Optical properties of Cr doped ZnAl₂O₄ nanoparticles with Spinel structure synthesized by hydrothermal method

Huang Shang-Pan¹ 2, Wei Zhi-Qiang¹ 2, Wu Xiao-Juan¹ 2 and Shi Ji-Wen¹ 2

¹State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Lanzhou University of Technology, Lanzhou 730050, People’s Republic of China
²School of Science, Lanzhou University of Technology, Lanzhou 730050, People’s Republic of China

E-mail: zqwei7411@163.com

Keywords: ZnAl₂O₄, chromium doped, microstructure, optical properties

Abstract

Zn₁₋ₓCrₓAl₂O₄ (x = 0, 0.01, 0.03, 0.05 and 0.07) nanoparticles were synthesized by hydrothermal method and heat treatment technology, and the effects of Chromium doping ratios on the microstructure, morphology, element distribution, 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). The experimental results show that Zn₁₋ₓCrₓAl₂O₄ nanoparticles possess cubic spinel structure without other impurity phases. The average crystallite size decrease and the lattice parameter increase with the increase of Cr doping concentration. The morphology of the samples exhibits irregular spherical or ellipsoid particles with uniform particle size. XEDS spectra display Cr³⁺ successfully used as doping agent replaced Zn²⁺ and entered ZnAl₂O₄ matrix. XPS spectra demonstrate that the doped Cr ions mainly occupy the tetrahedral sites in Zn₁₋₀.95Cr₀.05Al₂O₄ sample. UV–vis spectra indicate the band gap of the doped sample decrease and exhibit red shift with the increase of Cr ion concentration. The intensity of FT-IR spectra for Zn₁₋ₓCrₓAl₂O₄ samples decreases slowly and occurs red shift. PL spectra show the intensity decrease and occur luminescence quenching phenomenon for Cr doped sample.

1. Introduction

Spinel structure metal-oxide (AB₂O₄) is a kind of important functional semiconductor materials, which have attracted extensive attention due to its unique crystal structure, special properties and broad application prospect in the fields, such as catalysts, catalytic carriers, high-temperature ceramics, optical materials, sensors and dielectric materials [1–7], etc. In the formula AB₂O₄, A represents the tetrahedral position occupied by bivalent metal cations, and the tetrahedral gap formed by four oxygen ions, while B position represents the octahedral position occupied by the trivalent metal cations, and the octahedral void formed by six oxygen ions [8–10]. According to the metal cation distribution, the general chemical formula of spinel structure can be written as (A₁₋ₓBₓ)(AᵥB₄₋ᵥ)O₄, where (,) represents tetrahedral position, [ ] represents octahedral position, and x is the inversion coefficient. When x = 0, AB₂O₄ is orthospinel structure; x = 1, AB₂O₄ is anti-spinel structure, while 0 < x < 1, AB₂O₄ is the mixed spinel structure [11–13].

Among the spinel structure metal-oxide, ZnAl₂O₄ belonging to Fd3m space group with cubic structure and wide band gap energy (3.8 eV), ZnAl₂O₄ have attracted much attention due to their high temperature stability, high mechanical strength, low surface acidity, good cationic dispersion, excellent optical and dielectric properties [14–16]. The crystal structure and band structure of metal oxide semiconductors can be adjusted by modification of precious metals, composite with metal oxide semiconductor or carbon materials, metal ion doping and metal ion doping and synthesis of nano semiconductor materials [17–20]. As the acceptor or donor, the hole or electron is used to regulate the carrier type and concentration of the carrier, thus effectively
controlling the electrical, magnetic and optical properties of new semiconductor materials [21–24]. In recent years, ZnAl₂O₄ was selected as the semiconductor matrix, and its physical properties were adjusted through transition metal ion doping to improve the added value of spinel structure nanometer semiconductor materials [25, 26]. For instance, Zhu et al prepared Ag-ZnAl₂O₄ nanorods photocatalyst by hydrothermal method, because the rod-like structure with porous and has a high specific surface area, found that the photocatalytic activity of ag-supported ZnAl₂O₄ to gas-phase toluene was higher than that of other prepared samples and commercial P25 [27]. Qin et al reported Er³⁺ doped ZnO-ZnAl₂O₄ polyphase oxide prepared by co-precipitation method, compared with undoped ZnO-ZnAl₂O₄, the ultraviolet catalytic degradation activity of methyl orange was enhanced [28]. Wu, etc synthesized spinel structure Zn₁₋ₓNiₓAl₂O₄ nanocrystalline by sol-gel method, found the band gap decreases of the samples with the increase of Ni concentration due to the introduction of impurity level between the conduction band and valence band, and occurs sparked the photoluminescence quenching phenomenon [29]. Anand et al found that Ni doped ZnAl₂O₄ nanoparticles possess superparamagnetic, while undoped ZnAl₂O₄ possess diamagnetism [30]. Wu, etc reported the average crystallite size of Co-doped ZnAl₂O₄ nanoparticles decrease with the increase of Co doping concentration, and the PL spectra exhibit red-shift [31].

The crystal structure and band structure of semiconductor have been studied by controlling the preparation process, changing the doped elements and doping amount, and the physical properties of spinel structure metal-oxide are closely related to the synthesis route, annealing temperature and impurity content [32–34]. Compared with other traditional methods, hydrothermal method possesses more advantages due to its low expensive, the interaction of solvent and reactants at the molecular level, and generates new substances in the aqueous solution under high temperature and high-pressure condition, in addition, the products synthesized by hydrothermal method exhibit single morphology, uniform particle size and good dispersion [9, 24]. Many studies have been made on the properties of transition metal-doped spinel structure metal oxides, however, The purity of ZnAl₂O₄ nanoparticles prepared by hydrothermal method is not high, and the intermediate product needs further heat treatment, to our knowledge, few studies have been performed on the structural properties of Cr doped ZnAl₂O₄ nanoparticles and its correlation with optical properties.

In this paper, Zn₁₋ₓCrₓAl₂O₄ (x = 0, 0.01, 0.03, 0.05 and 0.07) were synthesized by hydrothermal method and heat treatment technology, and the effects of Cr-doping content on the crystal structure and optical properties of the samples were characterized by x-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), energy dispersive x-ray spectroscopy (EDX), fourier transform infrared spectroscopy (FTIR), x-ray photoemission spectroscopy (XPS), ultraviolet-visible (UV–vis) spectroscopy and photoluminescence spectra (PL), respectively.

2. Experimental

2.1. Preparation of Zn₁₋ₓCrₓAl₂O₄ nanoparticles

All chemicals used in this work were of analytical grade and were used without any further purification. Zn₁₋ₓCrₓAl₂O₄ nanopowders were prepared via hydrothermal method, as shown in figure 1. In a typical procedure, according to the chemical formula Zn₁₋ₓCrₓAl₂O₄ (x = 0, 0.01, 0.03, 0.05 and 0.07) and the molar ratio of metal cations Zn:Cr:Al = (1 − x):x:2, weighed stoichiometric amounts of Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and CrCl₃·6H₂O used as raw materials, dissolved in distilled water to obtain mixed metal salt.
solution, and evenly dispersed by magnetic stirring at room temperature. Meanwhile, dropped NaOH solution into the above solution to adjust the pH value of the mixed solution to be 12, subsequently a certain amount of CTAB slowly added to the above mixed solution, all the above processes are carried out under constant magnetic stirring. Then the resultant mixture was transferred to and sealed a 100 ml Teflon-lined stainless-steel autoclave and kept at 200 °C for 24 h. After the reaction was completed, the autoclave was naturally cooled down to room temperature. Thereafter, the resulting precipitate was separated centrifugally and washed several times with distilled water and absolute alcohol to remove excess surfactants and impurities, respectively, the precipitate was dried in a vacuum drying oven at 60 °C for 12 h to obtain the precursors. Finally, the Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ sample can be obtained by heat treatment the precursors at sintering temperature of 700 °C for 6 h.

2.2. Characterization

The crystal phases of the samples were identified by x-ray powder diffraction (Rigaku corporation, Japan, D/Max-2400) using Cu Kα radiation ($\lambda = 0.15406$ nm) operating at 40 kV and 30 mA in the diffraction angle range of 20–80° with scanning rate 0.005 °s$^{-1}$ and step size 0.02°. The morphology and microstructure were characterized by scanning electron microscope (SEM, JEOL JSM-6701F) and high-resolution transmission electron microscopy (HRTEM, JEM-2010). The chemical composition analysis of the products was measured by x-ray energy dispersive spectroscopy (XEDS). The optical absorption and bandgap energy of the samples were characterized by ultraviolet-visible (UV–vis) spectrophotometer (PERSEE TU-1901) using BaSO$_4$ as reference. Fourier transform infrared spectroscopy (FT-IR) analysis were performed by Nexus 670 FT-IR spectrophotometer in the range of 4000 – 500 cm$^{-1}$ using KBr powder. The composition and chemical states of elements were studied by x-ray photoelectron spectroscopy (XPS) measurement was carried out on a PHI-5702 multi-functional x-ray photoelectron spectrometer. The photoluminescence (PL) spectra were recorded by PerkinElmer spectrophotometer (LS-55) with an excitation wavelength of 320 nm.

3. Results and discussion

3.1. Structural characterization

Figure 2 show the XRD patterns of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ (x = 0, 0.01, 0.03, 0.05 and 0.07) samples. It is clearly observed from figure 2 that the diffraction peaks of pure ZnAl$_2$O$_4$ at 2θ = 31.5°, 36.8°, 44.9°, 47.3°, 56.2°, 58.1°, 65.3°, 73.6° and 77.3° are well indexed to (220), (311), (400), (331), (422), (511), (440), (620) and (533) crystal planes of single-phase ZnAl$_2$O$_4$ cubic spinel structure with lattice parameters $a = b = c = 0.8048$ nm, which is in accordance with that of the standard spectrum (JCPDS Card No. 05-0669). In addition, there is no extra diffraction peaks of other impurities such as Cr clusters or Cr oxides are detected within the detection limit of XRD, ZnAl$_2$O$_4$ is the only phase detected in all the heated samples. which indicating that all Cr ions are successfully incorporated into Zn$^{2+}$ ions sites without changing the parent ZnAl$_2$O$_4$ structure, and the purity of the product is relatively high.

The crystallite size of the samples is calculated using the most intense diffraction peak (311) by means of Scherrer formula: $D = \frac{K \lambda}{\beta \cos \theta}$, where $D$ is the crystallite size, $K = 0.9$ is the Scherrer constant, $\lambda = 1.54056$ Å is
the x-ray wavelength, \(B\) is the corrected full width at maximum and \(\theta\) is the diffraction angle. The average crystallite size of the samples was summarized in table 1. It is clear that the crystallite size gradually decreases with the increase of Cr doping concentration, indicating that Cr doping have a regulating effect on the crystallite size.

The interplanar crystal spacing and the lattice constants of the sample can be obtained according to the crystalographic calculation formula and the Bragg formula, the diffraction angle, lattice parameters, interplanar crystal spacing and crystallite size of \((311)\) peak for \(\text{Zn}_{1-x}\text{Cr}_x\text{Al}_2\text{O}_4\) samples as shown in table 1. It is obviously that the diffraction angle of the \((311)\) peak for doped samples is slightly shifted towards lower angle with the increase of Cr doping content, the lattice parameters and interplanar crystal spacing of doped samples decrease with Cr doped content increase. The lattice constant is distorted, and exhibit lattice expansion, which may be attributed to the incorporation of Cr ions are doped into \(\text{ZnAl}_2\text{O}_4\) host lattice, and ionic radius of \(\text{Cr}^{3+}\) (0.63 Å) smaller than \(\text{Zn}^{2+}\) (0.74 Å), which eventually led to the lattice distortion. These results show that the lattice parameters and particle size of the sample can be controlled by doping, and then the microstructure and physical properties of the sample can be controlled and adjusted.

### Table 1. XRD results of \(\text{Zn}_{1-x}\text{Cr}_x\text{Al}_2\text{O}_4\) samples.

| Sample | \(2\theta\) (°) | \(d_{hkl}\)/nm | \(a = b = c\) (nm) | \(D\)/nm |
|--------|----------------|----------------|--------------------|----------|
| \(x = 0\) | 36.88 | 0.2435 | 0.8076 | 24 |
| \(x = 0.01\) | 36.89 | 0.2434 | 0.8074 | 22 |
| \(x = 0.03\) | 36.85 | 0.2437 | 0.8082 | 21 |
| \(x = 0.05\) | 36.81 | 0.2439 | 0.8091 | 20 |
| \(x = 0.07\) | 36.79 | 0.2440 | 0.8095 | 21 |

3.2. Morphological studies

The typical SEM images of pure \(\text{ZnAl}_2\text{O}_4\) and \(\text{Zn}_{0.95}\text{Cr}_{0.05}\text{Al}_2\text{O}_4\) sample as shown in figure 3. It is obviously that the morphology of pure \(\text{ZnAl}_2\text{O}_4\) is mainly irregular spherical or ellipsoid particles with average particle size below 50 nm. Due to the existence of van der Waals force, coulomb force or chemical bond cooperation between nanoparticles, there is a certain degree of agglomeration phenomenon. Compared with pure samples, the morphologies of pure \(\text{ZnAl}_2\text{O}_4\) and doped \(\text{ZnAl}_2\text{O}_4\) samples are basically the same, but Cr doped sample show a tendency to possess smaller particle size and more uniform size distribution, and the doped ions do not have significant effect on the morphology of the products.

The microstructure and morphology of the as-prepared samples were performed by HRTEM, figure 4(a) shows a representative HRTEM images of \(\text{Zn}_{0.95}\text{Cr}_{0.05}\text{Al}_2\text{O}_4\), it can be seen that the morphology of \(\text{Zn}_{0.95}\text{Cr}_{0.05}\text{Al}_2\text{O}_4\) sample is mainly irregular ellipsoid particles with rough surface and irregular edges. Figure 4(b) represents the local magnification of \(\text{Zn}_{0.95}\text{Cr}_{0.05}\text{Al}_2\text{O}_4\) sample, it clearly find the orderly and flawless crystal plane stripes, and the interplanar spacing about 0.284 nm, which corresponds to the \((311)\) crystal planes of cubic spinel structure \(\text{ZnAl}_2\text{O}_4\), indicating that \(\text{Zn}_{0.95}\text{Cr}_{0.05}\text{Al}_2\text{O}_4\) are well-crystallized and grew selectively along the \((311)\) crystal planes, which is consistent with the XRD results.
The selected area electron diffraction (SAED) pattern of Zn$_{0.95}$Cr$_{0.05}$Al$_2$O$_4$ as shown in figure 4(c), the SAED pattern of the samples consists of a series of regular concentric rings with different clear and obvious radius due to the sample possess polycrystalline structure. The polycrystalline diffraction rings from inside to outside correspond to the crystal plane of ZnAl$_2$O$_4$ (220), (311), (400), (331), (422), (511) and (440), respectively. The results of SAED and HRTEM further indicated that the obtained samples with spinel structure, which further indicating that all Cr$^{3+}$ entered ZnAl$_2$O$_4$ lattice and replaced Zn$^{2+}$, which is consistent with the XRD analysis results.

Figure 4(d) is the particle size distribution diagram of Zn$_{0.95}$Cr$_{0.05}$Al$_2$O$_4$ nanoparticles, it can be seen from the figure that the particle size distribution is relatively uniform, mainly distributed in the range of 10–50 nm, and the average particle size is about 25 nm.

Figure 5 shows the XEDS spectra of pure ZnAl$_2$O$_4$ and Zn$_{0.95}$Cr$_{0.05}$Al$_2$O$_4$ samples. 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 (figure 5(a)), and the atomic percentage (At %) of Zn/Al/O is found to be 14.27 / 25.51 / 60.22%, respectively, as shown in inset of figure 5(a). Figure 5(b) confirms the existence of Cr elements in addition to Zn, Al and O element for Zn$_{0.95}$Cr$_{0.05}$Al$_2$O$_4$ sample, while no Cr element was found in the spectrum of pure ZnAl$_2$O$_4$. The quantitative atoms and weight percentages of the associated elements for Zn$_{0.95}$Cr$_{0.05}$Al$_2$O$_4$ sample from XEDS results as shown in inset of figure 5(b), reveals Zn/Al/O atomic percentage is 9.24 / 25.74 / 61.23%, 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. Which also confirmed the presence of Zn, Al, O and Cr elements only and shows the purity of the synthesized materials. XEDS results further verified the conclusion of XRD, indicating that Cr-doped spinel ZnAl$_2$O$_4$ nanocrystalline were successfully prepared by hydrothermal method, and Cr$^{3+}$ successfully used as doping agent replaced Zn$^{2+}$ and entered ZnAl$_2$O$_4$ matrix.
3.3. XPS analysis

In order to further determine the composition and element chemical states of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ samples, the sample was analyzed by X-ray photoelectron spectroscopy (XPS). Figure 6(a) shows the full XPS spectra, revealing the existence of Zn, Al, Cr, O, and C elements in Zn$_{0.05}$Cr$_{0.05}$Al$_2$O$_4$ sample. Figures 6(b)–(f) shows illustrates the high resolution XPS spectra of Zn 2p, Al 2p, O 1s, Cr 2p and C 1s, respectively. As seen from figure 6(b), the Zn 2p XPS spectrum shows two sharp peaks at 1022 and 1045 eV correspond to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$, respectively, which indicates that Zn exists in the combination state of +2 valence. The Al 2p peak of the sample appearing around 74.5 eV in figure 6(c). The C 1s XPS spectrum (figure 6(f)) presents the peak at 284.8 eV is attributed to the hydrogen reaction process without washing clean organic carbon. The O 1s peak about 532 eV shown in figure 6(d) can be fitted into three peaks at about 531.1, 532.5 and 533.7 eV respectively. The main peaks centered at 531.1 eV are attributed to the contribution of oxygen in the crystal lattice, which is the energy spectrum of Zn-O and Al-O bonds in ZnAl$_2$O$_4$ lattice. The peak at 532.5 eV is related to the oxygen defect in ZnAl$_2$O$_4$ crystal, which indicates that there are some oxygen vacancies in the sample. While the peak at 533.7 eV is caused by free oxygen on the surface of the sample or oxygen molecules in the pollutant surface of the hydrated oxide (such as adsorbed pollutants, chemical adsorbents and –CO$_3$, H$_2$O and O$_2$, etc.) [35]. Figure 6(e) is Cr 2p$_{3/2}$ XPS spectra, there are two main peaks appeared around 577.1 and 588.5eV, which correspond to the binding energy between Cr 2p$_{3/2}$ and satellite peaks, respectively. The Cr 2p$_{3/2}$ XPS spectra can be fitted into three peaks at 576.9, 577.3 and 588.5 eV respectively. Therefore, the peak at 576.9 eV corresponds to the Cr ion of the octahedron, and the peak at 577.3 eV corresponds to the Cr ion of the tetrahedron. The Cr 2p XPS results clearly show that the Cr ions mainly occupied the tetrahedral site, while only a small number of Cr ions occupy the octahedral position in Zn$_{0.95}$Cr$_{0.05}$Al$_2$O$_4$ sample.

3.4. UV–vis analysis

The UV–vis absorption spectra of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ samples recorded in range 250–850 nm as depicted in figure 7(a), pure ZnAl$_2$O$_4$ exhibit the absorption peak in the wavelength range of 300–400 nm. Compared to pure ZnAl$_2$O$_4$, doped Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ samples exhibit a broad absorption peak near 500 nm, which is the characteristic peak of Cr$^{3+}$ in the tetrahedral sites [36], this peak corresponds to the transition from 1A$_2$(F) to 2A$_g$(G) of 3d electron of Cr ion in the field of tetragonal crystal, and this peak causes the sample to appear green-blue [37]. With the increase of Cr concentration, the intensity of the absorption peak gradually increased. The UV–vis absorption spectra are consistent with the fitting results of Cr 2p in XPS, at low concentration, the proportion of Cr ion concentration at the tetrahedral position is relatively low. With the increase of Cr ion concentration, more Cr ions replace Zn ions at the tetrahedral position. Therefore, this will lead to further increase of characteristic peak strength of Cr ion at the tetrahedral position.

The band gap Eg of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ (x = 0, 0.01, 0.03, 0.05 and 0.07) samples can be calculated according to Tauc formula [38]: (αhv)$^{2} = A(hv – E_g)$ The relationship curve between (αhv)$^{2}$ and hv as shown in figure 7(b) The band gap Eg of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ (x = 0, 0.01, 0.03, 0.05 and 0.07) samples are 3.13 eV, 2.99 eV, 2.89 eV and 2.97 eV, respectively. The band gap of pure ZnAl$_2$O$_4$ (3.23 eV) is smaller than that of corresponding block ZnAl$_2$O$_4$ (3.8 eV) due to the quantum limiting effect. In addition, with the increase of Cr ion concentration, the band gap of the doped sample decrease and exhibit red shift. The phenomenon of redshift is mainly due to 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. Furthermore, the radius of Cr ion (0.063 nm) is less than that of Zn ion (0.074 nm), the band gap of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ samples from 0 to 7% gradually decreases with the increase of Cr ion concentration.
3.5. FT-IR analysis

FT-IR spectra of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ ($x = 0, 0.01, 0.03, 0.05$ and $0.07$) samples recorded in the range of 400–4000 cm$^{-1}$ as shown in figure 8. It can be seen that two obvious absorption peaks appear near 3448 and 1635 cm$^{-1}$ for all samples, FT-IR spectra of pure and doped ZnAl$_2$O$_4$ samples are basically the same. The wide absorption band near 3448.3 cm$^{-1}$ corresponds to the stretching vibration of O-H group, and the band at 1635 cm$^{-1}$ can be assigned to the bending vibration of H-O-H group, both of which are related to water molecules on the surface of the sample [26]. In addition, there are three sharp absorption peaks appear near 490 cm$^{-1}$, 553 and 689 cm$^{-1}$, which belong to the characteristic peaks of spinel structure ZnAl$_2$O$_4$. Among them, the peak at 553 cm$^{-1}$ are corresponds to the Zn–O bond asymmetric stretching vibration mode of the tetrahedron positions, while the peak at 490 and 689 cm$^{-1}$ are attributed to the Al-O bond asymmetric stretching vibration and the bending vibration mode of the octahedron positions, respectively [25]. In addition, with the increase of Cr concentration, the intensity of FT-IR spectra for Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ samples decreases slowly in the range of 400–700 cm$^{-1}$ region.

Figure 6. XPS spectrogram of Zn$_{0.95}$Cu$_{0.05}$Al$_2$O$_4$: (a) survey spectrum, (b) Zn 2p, (c) Al 2p, (d) O 1s, (e) Cr 2p and (f) C 1s.
and the peaks moving toward long wavelength direction and occurs red shift. This is mainly due to the cation distribution in ZnAl$_2$O$_4$ nanocrystals changes significantly when Cr ions entered ZnAl$_2$O$_4$ lattice and replaced Zn ions and the particle size reaches the nanoscale scale, some Al$^{3+}$ enters the A position of tetrahedron, and Cr$^{3+}$ enters the B position of octahedron, which leads to the generation of ion logarithm of super exchange between A and B [10], and introduce new interstitial structural defects in spinel structure, the new introduced structural defects will lead to redshift of the spectra, which is consistent with the UV–vis analysis results.

3.6. PL analysis

Figure 9 shows PL spectra of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ $(x = 0, 0.01, 0.03, 0.05$ and $0.07)$ samples with excitation wavelength of 300 nm at room temperature. It was observed that Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ samples exhibited three emission spectra at 406, 465, and 576 nm, respectively. Pure ZnAl$_2$O$_4$ exhibit 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 ZnAl$_2$O$_4$ (3.08 eV), indicating the sample possesses better crystallization. the blue emission peak centered at 465 nm for the samples is associated with oxygen vacancy. Compared with pure ZnAl$_2$O$_4$, 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$^{2+}$ ions by Cr$^{3+}$ ions in ZnAl$_2$O$_4$ lattice will introduce new impurity levels mainly between O vacancy level and valence band, leading to slight lattice distortion, resulting in energy change during energy level transition. In addition, the photoluminescence peak is attributed to the recombination of electron-hole related to intrinsic defects, the PL intensity of the doped sample decrease sharply and occur quenching phenomenon with the increase of Cr ion concentration. This is mainly due to the decrease of zinc gap and the increase of Cr$^{3+}$ concentration after the replacement of Zn$^{2+}$ by Cr$^{3+}$, the octahedral and tetrahedral gap.
formed by O atom accumulation are occupied by metal ions respectively, forming a compact structure, which is likely to form Zn, Al, O and other interstitial structural defects in spinel structure, photoelectron preferentially occupies the trap center caused by Cr$^{3+}$, leading to luminescence annihilation.

### 3.7. CIE analysis

Figure 10 shows the Commission International De l’Eclairage (CIE) chromaticity diagram of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ samples, which are calculated via fluorescence spectra under the excitation wave of 320 nm. The CIE coordinates values of Zn$_{1-x}$Cr$_x$Al$_2$O$_4$ ($x = 0, 0.01, 0.03, 0.05$ and $0.07$) nanoparticle are shown inset of figure 7, which are located in green-blue region. It can be seen from the chromaticity diagram, 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$_{1-x}$Cr$_x$Al$_2$O$_4$ nanoparticle exhibit excellent light-emitting ability.
4. Conclusion

Zn_{1−x}Cr_xAl_2O_4 nanoparticles with different doping ratios were successfully synthesized by hydrothermal method and heat treatment technology. The samples prepared by this method possess single phase cubic spinel structure, no other impurity phases were observed. The average crystallite size decrease and the lattice parameters increase with the increase of Cr doping concentration. The morphology of the samples exhibits irregular spherical or ellipsoidal particles with uniform particle size. XEDS spectra display Cr^{3+} successfully used as doping agent replaced Zn^{2+} and entered ZnAl_2O_4 matrix. XPS spectra demonstrate that the doped Cr ions mainly occupy the tetrahedral sites in Zn_{0.95}Cr_{0.05}Al_2O_4 sample. UV–vis spectra indicate with the increase of Cr concentration, the band gap of the doped sample decrease and exhibit red shift. The intensity of FT-IR spectra for Zn_{1−x}Cr_xAl_2O_4 samples decreases slowly in the range of 400–700 cm^{-1} and occurs red shift. PL spectra show the intensity decrease and occur quenching phenomenon for Cr doped sample. CIE indicate that the luminescent color can be adjusted by controlling Cr doping concentration.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51261015), Natural Science Foundation of Gansu Province, China (1308RJAZ238) and HongLiu First-Class Disciplines Development Program of Lanzhou University of Technology.

ORCID iDs

Huang Shang-Pan  ☞  https://orcid.org/0000-0002-7981-7632

References

[1] Xu Y, Fa P, Zhang B H, Gao J, Zhang J L and Wang X 2014 Mater. Lett. 123 142
[2] Joo O and Jung K 2003 B. Koram. Chem. Soc 28 86
[3] Ballarini A D, Bocanegra S A, Castro A A, Miguel S R and Scladza O A 2009 Catal. Lett. 129 293
[4] Bhavani P, Manikanand A, Paulraj P, Dinesh A, Durka M and Antony S A 2018 J. Nanosci. Nanotechnol. 18 4072
[5] Denisov I A, Volk Y V, Malarychev A M and Yumashev K V 2003 J. Appl. Phys. 93 3827
[6] Wu N, Huda A, Mohd S Z, Badariah B, Sahuqin D and Mohammad I 2013 T. Indian. Ceram. Soc 72 215
[7] Lucile C, Manuel G and Veronique I 2013 J. Mater. Chem. 15 419
[8] Sickafus K L, Wills J M and Grimes N W 2010 J. Am. Ceram. Soc 82 3279
[9] Zhu X L, Wei Z Q, Zhao W H, Zhang X D, Zhang L and Wang X 2018 J. Electron. Mater. 47 6428
[10] Zhu X L, Wei Z Q, Zhao W H, Zhang X D, Wu X J and Jiang H J 2018 Curr. Nanosci. 14 474
[11] Zhang L, Li J T, Zhao F and Gong G Z 2011 Chinese. Phys. B 20 412
[12] Cabello G, Lillo L, Caro C, Seguel M, Sandovàl C, Buono G E, Boris C A and Flores C M 2016 Mater. Res. Bull. 77 212
[13] Pathak N, Gupta S K, Sanjay K, Kadam R M and Natarajan V 2014 Dalton. T 43 9313
[14] Subhash Sand Kaushik P 2015 Mat. Sci. Eng: A 644 325
[15] Yue H Y, Fei W D and Wang L D 2008 J. Mater. Sci. 43 6233
[16] Mulwa W M, Dejene B F, Onani M O and Ouma C N M 2017 J. Lumin. 184 187
[17] Jiang J, He X, Du J, Pang X, Yang H and Wei Z 2018 Mater. Lett. 220 178
[18] Bi T T, Fang H Q, Jiang J L, He X X, Zhen X, Yang H, Wei Z Q and Jia Z F 2019 J. Alloy. Compd. 787 759
[19] Liang C, Liu Y, Li K, Wen J, Xing S, Ma Z and Wu Y 2017 Sep. Purif. Technol. 188 105
[20] Li J I, Wei Z Q, Ding M J, Ma L, Zhu X L and Liang H J 2019 J. Ceram. Soc. Jpn. 127 747
[21] Sun Z, Yao G, Liu M and Zheng S 2017 J. Taiwan. Inst. Chem. E 71 501
[22] Meena S, Renuka L, Anantharaju K S, Vidya Y S, Nagaswarupa H P, Prashanth S C and Nagabhushana H 2017 Mater. Today: Proceedings 4 I 1773
[23] Ahmed S A 2017 J. Mater. Sci-Mater. El. 28 3733
[24] Zhao W H, Wei Z Q, Zhang L, Wu X J and Wang X 2019 J. Electron. Mater. 48 6807
[25] Tsai T T, Fang Y S, Huang B and Pan B Y 2013 Ceram. Int. 39 3691
[26] Rapatically C, Kennedy I and Vijaya J 2014 Adv. Powder. Technol. 25 267
[27] Zhu Z, Zhao Q D, Li Y X, Li Y H, Sun C, Zhang G and Cao Y Q 2012 Chem. Eng. J. 203 43
[28] Qin Z Z, Liu W X and Li Z Z 2018 J. Mater. Sci-Mater. El. 29 8293
[29] Wu X J, Wei Z Q, Chen X J, Wang X, Yang H and Jiang J L 2014 J. Mater. Sci-Mater. El. 26 5761
[30] Anand G T, Kennedy I, Vijaya J, Kaviyaranjan K and Sukumar M 2015 Ceram. Int. 41 603
[31] Wu X J, Wei Z Q, Chen X J, Wang X, Yang H and Jiang J L 2017 Russ. J. Phys. Chem. A 91 2651
[32] Mathew T, Shiji N R, Sreekumar K, Rao B S and Cogniathil 2002 J. Catal. 210 405
[33] Basavaraj W, Priolkar K R, Goureit D, Sharma S K, Bessière A and Viana B 2013 Phys. Chem. Chem. Phys. 17 1790
[34] Basavaraj W, Sharma S, Bessière A, Viana B, Goureit D and Priolkar K 2013 J. Phys. D: Appl. Phys. 46 375041p1
[35] Kumar V, Swart H C, Ntwaeaborwa O M, Kroon R E, Terblans J J, Shaat S K K and Duvenhage M M 2013 Mater. Lett. 101 60
[36] Wu X J, Wei Z Q, Chen X J, Wang X, Yang H and Jiang J L 2015 J. Mater. Sci-Mater. El. 26 6606
[37] Janos R, Muntean E, Păcurariu C, Lază R, Bandas C and Delineescu G 2017 Dyes. Pigments 142 31
[38] Zhao W H, Wei Z Q, Zhang L, Wu X J and Wang X 2018 Mat. Sci. Semicon. Proc 88 173