Complexation Mechanism and Luminescence Properties of Spinel Nano-Zinc Aluminate Synthesized by Polyacrylamide Gel Postprint

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Abstract

Using an improved polyacrylamide gel method, ZnAl2O4 nanoparticles with approximately spherical morphology and uniform particle size were prepared, and three ZnAlO samples with different Zn/Al molar ratios were synthesized. XRD results demonstrate that when the Zn/Al molar ratio is 1:1.8 and 1:2, the samples obtained by calcining the dried gel at 900°C are pure-phase ZnAl2O4 powders. SEM results reveal that for the sample prepared with a Zn/Al molar ratio of 1:2, the particle size increases with rising calcination temperature, and severe agglomeration occurs at 900°C. Photoluminescence spectroscopy analysis indicates that a blue emission peak at 469 nm appears under an excitation wavelength of 352 nm. Based on these experimental results, the complexation mechanism and luminescence mechanism were investigated.

Full Text

Synthesis of Spinel Nano-ZnAl2O4 by Polyacrylamide Gel Method and Its Chelating Mechanism and Photoluminescence Performance

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Abstract

Spherical $ZnAl_2O_4$ nanoparticles with uniform size distribution were synthesized by a modified polyacrylamide gel method, and three ZnAlO samples with different Zn to Al molar ratios were prepared. X-ray diffraction analysis shows that pure-phase $ZnAl_2O_4$ powders can be obtained after calcination at 900°C for the two xerogel samples with mole ratios of Zn^{2+}:Al^{3+} = 1:1.8 and 1:2. Scanning electron microscope images reveal that the particle size of the sample with a mole ratio of 1:2 increases with increasing calcination temperature, with significant agglomeration observed at 900°C. The photoluminescence emission spectrum for $ZnAl_2O_4$ nanoparticles detected at λ = 352 nm shows a blue emission peak located at 469 nm. Finally, the chelating mechanism and luminescence mechanism of $ZnAl_2O_4$ nanoparticles are discussed based on the experimental results.

Keywords: inorganic non-metallic materials, polyacrylamide gel method, $ZnAl_2O_4$, blue-light emission, chelating mechanism

Introduction

Spinel-type zinc aluminate ($ZnAl_2O_4$) exhibits excellent thermal and chemical stability along with high quantum yield, making it promising for applications in catalysis, ceramics, and luminescence [1-3]. Material properties, particularly luminescence performance, are closely related to morphology, purity, and defects, while nanoscale materials often exhibit superior or entirely new properties compared to bulk materials [4]. However, preparing nanoscale $ZnAl_2O_4$ is challenging because $ZnAl_2O_4$ tends to agglomerate during crystalline transformation. The primary solution involves reducing synthesis temperature to minimize interparticle contact. Various methods have been reported for synthesizing $ZnAl_2O_4$ nanoparticles, including microwave synthesis [5], sol-gel methods [3,6], co-precipitation [7,8], and hydrothermal methods [9,10]. Among these, the sol-gel method offers advantages of simple processing, low synthesis temperature, and high crystalline quality. Ragupathi et al. [11] synthesized nanoscale $ZnAl_2O_4$ with excellent blue-green emission, while Silva et al. [12] observed strong blue emission at 488 nm in $ZnAl_2O_4$ nanoparticles prepared by sol-gel method.

Nevertheless, conventional sol-gel synthesis of $ZnAl_2O_4$ nanoparticles requires long processing times, necessitating the development of alternative preparation methods. The polyacrylamide gel method can effectively prevent interparticle agglomeration and offers significant advantages for preparing various nanoscale oxides, particularly magnetic nanoxides [13-15]. In this approach, a chelating agent first complexes metal ions in solution to form relatively stable complexes. Subsequently, acrylamide and methylenebisacrylamide monomers are added to the precursor solution along with a polymerization initiator. Triggered by temperature, the polymerization reaction rapidly increases gelation speed, yielding a gel within minutes to tens of minutes [16]. Additionally, during gel formation, the polymerization of acrylamide and methylenebisacrylamide creates a polymer network skeleton that provides growth space for chelates while confining them within the polymer network. Through drying and sintering processes, nanoscale particles with regular morphology, near-spherical shape, and uniform particle size can be obtained.

In this work, $ZnAl_2O_4$ nanoparticles were prepared using $Zn(NO_3)_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ as raw materials via the polyacrylamide gel method. By varying the Zn/Al ratio and using citric acid as a chelating agent, the chelating mechanism of citric acid with Zn and Al metal ions was investigated, and the fluorescence properties and luminescence mechanism of $ZnAl_2O_4$ nanoparticles were studied.

1.1 Sample Synthesis

Three samples were prepared with Zn:Al molar ratios of 1:1, 1:1.8, and 1:2 by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ in 15 mL deionized water, designated as S1, S2, and S3 respectively. After complete dissolution of the salts, citric acid was added at a molar ratio of 1.5:1 to the total cations to ensure full complexation with both metal ions. Subsequently, 20 g of glucose was added to prevent severe collapse of the gel during drying, followed by acrylamide monomer at a molar ratio of 9:1 to the cations. Once the solution became clear, methylenebisacrylamide was quickly added at a molar ratio of 1:5 to the acrylamide. Magnetic stirring was applied at each step to ensure complete dissolution. After the solution became homogeneous and clear, ammonia water was used to adjust the pH to approximately 3. Finally, the mixed solution was heated to 80°C to induce thermal polymerization, forming a white gel within several minutes. The obtained white gel was dried in an oven at 120°C for 24 h to form a xerogel, which was then ground into fine powder and sintered in a box furnace at various temperatures for 5 h to obtain the final products.

1.2 Sample Characterization

The phase structure of powder samples calcined at different temperatures was analyzed using a DX-2700 X-ray diffractometer (XRD). Thermal gravimetric (TG) and differential thermal analysis (DTA) of the xerogel were performed using an SDT Q600 simultaneous thermal analyzer at a heating rate of 10°C/min. Surface morphology of samples calcined at different temperatures was observed using a KYKY-EM3900 scanning electron microscope (SEM). Fourier transform infrared (FTIR) spectra were recorded using a Bruker IFS 66v/S spectrometer in the range of 400-4000 cm^{-1}. Photoluminescence spectra were measured using an RF-5301PC fluorescence spectrophotometer.

Results and Discussion

2.1 Effect of Different Zn/Al Ratios on Products

Figure 1a [Figure 1: see original paper] shows XRD patterns of ZnAlO xerogel samples with Zn:Al ratios of 1:1 (S-0) and 1:1.8 (S-01) calcined at 900°C. The product at Zn:Al = 1:1 consists of mixed phases: $ZnAl_2O_4$ (JCPDS No. 05-0669) and ZnO (JCPDS No. 36-1451), while pure $ZnAl_2O_4$ phase appears at Zn:Al = 1:1.8. Figure 1b presents XRD patterns of ZnAlO xerogel with Zn:Al = 1:2 calcined at 500, 600, 700, 800, and 900°C. The sample sintered at 500°C is amorphous, showing no characteristic peaks of spinel $ZnAl_2O_4$. As the temperature increases to 600°C, characteristic $ZnAl_2O_4$ peaks emerge. With further increases in calcination temperature, the diffraction peaks gradually intensify, indicating improved crystallinity. Using Jade 5.0 software, the full width at half maximum (FWHM) of the (311) plane for samples calcined at 600-900°C were determined to be 0.380, 0.444, 0.399, and 0.361 respectively. The FWHM initially increases then decreases with temperature, likely due to residual organic matter at 600°C causing peak broadening.

To obtain crystallite size, unit cell parameters, and volume, Jade 5.0 software was used to calculate interplanar spacing d for peaks (220), (311), (422), (511), and (440), with results listed in Table 1 . Unit cell parameters were calculated using Equation (1) and averaged across different diffraction peaks, with results also presented in Table 1.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

where d is interplanar spacing, h, k, l are Miller indices, and a is lattice constant. Table 1 shows that unit cell parameters decrease with increasing temperature, with an anomaly at 900°C, possibly due to high-temperature lattice expansion [17] or experimental error. To assess reliability, standard deviation was calculated using Equation (2).

$$\delta_a = \sqrt{\frac{\sum (a_i - \bar{a})^2}{n - 1}} \quad (2)$$

where δ is standard deviation, ā is average cell parameter, and n is the number of a values. The standard deviations are on the order of 10^{-3}, indicating reliable cell parameter calculations from different diffraction peaks.

Crystallite size was estimated using the Scherrer equation (3):

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where k is shape factor (0.9), D is crystallite size, λ is X-ray wavelength (0.15406 nm), is diffraction angle for peaks (220), (311), (422), (511), (440), and β

is corresponding FWHM. Average crystallite sizes are listed in Table 1, showing continuous increase with sintering temperature, with an anomaly at 700°C. Combined with cell parameter results, this suggests that changes in unit cell parameters during high-temperature sintering affect crystallite size.

2.2 Chelating Mechanism

As shown in Figure 1, different Zn/Al ratios lead to different products. Analysis of the gel formation process reveals that the polyacrylamide gel method involves three main reactions: chelation, cross-linking, and polymerization [13]. Cross-linking and polymerization primarily affect particle morphology without altering metal ion coordination. Figure 2 [Figure 2: see original paper] illustrates the chelation reaction between citric acid and Zn/Al ions. Citric acid is a hydroxyl-carboxyl type chelating agent; when excess citric acid is present, carboxyl groups dominate chelation. With appropriate metal ion amounts, both carboxyl and hydroxyl groups participate in chelation, while excess metal ions can only coordinate with OH^- ions in the precursor solution.

In $ZnAl_2O_4$ crystal, Al^{3+} has a coordination number of 6 while Zn^{2+} has 4, enabling citric acid to coordinate with Al^{3+} through 6 carboxyl/hydroxyl groups and with Zn^{2+} through 4 groups. Figure 2a shows the case of excess Zn^{2+}, where three citric acid molecules coordinate with two Al^{3+} ions via carboxyl groups and with Zn^{2+} via hydroxyl groups, while excess Zn^{2+} coordinates with OH^- ions. During reaction, Zn^{2+} coordinated with OH^- ions preferentially forms ZnO, with the remainder forming $ZnAl_2O_4$, as seen in sample S-0 (Figure 1a). With slight Zn^{2+} excess, another scenario may occur where Zn^{2+} substitutes for some Al^{3+} positions to form relatively stable complexes (Figure 2b), producing single-phase $ZnAl_2O_4$ at appropriate sintering temperatures (sample S-01, Figure 1a). When Zn/Al ratio is exactly 1:2, the chelation is illustrated in Figure 2c.

2.3 TG-DTA Analysis

To investigate the phase transformation process of $ZnAl_2O_4$ xerogel with temperature, Figure 3 [Figure 3: see original paper] shows DTA and TG curves for $ZnAl_2O_4$ xerogel (Zn:Al = 1:2, used for all subsequent experiments unless otherwise specified). From room temperature to 170°C, approximately 11.3% mass loss occurs, primarily from evaporation of adsorbed water molecules [18-20]. The DTA curve reveals three exothermic reactions. The first exothermic peak at 215°C, with ~11.9% mass loss, corresponds to decomposition of small molecular groups such as C–H, C–N, and C=O [18,19]. The second peak at 368°C, with ~22.5% mass loss, mainly involves decomposition of coordinated COO^- groups and residual C=O groups [20]. The most significant third exothermic process occurs between 420-650°C, peaking at 557°C, attributed to oxidation decomposition of polymer network side chains, main chains, and other organic residues, along with crystallization heat release [18-21], with ~49.8% mass loss. No further mass loss occurs above 650°C, indicating complete organic removal. These DTA results are consistent with XRD findings.

2.4 SEM Analysis

Figure 4 [Figure 4: see original paper] shows SEM images of $ZnAl_2O_4$ samples prepared by calcining xerogel at different temperatures. Particle size increases with calcination temperature. At 600°C, particles are nearly spherical, fine, and uniform (Figure 4a). At 700°C, particles become more dispersed (Figure 4b). At 800°C, obvious adhesion between particles appears, and at 900°C, significant agglomeration occurs (Figures 4c and 4d). Particle size distributions for four samples were statistically analyzed using Nano Measurer software, as shown in Figure 5 [Figure 5: see original paper]. Average particle sizes for samples calcined at 600, 700, 800, and 900°C are 15, 26, 32, and 38 nm respectively. These trends are consistent with XRD-calculated crystallite sizes, though the absolute values differ significantly, likely because SEM-observed particles consist of several crystallites [13].

2.5 FTIR Analysis

Figure 6 [Figure 6: see original paper] presents FTIR spectra of samples synthesized at different calcination temperatures. All samples show vibration peaks at 3460 and 1630 cm^{-1} due to adsorbed water molecules or hydroxyl groups, corresponding to O–H stretching and H–O–H bending modes [13]. Peaks at 2928 and 2854 cm^{-1} correspond to C–H stretching and symmetric $-CH_2$ stretching vibrations [22,23]. For the 500°C sample, weak peaks at 1385, 845, and 1550 cm^{-1} correspond to NO_3^- asymmetric stretching, bending vibrations, and $-NH_2$ bending mode [18,24]. When calcination temperature reaches 600°C, these peaks disappear, indicating complete $ZnAl_2O_4$ phase formation. In normal spinel structure, Zn–O and Al–O bonds exist as $[ZnO_4]$ and $[AlO_6]$ coordination, while inverse spinel contains some $[AlO_4]$ coordination. The 400-1000 cm^{-1} region corresponds to metal-oxygen bonds. Samples calcined at 600-900°C show characteristic $ZnAl_2O_4$ vibration peaks at 498, 557, and 665 cm^{-1}, where 557 and 665 cm^{-1} are $[AlO_6]$ stretching vibrations and 498 cm^{-1} is $[AlO_6]$ bending vibration [12], suggesting the prepared $ZnAl_2O_4$ has normal spinel structure.

2.6 Photoluminescence Analysis

Figure 7 [Figure 7: see original paper] shows excitation and emission spectra of $ZnAl_2O_4$ samples calcined at different temperatures. All samples exhibit an excitation peak at 352 nm with emission wavelength $\lambda = 469$ nm (Figure 7a). Notably, the sample calcined at 600°C also shows an excitation peak at 313 nm, likely due to combined effects of residual organics and $ZnAl_2O_4$. Although XRD does not directly detect organic peaks, TG/DTA, FTIR, and SEM results confirm residual organics at this temperature. Figure 7b shows blue emission peaks at 469 nm for nanoparticles calcined at different temperatures, possibly arising from lattice defects such as oxygen vacancies [11]. Emission intensity varies with calcination temperature, first increasing then decreasing then increasing again, a phenomenon also observed by Wang et al. [26] in Al_2O_3-C composites. The 600°C sample shows highest intensity; intensity decreases from 600°C to 800°C, likely due to defect recombination reducing defect concentration. The 900°C sample shows slightly higher intensity than the 800°C sample, possibly because higher temperature simultaneously reduces defect concentration (decreasing intensity) while improving crystallinity and reducing photon scattering by crystal defects (increasing intensity) [21]. The inset in Figure 7b shows emission spectra at λ = 313 nm and λ = 352 nm, both producing emission peaks at 469 nm without shifting peak position.

To further analyze the luminescence mechanism, Figure 8 [Figure 8: see original paper] illustrates the energy level diagram. The lower conduction band of $ZnAl_2O_4$ consists of Al^{3+} 2p orbitals and higher-lying Al^{3+} s orbitals, while the upper valence band comprises hybridized O^{2-} 2p and Zn^{2+} 3d orbitals [25], with V representing oxygen vacancies. Under 352 nm UV irradiation, electrons transition from the valence band to defect levels below the conduction band (position 1), forming near-band-edge absorption, then transfer to oxygen vacancy levels. Electrons at oxygen vacancy levels subsequently recombine radiatively with holes in the valence band, accompanied by blue emission at 469 nm (2.64 eV).

Conclusions

Modified polyacrylamide gel method successfully synthesized near-spherical $ZnAl_2O_4$ nanoparticles with uniform particle size. Varying the Zn/Al molar ratio produced different ZnAlO samples. For Zn:Al = 1:2 xerogel, $ZnAl_2O_4$ phase formed at 600°C, though some organics remained; organics were completely removed at 700°C. Particle size increased with sintering temperature, with significant agglomeration at 900°C. $ZnAl_2O_4$ xerogel sintered at various temperatures exhibited blue emission at 469 nm. Luminescence intensity generally decreased with increasing calcination temperature, with an anomaly at 900°C.

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