Effect of calcination temperature on structural and optical properties of MAl$_2$O$_4$ (M = Ni, Cu, Zn) aluminate spinel nanoparticles

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Effect of calcination temperature on structural and optical properties of \( \text{MAI}_2\text{O}_4 \) \((M = \text{Ni, Cu, Zn})\) aluminate spinel nanoparticles

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Received: September 28, 2018; Revised: January 11, 2019; Accepted: January 18, 2019

Abstract: NiAl\(_2\)O\(_4\), CuAl\(_2\)O\(_4\), and ZnAl\(_2\)O\(_4\) aluminate spinel nanoparticles were synthesized by sol-gel auto combustion method using diethanolamine (DEA) as a fuel. The effects of calcination temperature on structure, crystallinity, morphology, and optical properties of MAI\(_2\)O\(_4\) \((M = \text{Ni, Cu, Zn})\) have been investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), UV–visible diffuse reflectance spectroscopy (UV-DRS), and photoluminescence (PL) spectroscopy. The XRD and FT-IR results confirm the formation of single-phase spinel structure of NiAl\(_2\)O\(_4\), CuAl\(_2\)O\(_4\), and ZnAl\(_2\)O\(_4\) at 1200, 1000, and 600 °C, respectively. The direct band gap of these aluminate spinels, calculated from UV-DRS spectra using the Kubelka–Munk function, is found to increase with calcination temperature. The PL spectra demonstrate that NiAl\(_2\)O\(_4\) gives the highest blue emission intensity, while CuAl\(_2\)O\(_4\) and ZnAl\(_2\)O\(_4\) exhibit a very strong violet emission. During fluorescence process, the ZnAl\(_2\)O\(_4\) emits visible light in only violet and blue regions, while NiAl\(_2\)O\(_4\) and CuAl\(_2\)O\(_4\) emissions extend to the green region. It seems therefore that the transition metal type and intrinsic defects in these aluminate powders are responsible for these phenomena.

Keywords: NiAl\(_2\)O\(_4\); CuAl\(_2\)O\(_4\); ZnAl\(_2\)O\(_4\); sol-gel auto combustion; diethanolamine (DEA); photoluminescence (PL)

1 Introduction

Metal aluminate spinels with the formula MAI\(_2\)O\(_4\), where M represents a divalent metal ion, have attracted great attention for various applications owning to their high chemical and thermal stabilities, high mechanical resistance, high quantum yields with hydrophobic qualities, large surface area, and low surface acidity [1–3]. They have been widely used as photocatalysts, refractories, pigments, sensor, and magnetic, optical, and electrode materials including lubricant additive [4–7]. It has long been known that the synthesis method can affect the purity, crystallinity, surface area, particle size, and morphology of nanocrystalline MAI\(_2\)O\(_4\), which exert a significant influence on their optical and catalytic properties [8–10]. MAI\(_2\)O\(_4\) can be prepared by various techniques including solid-state reactions, co-precipitation synthesis, sol-gel method, solvothermal method, hydrothermal method, microwave-assisted hydrothermal
method, and polymeric precursor synthesis [8–10]. Each of these techniques requires its own specialized equipment, imposing significant cost, while further drawbacks include the low surface area of product and lack of homogeneity [3,11]. The sol-gel auto combustion method has been demonstrated to produce homogeneous high-purity nanoparticles with rapid heating and short reaction time [12–14]. This synthesis method combines the chemical sol-gel and combustion process, representing a quick, accessible technique with low energy costs and ideal for the synthesis of materials based on metal oxides. Various organic compounds can be employed as the fuel, but these have been conventionally limited to urea, citric acid, tartaric acid, and glycine [15,16]. In our previous studies, we have recently demonstrated the potential use of diethanolamine (DEA) as a novel fuel for sol-gel auto combustion synthesis of nanocrystalline NiAl2O4, CuAl2O4, and ZnAl2O4 aluminate spinels [17]. The obtained nano-size aluminate particles exhibited a single phase cubic spinel structure with excellent photocatalytic degradation of phenol rhodamine B (RhB), heteropolyaromatic methylene blue (MB), azoic methyl orange (MO), and methyl red (MR) under ultraviolet irradiation. NiAl2O4 and CuAl2O4 are found to exhibit higher photocatalytic activities than ZnAl2O4 due to the difference in band gap energy. The $E_g$ value of ZnAl2O4 (5.5 eV) is much larger than those of NiAl2O4 and CuAl2O4 (3.45 and 3.00 eV, respectively), which would limit the UV absorption region to very short wavelengths. It is obvious that the optical properties should play an important role in the photocatalytic performance of these materials. However, a comparative study of the influence of calcination temperature on the structure and optical properties of these materials has not yet been clarified. Aguilar et al. [18] studied the phase evolution of Cu–Al–O powders which were prepared by the Pechini method and calcined at different temperatures. CuAl2O4 and CuO were observed as intermediate phases at 900 and 1000 °C before transforming to CuAlO2 final phase at 1100 °C. Nazemi et al. [19] investigated the effect of calcination temperature on NiAl2O4 powders synthesized by mechano-chemical process. The single phase NiAl2O4 spinel powders were obtained at 1400 (unmilled powders) and 1100 °C (15 h milled powders); however, their optical properties have not been examined. Cornu et al. [20] studied the luminescence properties of ZnAl2O4 particles which were prepared using the Pechini or co-precipitation synthetic route and treated at different temperatures between 600 and 1350 °C. It was found that the transformation of amorphous precursor to ZnAl2O4 spinel phase occurred after heat treatment at 600 °C and various luminescence emissions linked to the presence of defects in the matrix structure. To the best of our knowledge, there have been no studies comparing the effect of calcination temperature on the structural and optical properties of NiAl2O4, CuAl2O4, and ZnAl2O4 aluminate spinels which were prepared by the same synthesis method.

In the present study, the NiAl2O4, CuAl2O4, and ZnAl2O4 aluminate spinels were synthesized by the sol-gel auto combustion method and calcined at different temperatures (600, 800, 1000, and 1200 °C). The effects of divalent metal ions and calcination temperatures on the structure, surface morphology, and optical properties of aluminate spinel (MA12O4 (M = Ni, Cu, Zn)) have been investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–visible diffuse reflectance spectroscopy (UV-DRS), and photoluminescence (PL) spectroscopy techniques. The optical properties and photoluminescence mechanisms of these metal aluminates are elucidated.

## 2 Experimental

### 2.1 Materials

The raw materials used for the preparation of NiAl2O4, CuAl2O4, and ZnAl2O4 aluminate spinels include Ni(NO3)$_2$·6H2O (nickel nitrate hexahydrate), Cu(NO3)$_2$·3H2O (copper nitrate trihydrate), Zn(NO3)$_2$·6H2O (zinc nitrate hexahydrate), Al(NO3)$_3$·9H2O (aluminum nitrate nonahydrate), and C$_2$H$_4$NO$_2$ (diethanolamine, DEA). All chemical reagents are of analytical grade and used as received without further purification.

### 2.2 Preparation of NiAl2O4, CuAl2O4, and ZnAl2O4

The NiAl2O4, CuAl2O4, and ZnAl2O4 nanoparticles were synthesized by the sol-gel auto combustion method [17]. First, stoichiometric amounts of metal nitrate and aluminum nitrate were dissolved in absolute ethanol to obtain a 0.2 mol/L solution. Then, an appropriate amount of DEA was added as fuel into the solution. The mixture was heated to 200 °C while stirring constantly. The mixed solution transformed into a condensed gel,
which self-ignited to produce a pearl white foamy product for ZnAl$_2$O$_4$ and dark brown powders for NiAl$_2$O$_4$ and CuAl$_2$O$_4$. Finally, the as-synthesized powders were calcined in air at 600, 800, 1000, and 1200 °C for 4 h.

2.3 Characterizations

The phase composition of the obtained powders was analyzed by XRD using a PANalytical X’Pert PRO MPD diffractometer and with Cu Kα radiation (λ = 1.5406 Å). The XRD patterns were collected from 20° to 80° with scanning steps of 0.04° and time step of 0.1 s. The FT-IR spectra of samples were recorded on a thermo scientific infrared spectrometer (Nicolet 6700) with KBr pellets in transmission mode, in the frequency range of 400–4000 cm$^{-1}$. Particle size and morphology were investigated by scanning electron microscopy (SEM, LEO 1450VP) and transmission electron microscopy (TEM, TECNAI G2). The samples were coated with gold for better visibility of the surface morphology for SEM measurement. In the process of preparing the TEM specimen, a small amount of the powder was dispersed in ethanol in an ultrasonic bath, and a few drops of the resulting suspension were placed on to a carbon-coated copper grid. UV–visible diffuse reflectance spectra were recorded using an Agilent Cary 5000 UV–Vis NIR spectrometer with an attached diffuse reflectance accessory in the wavelength range of 200–1000 nm to determine the energy band gap of the samples. Room temperature PL properties were studied by Perkin Elmer LS55 fluorescence spectrophotometer.

3 Results and discussion

3.1 XRD analysis

XRD was used to identify the crystal structure and phase evolution of NiAl$_2$O$_4$, CuAl$_2$O$_4$, and ZnAl$_2$O$_4$ powders after calcination at various temperatures (600, 800, 1000, and 1200 °C). Figure 1(a) shows the development of NiAl$_2$O$_4$ spinel structure. The as-synthesized powders exhibit diffraction peaks corresponding to NiO and Al$_2$O$_3$ phases, in agreement with JCPDS Nos. 45-0937 and 46-1212, respectively [21]. The characteristic peaks of NiAl$_2$O$_4$ first appear after calcination at 800 °C. As the calcination temperature rises, the intensity of NiAl$_2$O$_4$ peaks gradually increases at the expense of NiO and Al$_2$O$_3$. The powders calcined at 1000 °C consist of the major phase NiAl$_2$O$_4$ with a trace amount of NiO. At the calcination temperature of 1200 °C, NiO completely disappears and a single phase NiAl$_2$O$_4$ is obtained. The observed diffraction peaks are assigned to a cubic spinel structure of nickel aluminate (JCPDS No. 10-0339) [22–24]. The strong sharp diffraction peaks indicate that NiAl$_2$O$_4$ calcined at 1200 °C has a long-range ordered structure. These results correlate well with the previous study by Nazemi et al. [19] who
found that a mixture of NiO and Al₂O₃ powders transformed to the single phase NiAl₂O₄ spinel powders after calcination above 1000 °C, at 1100 °C for 15 h milled powders, and at 1400 °C for unmilled powders. For the CuAl₂O₄ samples (Fig. 1(b)), a monoclinic structure of CuO (ICPDS No. 45-0937) and a small impurity phase of Al₂O₃ [25,26] are found in the as-synthesized powders. When the powders are calcined at 600 °C, the XRD peak intensity of CuO increases while the characteristic peaks of Al₂O₃ disappear. At 800 °C, the formation of CuAl₂O₄ phase occurs but the CuO trace still remains. Similar phase evolution has been observed for Cu–Al–O powders which were prepared by the Pechini method and calcined at different temperatures [18]. Aguilar et al. [18] identified CuAl₂O₄ and CuO as intermediate phases at 900 and 1000 °C before transforming to CuAl₂O₄ final phase at 1100 °C. Mindru et al. [27] also found the presence of CuO as an impurity phase in the CuAl₂O₄ samples calcined at 900 °C. In the present study, a single phase CuAl₂O₄ aluminate spinel (ICPDS No. 33-0448) is obtained after calcination at 1000 °C [23,28]. The formation process of ZnAl₂O₄ spinel structure is different from those of NiAl₂O₄ and CuAl₂O₄. The as-synthesized ZnAl₂O₄ powders are amorphous which later transform into a highly crystalline ZnAl₂O₄ aluminate spinel structure (ICPDS No. 05-0669) [29–31] after calcination at 600 °C. This is in agreement with previous studies by Cornu et al. [20]. They also found that the amorphous precursor, obtained from the Pechini or co-precipitation synthetic route, transformed into ZnAl₂O₄ spinel phase after heat treatment at 600 °C. Further increasing calcination temperature leads to a crystalline spinel structure with sharp, narrow, and high-intensity peaks, indicating an increase in crystallinity and particle size of ZnAl₂O₄.

In addition, the average crystallite size (D) of single-phase spinel samples can be estimated from the full width at half maximum of the strongest diffraction peak (311) by applying Debye–Scherrer equation:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

where \( D \) is the average crystallite size, \( \lambda \) is the wavelength of the X-ray source (Cu Kα, 1.54 Å), \( \beta \) is the integral breadth of the (311) diffraction peak, and \( \theta \) is the Bragg’s diffraction angle. The width of the Bragg peak is the combination of both sample and instrument broadening effects. The latter can be determined using the following relationship:

\[ \beta = (\beta_{\text{measured}}^2 - \beta_{\text{instrumental}}^2)^{\frac{1}{2}} \]  

Consequently, interplanar spacing (\( d_{\text{hkl}} \)) and lattice parameter (a) of these samples are determined using Eqs. (3) and (4), respectively:

\[ d_{\text{hkl}} = \frac{\lambda}{2 \sin \theta} \]  

\[ a = d_{\text{hkl}}(h^2 + k^2 + l^2)^{\frac{1}{2}} \]  

The calculated results are presented in Table 1. The lattice parameter of aluminate spinels is in the order of NiAl₂O₄ < CuAl₂O₄ < ZnAl₂O₄, which should be related to the difference in ionic radius of transition metals. The average crystallite sizes of NiAl₂O₄, CuAl₂O₄, and ZnAl₂O₄ (calcined at 1000 °C) are 42, 62, and 42 nm, respectively. The results of ZnAl₂O₄ powders correlate well with those reported by Ianoș et al. [12] and Visinescu et al. [14] who applied a combustion synthesis method using starch and urea as fuel. Moreover, the average crystallite size and lattice parameter of ZnAl₂O₄ are found to increase with the calcination temperature. Similar results have been reported by Cornu et al. [20] whose as-synthesized ZnAl₂O₄ spinel powders were calcined at different temperatures. They found that the crystallite size significantly increased from 4.7 to 57.8 nm when the calcination temperature was raised from 600 to 1000 °C. Parra and Haque [32] also mentioned that when the temperature increases, the nucleation rate of the particles increases more rapidly. This can be explained by the increase in supersaturation of the reaction products, which accelerates the crystal core forming reaction within a short time. The crystallite size thus increases as a result of this process. For NiAl₂O₄ and CuAl₂O₄, they show similar lattice parameters and larger crystallite sizes compared to those obtained by the combustion method using glycine as fuel and calcined at lower temperatures (600 and 900 °C) [26,33]. This difference is likely due to the variation in calcination temperatures and different types of fuel. A similar observation has been reported for CoAl₂O₄ ceramic pigment prepared by means of solution combustion synthesis method using different fuels [34]. The crystallite size of aluminate sample synthesized with urea (9 nm) is obviously smaller than that of glycine (19 nm). Gilabert
Table 1 Average crystallite size ($D$), interplanar distance ($d$), lattice parameter ($a$), and band gap value ($E_g$) of single-phase NiAl$_2$O$_4$, CuAl$_2$O$_4$, and ZnAl$_2$O$_4$ powders

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D$ (nm)</th>
<th>$d_{311}$ (Å)</th>
<th>$a$ (Å)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl$_2$O$_4$ (1200 °C)</td>
<td>42</td>
<td>2.428</td>
<td>8.053</td>
<td>3.45</td>
</tr>
<tr>
<td>CuAl$_2$O$_4$ (1000 °C)</td>
<td>62</td>
<td>2.435</td>
<td>8.076</td>
<td>3.00</td>
</tr>
<tr>
<td>ZnAl$_2$O$_4$ (1000 °C)</td>
<td>42</td>
<td>2.440</td>
<td>8.092</td>
<td>5.50</td>
</tr>
<tr>
<td>ZnAl$_2$O$_4$ (800 °C)</td>
<td>35</td>
<td>2.439</td>
<td>8.089</td>
<td>5.42</td>
</tr>
<tr>
<td>ZnAl$_2$O$_4$ (600 °C)</td>
<td>30</td>
<td>2.438</td>
<td>8.086</td>
<td>5.35</td>
</tr>
</tbody>
</table>

et al. [34] stated that the main difference between fuels lies in the molar ratio of emitted gases/spinel formed. The higher the amount of gaseous products released during combustion, the higher the porous voluminous masses are obtained, but the lower the maximum temperature they achieve in the process because they lose more heat. In the case of urea and glycine, the ratio is approximately 31 and 26 mol gas/spinel, respectively.

3.2 FT-IR spectroscopy analysis

The typical transmittance FT-IR spectra of as-synthesized and calcined NiAl$_2$O$_4$, CuAl$_2$O$_4$, and ZnAl$_2$O$_4$ powders are shown in Fig. 2 as a series of transmission peaks in the range of 400–4000 cm$^{-1}$. FT-IR analysis was performed to investigate the formation of metal aluminate spinel structure and the surface functional group. All the samples contain common absorption bands around 3462, 2922, 2850, 2337, 1633, 1385, 1200, and 1118 cm$^{-1}$. Broad bands near 3462 and 1633 cm$^{-1}$ are attributed to –OH stretching vibrational modes and bending vibrational mode of absorbed water molecules, respectively [35]. Several IR studies of metal aluminate spinels noticed the water absorption peaks and stated that the high surface area of these materials could result in rapid adsorption of water from the atmosphere during pellet compression and IR measurements [35,36]. Small peaks at about 2922 and 2850 cm$^{-1}$ belong to C–H stretching vibration [1]. The absorption band at 2337 cm$^{-1}$ is possibly related to the presence of CO$_2$ on the powder surface, while a small peak at 1385 cm$^{-1}$ can be attributed to the residual nitrogen groups resulting from the combustion reaction [36]. The peaks in the 1200 cm$^{-1}$ region can be interpreted as vibrations of the C–C bond, and bands at around 1118 cm$^{-1}$ can be attributed primarily to oxygen groups with a single C–O bond [37,38]. Shanaj and John [39] reported that these organic impurities could be reduced by increasing calcination time. This affected the improvement of absorption and transmittance efficiency resulting in an extensive number of electrical, optical, and catalytic applications. In the FT-IR spectrum of as-synthesized NiAl$_2$O$_4$ powders (Fig. 2(a)), several small absorption bands located in the range of 400–1000 cm$^{-1}$ are assigned to the vibrational modes of NiO and Al$_2$O$_3$ [40,41]. These impurity bands remain in the samples calcined at 600 and 800 °C. By increasing the calcination
were examined using SEM, as shown in Fig. 3. SEM which are assigned to the Cu–O, Al –O, and Cu–O–Al stretching modes of Ni–O, Al–O, and Ni –O–Al bonds indicate the amorphous character of the sample [35,36,47]. After calcination at 600 °C, three well-defined characteristic bands describing the formation of the ZnAl2O4 spinel structure are observed in the range of 400–800 cm⁻¹. The bands located at 662, 555, and 499 cm⁻¹ are attributed to the vibrations of Zn–O, Al–O, and Zn–O–Al bonds in ZnO4 tetrahedra and AlO6 octahedral groups in the spinel structure [9,35,44]. These bands become sharper as the calcination temperature increases to 800 and 1000 °C, suggesting a high degree of crystallinity of zinc aluminate. No other impurity phases are found in the samples.

3.3 SEM analysis

The morphologies of as-synthesized and calcined NiAl2O4, CuAl2O4, and ZnAl2O4 powders (no grinding) were examined using SEM, as shown in Fig. 3. SEM images of as-synthesized NiAl2O4 (Fig. 3(a)) and CuAl2O4 (Fig. 3(f)) show agglomerated particles with a rounded shape lying over a smooth surface. Two phases can be distinguished, which is consistent with XRD results revealing the coexistence of Al2O3 phase with their corresponding metal oxide phase, i.e., NiO and CuO for the as-synthesized NiAl2O4 and CuAl2O4, respectively. The particle size of spherical agglomerates is found to decrease with increasing temperature. Upon calcination at 800 °C (Figs. 3(c) and 3(h)), NiAl2O4 and CuAl2O4 samples are composed of several tiny spherical particles with grain sizes below 50 nm. A further increasing calcination temperature causes the formation of small spherical nanoparticles which are closely packed together with a homogeneous size distribution (Figs. 3(d), 3(e), and 3(i)). The average particle size of pure NiAl2O4 and CuAl2O4 nanopowders obtained at their respective optimum temperatures (1200 and 1000 °C) are in the ranges of 20–50 nm and 100–200 nm. Regarding the development of ZnAl2O4 morphology, SEM image of as-synthesized amorphous powders (Fig. 3(j)) illustrates the presence of agglomerated particles with diverse sizes and shapes. As the calcination temperature increases to 1000 °C (Fig. 3(d)), the ZnAl2O4 particles become more uniform and spherical with mean particle size ca. 50 nm. In addition, the release of volatile gases such CO2, N2, O2, and H2O during the combustion process should be one of the main factors that create pores in the NiAl2O4, CuAl2O4, and ZnAl2O4 powders. This interconnected pore structure is important for catalytic applications.

3.4 TEM analysis

In order to further confirm the nano-scale morphology of NiAl2O4, CuAl2O4, and ZnAl2O4 powders, TEM studies were carried out. Figure 4 illustrates TEM micrographs of the single-phase NiAl2O4 (Fig. 4(a)), CuAl2O4 (Fig. 4(b)), and ZnAl2O4 (Fig. 4(c)) powders calcined at 1200, 1000, and 1000°C, respectively. It was found that all samples were composed of polyhedral particles with particle size in the range of 40–60 nm.

3.5 UV-DRS analysis

To understand the excitons and interband transitions, the UV-DRS spectra of NiAl2O4, CuAl2O4, and ZnAl2O4 powders calcined at different temperatures were measured in a wavelength range of 200–1000 nm, as shown in Fig. 5. Each metal aluminate displays different spectral profile with characteristic absorption bands. Figure 5(a) shows the UV-DRS spectra of as-synthesized and calcined
NiAl$_2$O$_4$ powders. The powders calcined at 600 °C exhibit a broad absorption band with reflectance values of 10%–15% over the UV region up to the NIR region. After heating to 800 °C, three small bands corresponding to the formation of NiAl$_2$O$_4$ spinel structure occur at about 380, 600, and 645 nm [22]. These characteristic bands become stronger when the calcination temperature increases to 1200 °C. Many intense convoluted bands are located at about 240, 260, 380, 600, and 645 nm. The reflectance of both samples also increased sharply at wavelengths of 350–550 nm and 650–1000 nm up to maximum values of 37.5% and 47.5%, respectively.
This spectral evolution confirms the complete formation of a NiAl₂O₄ spinel structure [48]. The broad absorption bands located at 240 and 260 nm originate from the fundamental band-to-band electron transition between filled O 2p orbitals and empty Al 3s with the possibility of Al 3p wave function mixing. The additional shoulder observed at 320 nm is associated with electronic excitations between filled O 2p and empty Ni 4s orbitals [49]. This usually depends on the intrinsic defects of the sample. The high-energy band at 380 nm is associated with both the charge transfer bands and 3A₂g→3T₁g spin allowing transition for octahedral coordination of Ni²⁺ cations [48]. The bands at about 600 and 645 nm can be attributed to 3T₁→3T₂ (3P) spin allowing transition. These doublet d–d bands can be related to Ni²⁺ in tetrahedral and octahedral sites, respectively [3,49], which would confirm an inverse spinel structure of NiAl₂O₄. For the CuAl₂O₄ samples (Fig. 5(b)), the UV-DRS spectrum of as-synthesised powders also exhibits a broad absorption band with about 10%–12.5% reflectance value covering spectra ranging from the UV up to the NIR region without any prominent features. An increase in calcination temperature to 600 °C results in the appearance of three small absorption bands at about 290, 440, and 750 nm [50]. These bands become stronger and more visible when CuAl₂O₄ samples are calcined at 800 °C. Further heating to 1000 °C, the characteristic band of CuO at 750 nm disappears, which would suggest the complete formation of the CuAl₂O₄ spinel structure. The high energy band at 290 nm is related to the fundamental electron transition between filled O 2p orbitals and empty Al 3s orbitals (which can be mixed with the 3p orbital), while the band at about 440 nm is associated with the charge transfer between O and Cu²⁺ occupied octahedral sites [51,52]. The new broad shoulder at around 800 nm corresponds to the Cu²⁺ d–d transitions in a tetragonally-distorted octahedral geometry around Cu²⁺ ions [27]. Moreover, it can be clearly seen that the reflectance percentage in the high wavelength VIS region (600–800 nm) and NIR region (800–1000 nm) of CuAl₂O₄ samples tends to increase with increasing calcination temperatures while that of the UV region (200–400 nm) and low wavelength VIS region (400–600 nm) is comparable (10%–12.5%) for all samples. Even though there are various hypotheses that have been proposed in order to explain the strong variation of the absorption band intensity, reasonable results were presented by le Nestour et al. [53]. Their CuAl₂O₄ samples prepared at 700 and 1000 °C exhibited different absorption behaviors in both VIS and NIR regions. Based on their electron paramagnetic resonance (EPR) spectra, they concluded that the Cu⁺/Cu⁰ mixed valencies and defects such as oxygen vacancies in the anion network of sample prepared at low temperature were responsible for this phenomena. The intra-atomic transition (3d¹⁰→4s¹) in these monovalent copper cations (Cu⁺) affect the increase in absorption intensity at around 780 nm. On the contrary, the calcination at 1000 °C leads to the oxidation reaction Cu⁺→Cu²⁺ + e⁻. This increase of Cu²⁺ directly affects the inter-atomic d–d charge transfer between divalent and monovalent copper cations (Cu²⁺/Cu⁺ intervalency transitions) that may be responsible for the variation of the absorption band from about 800 to 1000 nm. In the ZnAl₂O₄ samples (Fig. 5(c)), the reflectance of all samples increases with increasing calcination temperature in the overall wavelength region. The UV-DRS spectrum of amorphous powders shows a broad absorption band covering a range from the ultraviolet (UV) region up to the near-infrared (NIR) region without any significant features. After calcination at 600 °C, ZnAl₂O₄ powders exhibit absorption bands at about 200, 250, 320, and 350 nm. The high-energy bands of ZnAl₂O₄ aluminate spinel are related to fundamental band-to-band electron excitation between filled O 2p orbitals and empty Al 3s orbitals, with the possibility of Al 3p wave function mixing [8,14]. The broad shoulder observed in the 320–350 nm wavelength region is typically associated with electronic transition between filled O 2p and empty Zn 4s orbitals depending on the intrinsic properties (spinel defects) [8,15]. This shoulder band is found to shift to a higher energy with increasing calcination temperatures. Both ZnAl₂O₄ samples calcined at 800 and 1000 °C show the maximum reflectance of 98% over the spectral range of 500–1000 nm. The significant increase in reflectance value in the VIS regions rendered these powders brighter and whiter when compared to ivory-colored samples calcined at 600 °C, as illustrated in Fig. 6. Similar observation was reported by Cornu et al. [54], of which ZnAl₂O₄ powders were synthesized using Pechini method and calcined at different temperatures ranging from 600 to 1350 °C [54]. They found that reflectance percentages of ZnAl₂O₄ in the UV region (300–400 nm) and VIS region (400–550 nm) tended to increase with increasing calcination temperature and reached a maximum value of about 95%, while no modification was observed in the 200–300 nm region. They explained that these occurrences should be related to the disappearance of six fold-coordinated zinc ions. The Zn–O charge transfer band of six fold-coordinated zinc ions located at
Fig. 6 Photographs of NiAl\textsubscript{2}O\textsubscript{4}, CuAl\textsubscript{2}O\textsubscript{4}, and ZnAl\textsubscript{2}O\textsubscript{4} powders calcined at different temperatures.

400–500 nm disappear while only the Zn–O charge transfer band of four fold-coordinated zinc ions remains visible below 300 nm, which confirms the complete formation of a ZnAl\textsubscript{2}O\textsubscript{4} spinel structure.

3.6 Optical band gap analysis

The optical band gaps of NiAl\textsubscript{2}O\textsubscript{4}, CuAl\textsubscript{2}O\textsubscript{4}, and ZnAl\textsubscript{2}O\textsubscript{4} aluminate spinels are calculated from UV-DRS spectra. The Kubelka–Munk function is first applied to convert diffuse reflectance into an equivalent absorption coefficient for powder samples.

\[
\alpha = F(R) = \frac{(1-R)^2}{2R}
\]

where \(F(R)\) is the Kubelka–Munk function, \(\alpha\) is the absorption coefficient, and \(R\) is the reflectance. Therefore, the optical band gap can be determined by Tauc relation.

\[
F(R)hv = A(hv - E_g)^n
\]

where \(hv\) is light energy, \(A\) is constant, \(E_g\) is band gap energy, \(n = 1/2\) for direct band gap. Figure 7 displays the plots of \((F(R)hv)^2\) versus \(hv\) for NiAl\textsubscript{2}O\textsubscript{4}, CuAl\textsubscript{2}O\textsubscript{4}, and ZnAl\textsubscript{2}O\textsubscript{4} powders calcined at various temperatures. The extrapolation of Tauc plot to \(x\) axis provides the value of direct band gap energy \((E_g)\). These results show that the band gap energies of all metal aluminate samples increase with increasing calcination temperature (Table 1). The NiAl\textsubscript{2}O\textsubscript{4}, CuAl\textsubscript{2}O\textsubscript{4}, and ZnAl\textsubscript{2}O\textsubscript{4} calcined at the highest temperature exhibit a direct band gap of 3.45, 3.00, and 5.50 eV, respectively. The \(E_g\) value of our NiAl\textsubscript{2}O\textsubscript{4} aluminate spinel (3.45 eV) agrees well with the previous study reported by Gouda and Bayoumy [55] who applied combustion method using citric acid as fuel (3.4 eV). For the pure ZnAl\textsubscript{2}O\textsubscript{4} powders calcined at 600–1000 °C, they exhibit \(E_g\) values in the range of 5.35–5.50 eV which are slightly higher than those obtained by using urea as fuel (5.1 eV) [49]. However, the band gap energy of our CuAl\textsubscript{2}O\textsubscript{4} powders is found to be larger than those prepared by conventional and microwave combustion methods using aloe vera extract as fuel (2.34–2.50 eV) [51,52]. This blue shift in the optical band gap may be attributed to the difference in particle size and size distribution which can cause inhomogeneous broadening of the optical spectra. Furthermore, the change in the band gap values would explain the color variation of metal aluminates with calcination temperature, as shown in Fig. 6. The band gap value of the as-synthesized NiAl\textsubscript{2}O\textsubscript{4} sample is 1.65 eV, while increasing the calcination temperature to 1200 °C the band gap expands to 3.45 eV. These
results are directly related to a blue shift of the absorption wavelength which enhances the cerulean blue color of the pure NiAl$_2$O$_4$ samples. A blue shift in absorbance wavelength also causes the change of color in CuAl$_2$O$_4$ samples from the black as-synthesized powders to black olive and red-brown CuAl$_2$O$_4$ powders. Thus, the color variation can be a direct evidence for the impact of calcination temperature on the respective aluminates.

3.7 PL analysis

PL spectra were recorded to investigate the recombination phenomena in the samples. From these spectra, it is possible to obtain the information of band gap with the relative energy position of sub-band gap defect states \[56\] in materials which can be influenced by the synthesis condition \[49\]. Figure 8 shows the room temperature normalized PL spectra of single-phase NiAl$_2$O$_4$ (Fig. 8(a)), CuAl$_2$O$_4$ (Fig. 8(b)), and ZnAl$_2$O$_4$ (Fig. 8(c)), recorded with 225 nm excitation wavelength. All samples show violet, blue, and green emission bands from 360 to 560 nm. NiAl$_2$O$_4$ exhibits weak broad luminescence bands with a sharp blue emission peak at 475 nm. Whereas, ZnAl$_2$O$_4$ and CuAl$_2$O$_4$ powders show high intensity of violet emission centered at about 425 and 440 nm, respectively. The intensity of the PL peak is known to be controlled by the number of charge transfers and surface defects, including the existence of some organic residual (e.g., NO$_3^-$ and CO$_2$) previously observed in the FT-IR results \[57,58\]. The emission peaks that occurred in the PL spectra of each metal aluminate samples are attributed to the recombination of electrons and photogenerated holes involving various structural defects, such as the ionized charge states of intrinsic defects, oxygen vacancies, metal (Ni, Cu, Zn) vacancy, metal interstitials, and oxygen antisites. Rapid combustion during the sol-gel auto combustion method usually generates these structural defects, which act as deep defect donors in semiconductor oxides and contribute to the optical emission \[59\]. The intensities ($I$) of the strongest emission peak of the as-synthesized and calcined aluminate samples, including their fluorescence lifetime ($\tau$), are tabulated in Table 2. The fluorescence intensity values of single-phase aluminate samples are in accordance with Wang et al. \[58\], Kool et al. \[60\], and He et al. \[61\] whose NiAl$_2$O$_4$, CuAl$_2$O$_4$, and ZnAl$_2$O$_4$ samples were prepared by the modified sol-gel and co-precipitation methods. Moreover, the fluorescence lifetime tends to increase with increasing...
Table 2  Photoluminescence intensity ($I$) and fluorescence lifetime ($\tau$) of (a) NiAl$_2$O$_4$, (b) CuAl$_2$O$_4$, and (c) ZnAl$_2$O$_4$ powders calcined at different temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-syn.</th>
<th>600 °C</th>
<th>800 °C</th>
<th>1000 °C</th>
<th>1200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I$ (a.u.)</td>
<td>$\tau$ (ms)</td>
<td>$I$ (a.u.)</td>
<td>$\tau$ (ms)</td>
<td>$I$ (a.u.)</td>
</tr>
<tr>
<td>NiAl$_2$O$_4$</td>
<td>264</td>
<td>0.3752</td>
<td>287</td>
<td>0.4757</td>
<td>326</td>
</tr>
<tr>
<td>CuAl$_2$O$_4$</td>
<td>318</td>
<td>0.1803</td>
<td>320</td>
<td>0.2384</td>
<td>344</td>
</tr>
<tr>
<td>ZnAl$_2$O$_4$</td>
<td>316</td>
<td>0.0642</td>
<td>1302</td>
<td>0.2139</td>
<td>1490</td>
</tr>
</tbody>
</table>

calcination temperature. Yin et al. [62] reported that these occurrences may be related to the increase of crystal field effects on the energy level within the matrix leading to the transition change and having an impact on the lifetime of the excited state electrons.

All the PL spectra between 360 and 560 nm can be deconvoluted into several emission peaks centered at 382 nm (3.25 eV), 402 nm (3.08 eV), 423 nm (2.03 eV), 443 nm (2.8 eV), 471 nm (2.63 eV), 493 nm (2.52), and 516 nm (2.4 eV) which are denoted by UV-violet, violet-I, violet-II, violet-blue, blue, blue-green, and green emissions, respectively. Deconvolution of the PL spectrum for NiAl$_2$O$_4$ is depicted in Fig. 8(a). A good fit is achieved with five Gaussian components centered at 380 nm (UV-violet), 430 nm (violet-II), 471 nm (blue), 495 nm (blue-green), and 513 nm (green). The single-phase CuAl$_2$O$_4$ spectrum (Fig. 8(b)) gives seven emission peaks at 384 nm (UV-violet), 407 nm (violet-I), 419 nm (violet-II), 442 nm (violet-blue), 467 nm (blue), 490 nm (blue-green), and 518 nm (green). For ZnAl$_2$O$_4$ aluminate calcined at 600 °C (Fig. 8(c)), the PL spectrum is deconvoluted into four emission peaks centered at 397 nm (violet-I), 421 nm (violet-II), 444 nm (violet-blue), and 476 nm (blue).

To better understand the fluorescence mechanism of the NiAl$_2$O$_4$, CuAl$_2$O$_4$, and ZnAl$_2$O$_4$ samples, a schematic band diagram as shown in Fig. 9 is created to show the excitation and emission processes. When the $E_g$ value of metal aluminates (3.45 eV for NiAl$_2$O$_4$, 3.00 eV for CuAl$_2$O$_4$, and 5.35 eV for ZnAl$_2$O$_4$) is lower than the excitation wavelength ($\lambda_{ex} = 225$ nm, 5.51 eV), an electron in the valence band (VB) can be excited to higher energy levels in the conduction band (CB) and then falls to the conduction band maximum (CBM) through internal conversion (IC) (Fig. 9(a)) and vibrational relaxation (VR). The electron at CBM can then radiatively recombine with a hole in the valence band or defect states in the band gap resulting in the UV-violet, violet-I, violet-II, violet-blue, blue, blue-green, and green light emissions.

Fig. 9  Fluorescence mechanism, presenting various PL emission components originated due to electronic transitions between different defect levels and the band edges of aluminate powders.
The origin of the individual components of luminescence emission has been analyzed from the available energy positions of various defect centers existing within the Zn–O, Ni–O, and Cu–O systems [53,63–66]. The UV-violet emission luminescence peak at about 380 nm (≈3.26 eV) can be attributed to electron transition from the CB to a single ionized oxygen vacancy (V_{O}^{+}) as the responsible acceptor defects located at 0.27 eV above the VB (Fig. 9(b)) [67]. Two satellite components of violet luminescence are visible in each spectrum. The violet-I luminescence peak at 397 to 407 nm (3.05 to 3.12 eV) occurs through possible transition of electrons trapped at metal interstitial (M_{i}) defects to the VB (Fig. 9(c)), while the violet-II luminescence peak at 419 to 430 nm (2.88 to 2.96 eV) arises through possible electron transition between the ionized metal interstitial (M_{i}^{+}) defects level and the VB (Fig. 9(d)). This assumptions is in agreement with the previous study reported by Zeng et al. [68] that the blue emission can be interpreted by the transition of extended metal interstitials (M_{i}) states lying below the conduction band minima. Kim et al. [69] have also calculated the formation enthalpy of a complex of V_{O} and doubly ionized M_{i}^{++} defect. They found that each complex will generate pairs of M_{i}^{+} and V_{O}^{0} states differing slightly in energy from other complex. The electron–hole recombination between these M_{i}^{+} states and the VB led to the origin of violet-blue emission. Regarding the origin of the blue emission, several hypotheses have been proposed including electron transition from oxygen vacancies (V_{O}) to the VB, metal interstitials (M_{i}) to metal vacancies (V_{M}), and M_{i} to the VB or −OH groups at the particle surface which vary according to the synthesis techniques [70–73]. The blue emission was observed for ZnO particles synthesized by sol-gel method in the presence of Li^{+} cations and excessive OH– anions that caused a stoichiometric excess of oxygen favoring the formation of specific defects, including interstitial oxygen (O_{i}), oxygen antisite (O_{Zn}), and different zinc vacancies (V_{Zn}^{O}; V_{Zn}; V_{Zn}^{2−}) [74]. Since most of these defects are acceptors in nature, the possible path for the blue emission is the conduction-band-to-acceptor transitions. Moreover, the density functional theory (DFT) calculation confirmed that energy levels of O_{i}, O_{Zn}, V_{Zn}^{O}, V_{Zn}, and V_{Zn}^{2−} are 3.06, 2.66, 0.56, 2.28 and 2.38 eV below the CB, respectively. The previous research on the defect-related photoluminescence behavior of Ni–O and Cu–O systems by Anbuselvan et al. [75,76] also gave concordant results for the blue emission. Therefore, the blue luminescence peak of our metal aluminates appearing at 2.61 to 2.66 eV (467–476 nm) can be attributed to oxygen antisites (O_{M}) as the responsible acceptor defects (Fig. 9(e)). Van Dijken et al. [77], Mochizuki and Saito. [78], and Zhao et al. [76] explained the phenomenon of the origin of green emission at around 500 nm by the recombination of a shallowly trapped electron with a deeply trapped hole. The photogenerated hole is first trapped at the surface of the nanoparticles by surface defects such as O^{2−}/O^{−} and then migrates to vacancy levels located deep in the particle leading to the formation of a deep hole trapped level above the VB (Fig. 9(f)). Emission at around 500 nm (~2.48 eV) occurs when the photogenerated hole trapped in the deep oxygen vacancy recombines with the photogenerated electron trapped in a shallow level located just below the CB.

4 Conclusions

NiAl_{2}O_{4}, CuAl_{2}O_{4}, and ZnAl_{2}O_{4} aluminates nanoparticles were successfully synthesized by the sol-gel auto combustion method using DEA as a fuel. The calcination temperature is found to strongly influence the phase formation, particle size, optical, and fluorescence properties of the final product. The XRD results affirm that the formation of single-phase NiAl_{2}O_{4}, CuAl_{2}O_{4}, and ZnAl_{2}O_{4} spinel structures occurs at 1200, 1000, and 600 °C, respectively. The characteristic IR absorption bands in the frequency range of 400–800 cm^{-1} confirm the formation of a spinel structure, while SEM and TEM images depict the formation of well-developed nanosized grains. Their porous structures would enable these alumina spinels to serve as a potential candidate in the adsorption and catalytic applications. The UV–visible diffuse reflectance spectra illustrate dramatic improvement of reflectance in the visible and infrared regions up to 90% for the ZnAl_{2}O_{4} sample calcined at 1000 °C and around 40% for the single-phase NiAl_{2}O_{4} sample; meanwhile, all CuAl_{2}O_{4} samples show strong absorption in both UV and visible regions with maximum value of 90%, while improvement of reflectance in the infrared region of up to 30% is obtained with increasing calcination temperature. The optical band gap values of all samples are found to increase with increasing calcination temperature. The photoluminescence analysis of metal aluminate spinels reveals that the ZnAl_{2}O_{4} powders exhibit interesting abilities for applications in
violet and blue light-emitting devices, while NiAl$_2$O$_4$ and CuAl$_2$O$_4$ powders are capable to provide violet, blue, and green emissions for potential use as fluorescent materials. Moreover, the sol-gel auto combustion method can be considered a very effective and useful technique to synthesize other metal aluminate nanoparticles with good optoelectronic properties.

Acknowledgements

This work has been financially supported by Faculty of Science at Sriracha, Kasetsart University, Sriracha Campus and the Kasetsart University Research and Development Institute (KURDI), Bangkok, Thailand.

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