of \( \text{Zn}^{2+} \) in the \( \text{ZnAl}_2\text{O}_4 \) matrix without affecting the crystalline nature of pure \( \text{ZnAl}_2\text{O}_4 \), and the hydrothermal condition have no significant effects on the structure and purity of \( \text{ZnAl}_2\text{O}_4 \). Furthermore, the sharp diffraction peaks of the XRD patterns exhibit the as-prepared samples possess good crystallization.

The crystallite size of the samples was calculated using the most intense diffraction peak (311) by means of Scherrer formula: 
\[
D = \frac{K\lambda}{B \cos \theta},
\]
where \( D \) is the crystallite size, \( K \) is a constant (0.90), \( \lambda \) is the wavelength of Cu K\( \alpha \) (1.5406 nm), \( B \) is the full width half maximum (FWHM) intensity usually in radians and the Bragg’s diffraction angle in degrees, respectively. The average crystallite size of the samples is summarized in Table 1. It is obviously that the crystallite size gradually decreases with the increase of Mn doping concentration, which indicates that Mn doping has a regulating effect on the crystallite size, which may due to the uneven stress or strain of the particle growth process or the local structural deformation during the material formation process.

The interplanar spacing and the lattice constant of the samples can be obtained according to the crystallographic calculation formula and the Bragg formula, the diffraction angle, lattice constant, interplanar spacing and crystallite size of (311) peak of pure \( \text{ZnAl}_2\text{O}_4 \) and \( \text{Zn}_{0.95-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) samples are also presented graphically in Table 1. It is obviously that the (311) peak for doped samples shift slightly towards lower diffraction angle with the increase of Mn doping content, and the lattice constant and interplanar spacing of doped samples decrease with the increase of Mn doped content. The lattice constant is distorted and show lattice expansion. The difference of lattice parameter reflects the inhomogeneity of ion radius and the inhomogeneity of substituted ions in the matrix material, which may be attributed to the incorporation of Mn and Cr ions into \( \text{ZnAl}_2\text{O}_4 \) host lattice, and the ionic radius of \( \text{Mn}^{2+} \) ions (0.67 \( \text{Å} \)) and \( \text{Cr}^{3+} \) ions (0.63 \( \text{Å} \)) smaller than that of \( \text{Zn}^{2+} \) ions (0.74 \( \text{Å} \)), eventually lead to the lattice distortion. These results show that the lattice parameter and particle size of the samples can be controlled by transition metal ions doping, and the microstructure and physical properties of the samples can be controlled and adjusted.

### Table 1. Interplanar spacing, lattice constant, grain size and full width at half maximum of pure \( \text{ZnAl}_2\text{O}_4 \) and \( \text{Zn}_{0.95-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) samples

| Sample | \( 2\theta \) (°) | FWHM | \( d_{hkl}/\text{nm} \) | \( a=b=c \) (nm) | \( D/\text{nm} \) |
|--------|----------------|-------|------------------------|----------------|-------------|
| \( x=0 \) | 36.88 | 0.3380 | 0.2435 | 0.8077 | 24.50 |
| \( x=0.01 \) | 36.76 | 0.4510 | 0.2443 | 0.8103 | 18.35 |
| \( x=0.03 \) | 36.77 | 0.4860 | 0.2442 | 0.8099 | 17.03 |
| \( x=0.05 \) | 36.70 | 0.5390 | 0.2447 | 0.8116 | 15.36 |
| \( x=0.07 \) | 36.70 | 0.5830 | 0.2447 | 0.8116 | 14.20 |

### 3.2 Morphological studies

The typical SEM images of pure \( \text{ZnAl}_2\text{O}_4 \) and \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) samples was shown in Fig. 3. It is obviously that the morphology of pure \( \text{ZnAl}_2\text{O}_4 \) mainly irregular spherical or ellipsoid particles with average particle size below 50 nm. Figure 3(b) shows the particle size distribution diagram of pure \( \text{ZnAl}_2\text{O}_4 \) nanoparticles, from the histogram analysis, and it can be seen that the particle size mainly ranges from 20 to 45 nm with average particle size about 32 nm. As can be seen from Figs. 3(a) and 3(c), pure and doped \( \text{ZnAl}_2\text{O}_4 \) samples exhibit similar morphology, the SEM image of \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) samples also represent the irregular spherical or ellipsoid shape. Figure 3(d) shows the particle size distribution diagram of \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \), which the particle size distribution is in the range of 18–30 nm with average particle size about 23 nm. The morphology of doped \( \text{ZnAl}_2\text{O}_4 \) samples without changing compared with that of pure samples. However, Cr or Mn doped samples show a tendency to possess smaller particle size and more uniform size distribution, which is in good agreement with the XRD results.

HRTEM images in Fig. 4 provide more details of the basic unit of \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) nanoparticles. Figure 4(a) shows the representative HRTEM images of \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \). It is obviously that the morphology of doped samples is spherical shape with uniform size distribution, in addition, and some particles possess a degree of agglomeration, which may be due to grain boundary aggregation or the interaction of van der Waals force, coulomb force or chemical bond among nanoparticles to attain thermodynamic stability. Figure 4(b) represents the local amplification of \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) samples, and it clearly exhibits the ordered and perfect crystal plane stripes with interplanar spacing about 0.248 nm, which is ascribed to the (311) crystal planes of cubic spinel structure \( \text{ZnAl}_2\text{O}_4 \), and indicating that \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) is well-crystallized and grows selectively along the (311) crystal planes. This result is consistent with the fact that (311) facet possesses the highest intensity in the XRD.

The selected area electron diffraction (SAED) pattern of \( \text{Zn}_{0.90-x}\text{Cr}_{0.05+x}\text{Mn}_{x}\text{Al}_2\text{O}_4 \) as shown in Fig. 4(c), the SAED
pattern of the samples consists of a series of concentric rings with different radius due to the sample possess polycrystalline structure. The polycrystalline diffraction rings from inside to outside can be indexed to the (220), (311), (400), (331), (422), (511) and (440) crystal plane of ZnAl$_2$O$_4$, respectively. The results of SAED and HRTEM further indicate that the obtained samples with spinel structure, these results further indicating that both Cr$^{3+}$ and Mn$^{2+}$ enter ZnAl$_2$O$_4$ lattice and replace Zn$^{2+}$, which is consistent with the XRD analysis results.

Figure 5 illustrates the XEDS spectrum of pure ZnAl$_2$O$_4$ and Zn$_{0.90}$Cr$_{0.05}$Mn$_{0.05}$Al$_2$O$_4$ samples. The spectra show that the basic signals of the samples are consistent with the expected stoichiometry. The XEDS data quantification results provide the percentage of the element with energy distribution in the matrix, and obtain the composition of the sample. From the XEDS spectra, it is observed that pure ZnAl$_2$O$_4$ samples mainly exhibit characteristic peaks corresponding to Zn, Al and O elements in Fig. 5(a), and the relative atomic percentage (At %) of Zn, Al and O...
are 14.27, 25.51 and 60.22%, respectively, as shown in inset of Fig. 5(a), representing the Zn:Al:O ratio as 1:2:4. No additional impurity peaks are observed, which confirmed the presence of Zn, Al and O elements only and shows the purity of the synthesized materials. Figure 5(b) confirms the existence of Cr and Mn elements in addition to Zn, Al and O element for Zn0.90Cr0.05Mn0.05Al2O4 samples. The quantitative atoms and weight percentages of the associated elements for Zn0.90Cr0.05Mn0.05Al2O4 samples from XEDS results as shown in inset of Fig. 5(b), reveals Zn, Cr, Mn, Al and O relative atomic percentage are 14.3, 1.16, 0.82, 27.46 and 56.27%, respectively. The Atomic% and Weight% of the constituent elements are found to be almost close to the nominal stoichiometry within the range of experimental error. XEDS results further validate the conclusion of XRD, indicating that Cr and Mn doped spinel ZnAl2O4 nanocrystalline were successfully prepared by hydrothermal method, and Cr and Mn ions successfully replaced Zn2+ and entered ZnAl2O4 matrix.

### 3.3 XPS analysis

The chemical state and chemical composition of Zn0.90Cr0.05Mn0.05Al2O4 nanoparticles were studied by XPS. Figures 6(a)–6(e) display the high-resolution XPS spectra of Zn2p, O1s, Al2p, Cr2p and Mn2p, respectively. Figure 6(a) shows the Zn2p XPS spectrum, and two obvious peaks at 1022 and 1045 eV are observed in the spectrum, which are assigned to Zn2p3/2 and Zn2p1/2. Figure 6(b) shows the Zn2p XPS spectrum can be fitted into two peaks at 1022 and 1045 eV, which are correspond to Zn elements in ZnAl2O4, which contributed to the excitation of photoelectron and Al-O bond. The peak at 1045 eV is related to the oxygen defect in ZnAl2O4 crystal, which indicates that there are some oxygen vacancies in the sample. While the peak at 1022 eV is assigned to the free chemisorbed oxygen on the surface of the sample or oxygen molecules in the pollutant surface of the hydrated oxides.35) As shown in Fig. 6(d), Mn2p XPS spectrum presents two obvious peaks at 642 and 653.4 eV, which are assigned to the binding energies of Mn2p3/2 and Mn2p1/2, respectively. The Mn2p3/2 XPS spectra can be fitted into two peaks at 641.7 and 644 eV, which are correspond to Mn ions of the octahedron and tetrahedron positions, respectively, while the Mn2p1/2 XPS spectra can be fitted into two peaks at 652.7 and 655.1 eV, which are attributed to Mn ion of the octahedron and tetrahedron positions, respectively. This implies the existence of Mn3+ and Mn2+ oxidation states,32,33)

Figure 6(e) shows Cr2p3/2 XPS spectra, there are two main peaks at 576.9 and 586.8 eV, which correspond to the binding energy between Cr 2p3/2 and satellite peaks, respectively. The Cr 2p3/2 XPS spectra can be fitted into three peaks at 573.5, 576.7 and 578.7 eV respectively. Therefore, the peak at 576.9 eV corresponds to the Cr ion of the octahedron, and the peak at 576.7 eV corresponds to the Cr ion of the tetrahedron. The results of Cr2p XPS show that Cr ions mainly occupy the octahedral site, and only a small number of Cr ions occupies the octahedral position in Zn0.90Cr0.05Mn0.05Al2O4 samples.

### 3.4 UV–vis analysis

Figure 7 show the UV–Vis absorption spectra of pure ZnAl2O4 and Zn0.95–xCr0.05Mn0.05Al2O4 (x = 0.01, 0.03, 0.05 and 0.07) samples recorded in range 250–850 nm. As shown in Fig. 7(a), pure ZnAl2O4 exhibit the absorption band in the wavelength range of 250–400 nm. Compared with pure ZnAl2O4 nanoparticles, the doped samples reveal stronger absorption bands in the ultraviolet and visible light regions, and the absorption edge reach 550 nm, indicating that doped samples are partially absorbed in the visible region. In addition, the absorption intensity of doped samples in the ultraviolet region significantly increased, and the light absorbing edge moving toward long wavelength direction with the increase of Mn concentration due to the interaction between Cr and Mn ions with ZnAl2O4, which contributed to the excitation of photo-generated carries.

The UV–Vis absorption spectra is consistent with the fitting results of Mn2p in XPS, at low concentration, the
proportion of Mn ion concentration at the tetrahedral position is relatively low. As the concentration of manganese increases, more Mn ions replace Zn ions at the tetrahedral position. As a result, the characteristic peak strength of Mn ions in tetrahedral position will further increase. The bandgap $E_g$ and absorption coefficient ($\alpha$) of the samples can be calculated according to Tauc formula: \[ \alpha(h\gamma - E_g)^2 = A(h\gamma - E_g), \]
where $\alpha$, $h\gamma$, $A$ and $E_g$ represent the absorption coefficient, the photon energy, constant dependent on the effective masses of electron–hole pairs and material refractive index and the band gap of materials, respectively. The bandgap $E_g$ of pure ZnAl$_2$O$_4$ and Zn$_{0.95-x}$Cr$_{0.05}$Mn$_x$Al$_2$O$_4$ samples ($x = 0.01, 0.03, 0.05$ and $0.07$) are $3.09$, $2.96$, $2.89$ and $2.41$ eV, respectively.

The band gap of the doped samples are smaller than that of pure ZnAl$_2$O$_4$ due to the quantum limiting effect. In addition, the band gap of the doped sample decreases gradually and exhibits red shift with the increase of Mn ion concentration. The redshift phenomenon is mainly caused by the sp-d interaction between the electrons in the band and the local electrons in the d-shell of the substituted cation, which makes the conduction band potential decrease and the valence band potential increase, thus leading to the decrease of the band gap, and which may also be attributed to the charge compensation due to the defect associated oxygen vacancy, with the further increase of Mn ion concentration, more Mn ions occupy interstitial sites, and the band gap decreases slightly.

### 3.5 FT-IR analysis

FT-IR spectra of pure ZnAl$_2$O$_4$ and Zn$_{0.95-x}$Cr$_{0.05}$Mn$_x$Al$_2$O$_4$ ($x = 0.01, 0.03, 0.05$ and $0.07$) samples recorded in the range of $400$–$4000$ cm$^{-1}$ as shown in Fig. 8. It can be observed that there are two sharp absorption peaks appear near $543$ and $678$ cm$^{-1}$, which belong to the characteristic peaks of spinel structure ZnAl$_2$O$_4$. Among them, the peak

![Fig. 6. XPS spectra of Zn$_{0.90}$Cr$_{0.05}$Mn$_{0.05}$Al$_2$O$_4$ nanoparticles (a) Zn 2p, (b) Al 2p, (c) O 1s, (d) Mn 2p and (e) Cr 2p.](image-url)
at 543 cm⁻¹ are corresponds to the symmetric bending vibration mode of the Zn–O bond in A position of the tetrahedron, while the peak at 678 cm⁻¹ are attributed to the symmetric stretching vibration mode of Al–O bond in B position of the octahedron, respectively.39),40) Further-
more, these results obtained in the analysis of FTIR is also an indication of spinel structure formation for the sample, which are in good agreement with the results concluded in the XRD analysis.41)

In addition, with the increase of Mn concentration, the intensity of FT-IR spectra for doped samples decreases slowly in the range of 500–700 cm⁻¹ region, and the peaks moving toward long wavelength direction and occur red shift. This is mainly because the cation distribution in ZnAl₂O₄ nanocrystals change significantly when Cr and Mn ions enter ZnAl₂O₄ lattice and replaced Zn ions and the particle size reach the nanoscale scale, some Al³⁺ enter the A position of tetrahedron, and few Cr and Mn ions enter the B position of octahedron, which lead to the generation of ions logarithm of super exchange between A and B,34) and introduce new interstitial structural defects in spinel structure. This red shift occurs due to the dopants of Cr and Mn which may introduce new structural defects, which is consistent with the UV–Vis analysis results.

### 3.6 PL analysis

Fig. 9 show PL spectra of pure ZnAl₂O₄ and Zn₀.₉₅₋ₓCrₓMnₓAl₂O₄ (x = 0.01, 0.03, 0.05 and 0.07) samples. It is evident that all samples exhibit three emis-
mion band centered at 406, 465, and 576 nm, respectively. Pure ZnAl₂O₄ show a broad blue emission band centered at 406 nm (3.05 eV), which can be attributed to excitonic NBE emission, and the emission energy is close to the band gap of ZnAl₂O₄ (3.08 eV), indicating the sample pos-

sesses better crystallization. The blue emission peak cen-
tered at 465 nm for the samples is associated with oxygen vacancy. The yellow and green light at 500–600 nm (2.07–2.48 eV) corresponds to the transition between Zn vacancy and Al vacancy level to O vacancy level.

Compared with pure ZnAl₂O₄, the blue peak of doped sample moves in the direction of long wave and occurs red shift, which may be due to the substitution of Zn ions by Cr and Mn ions, leading to slight lattice distortion, result-
ing in energy change during energy level transition. In addition, with the increase of Mn ion concentration, the PL intensity of doped samples decreases sharply and occurs quenching phenomenon, which suggests that the migration and separation of photogenerated electrons and holes in doped nanoparticles can be promoted after the introduction of Cr and Mn ions. This is mainly due to the decrease of the interstitial zinc defects in spinel structure after the replacement of Zn ions by Cr and Mn ions. The opto-electronics preferentially occupy the center of the trap caused by Cr and Mn, resulting in luminescence annihilation. The lower the fluorescence intensity of the samples correspond to the lower the recombination probability of photogenerated charge. The unique optical properties of Zn$_{0.95-x}$Cr$_{0.05}$Mn$_x$Al$_2$O$_4$ nanocrystals due to the recombination of free electron and hole pairs by the exciton–exciton disordered collision process. In addition, the photoluminescence peak is attributed to the recombination of electron–hole related to lattice vacancy and interstitial defects.

3.7 CIE analysis

The effects of Cr and Mn doping content on the chromaticity distribution and the light-emitting ability of the samples are evaluated by standard Commission Internationa l’Eclairage (CIE). Figure 10 show the CIE color coordinate diagram of pure ZnAl$_2$O$_4$ and Zn$_{0.95-x}$Cr$_{0.05}$Mn$_x$Al$_2$O$_4$ samples, the CIE coordinate (x, y) values obtained from the color calculator software are shown inset of Fig. 9. It can be seen from the chromaticity diagram (Fig. 10), the color coordinates are located in green-blue region, the chromaticity distribution of the sample can be controlled by controlling the doping concentration of the sample, and the peak decreases regularly with the increase of the doping concentration, demonstrating Zn$_{0.95-x}$Cr$_{0.05}$Mn$_x$Al$_2$O$_4$ nanoparticles exhibit excellent light-emitting ability.

4. Conclusion

(1) Pure ZnAl$_2$O$_4$ and co-doped Zn$_{0.95-x}$Cr$_{0.05}$Mn$_x$Al$_2$O$_4$ (x = 0.01, 0.03, 0.05 and 0.07) nanoparticles were obtained via simple hydrothermal method and heat treatment technology, the samples prepared by this method maintain single-phase cubic spinel structure with good crystallization. The average crystallite size decrease and the lattice parameters increase as Mn doped concentration increase.

(2) The morphology of all the samples exhibit irregular spherical or ellipsoid particles with small particle size and good dispersion. Cr and Mn ions are successfully substituted for the lattice site of Zn$^{2+}$ to generate ZnAl$_2$O$_4$ nanocrystals and mainly occupy the tetrahedral sites of the doped samples.

(3) Cr and Mn co-doped samples possess excellent visible light absorption ability, and the band gap of doped samples decrease with the increase of Mn ion concentration and occur red shift. PL spectra occur luminescence quenching phenomenon and FT-IR spectra occur red shift for doped samples. CIE indicate that the luminescent color can be adjusted by controlling Mn doping concentration.

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