Preparation and optical properties of nanoscale MgAl$_2$O$_4$ powders doped with Co$^{2+}$ ions

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**Abstract**

Co$^{2+}$-doped MgAl$_2$O$_4$ nanocrystalline powders were prepared by co-precipitation method. The gels and/or calcined samples were characterized by means of thermogravimetry and differential scanning calorimetry (TG/DSC), X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier transform infrared (FTIR) spectrum and near-infrared absorption spectrum. MgAl$_2$O$_4$ nanocrystals were produced by calcining the gel above 800°C, with the crystallite size of 10–30 nm in the temperature range of 800–1100°C. The influence of pH value of precipitant solution on the dispersing of powders was studied and the result showed that Co:MgAl$_2$O$_4$ nanocrystalline powders exhibited good dispersion when pH = 11. The absorption spectrum of Co$^{2+}$-doped MgAl$_2$O$_4$ exhibited a broad absorption band in the wavelength range of 1200–1600 nm, which indicated that Co$^{2+}$ ions substituted for the tetrahedrally coordinated Mg$^{2+}$ ions in the MgAl$_2$O$_4$ lattice.

**1. Introduction**

Considerable interest has been noted in materials doped with tetrahedrally coordinated Co$^{2+}$ ions. This fact occurs due to their use as passive Q-switches for Er$^{3+}$:glass laser or the possible candidates for tunable solid state laser materials because of their excellent absorption and emission properties [1–6]. Oxide spinels comprise a very large group of structurally related compounds [7–9]. Co$^{2+}$-doped spinel crystal, such as MgAl$_2$O$_4$, ZnAl$_2$O$_4$, can exhibit absorption and luminescence properties [3,5].

Recently, transparent ceramic materials have attached much attention because they have several remarkable advantages over single crystals. For example, ceramic samples with high doping concentration and large size can be more easily fabricated, whereas this is usually difficult for crystals. The cost of ceramics can be potentially much lower than their single-crystal counterparts because of their faster fabrication process and possibility of mass production. The preparation process of highly transparent ceramics is technically quite difficult, containing powder synthesis and sintering. The key step is to synthesize high pure, ultrafine and highly dispersed nanocrystalline powders.

Several wet chemical routes have been adopted to synthesize doped and undoped spinel powders [10–16], such as precipitation, hydrothermal method and sol–gel method. Although the sol–gel method is the most widely employed chemical route to mixed metal oxides, it has some disadvantages, for example the pH control, the cost of the materials and the unstability of the sol in the air. Co-precipitation is one of the most promising techniques because of air- and moisture-stable precursor powders can be prepared on a large scale in water rather than in organic chemicals. In this work, Co-doped MgAl$_2$O$_4$ precursors were synthesized by using ammonium hydrogen carbonate (hereafter referred to as AHC) as precipitant via co-precipitation method. Phase evolution of the precursors and the influence of pH on the dispersing of nanoparticles were studied.

**2. Experimental**

Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_2$·6H$_2$O were used as starting materials and AHC was used as precipitant. For multi-cation precipitation, the reverse-strike technique (adding multi-cation solution to the precipitant solution) has the advantage of higher cation homogeneity in the precursors and was used in this study. Firstly, the multi-cation solution was obtained by dissolving Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_2$·6H$_2$O
in deionized water. The cationic molar ratio for Co:Mg:Al is 0.01:0.99:2. Then the solution was added drop-wise into the precipitant solution under magnetic stirring at 50 °C. The initial pH of ACH solution was adjusted to be 8, 9, 10, 11 with ammonia water, respectively. The resultant suspension was filtered using suction filtration, washed four times with deionized water, rinsed with ethanol, and then dried at 40 °C. The precursors obtained via the above-mentioned procedure were calcined in air at the temperature range of 400–1100 °C for 2 h.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyzes of the precursor were performed using a DSC/TGA analyzer (Model Q600 SDT) in flowing nitrogen atmosphere with a heating rate of 10 °C/min. The X-ray diffraction (XRD) patterns of the obtained powder were carried out by a Japan Rigaku D/Max-rA diffractometer, operated at 28 KV and 40 mA, using a Cu-target tube (λ = 0.15418 nm) and a graphite monochrometer. The TEM was performed on an H-800 transmission electron microscope. The infrared (IR) spectrum was obtained in the 4000–400 cm⁻¹ region by using a Nicolet 750 FTIR spectrometer at room temperature. The optical absorption spectrum was measured with a Hitachi model U-3500 recording spectrophotometer.

### 3. Results

Fig. 1 shows the IR spectrum of the precursor. The band near 3477 cm⁻¹ is due to the stretching vibration of H₂O. The peak at 1629 cm⁻¹ is from the bending vibration of H₂O. The peaks at 1539, 1390 cm⁻¹ can be attributed to NH₄⁺ and CO₃²⁻ ions, respectively. The peaks at 1028 cm⁻¹ is due to NO₃⁻ vibration.

The XRD patterns of the Co:MgAl₂O₄ precursor and the calcined powders at 400–1100 °C are shown in Fig. 2. From the figure, it is proved that NH₄Al(OH)₂CO₃·H₂O and Mg₆Al₂(CO₃)(OH)₁₆·4H₂O are formed in the precursor. The broad peaks in the XRD patterns of the powder calcined at 400–700 °C correspond to periclase (MgO) (JCPDS, 45-946), decomposed from hydrotalcite. When the sample was heated to 800 °C, the XRD spectra exhibit broadened diffraction peaks indicating the nanocrystalline nature. All the peaks were perfectly indexed to crystalline MgAl₂O₄ (JCPDS, 21-1152) and no other phase was observed. The intensity of the diffraction peaks increased as the calcinations temperature increased, indicating crystallite growth. The average grain sizes of the powders sintered at 800–1100 °C were calculated to be about 10–30 nm by means of the Scherrer formula: 

\[ D = \frac{0.9 \lambda}{β \cos θ} \]

where \( λ \) is the X-ray wavelength (0.15418 nm), \( θ \) is the diffraction angle, and \( β \) is the full-width at half-maximum (FWHM) intensity of the diffraction line.

Fig. 3 shows the TG/DSC curves obtained for the dried powder. The endothermic peak at 240 °C in the DSC curve can be explained by the removal of bound water. The exothermic peak at 665 °C may due to the formation of MgO. The weak exothermic peak at 819 °C corresponds to the crystallization of the MgAl₂O₄ spinel. No distinct weight loss is observed at temperature higher than 820 °C because of the mass formation of spinel.

### 4. Discussion

The chemical reactions of AHC hydrolysis in base solution are as follows:

\[ \text{NH}_4\text{HCO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} + \text{H}_2\text{CO}_3, \]

\[ \text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-}. \]

Thus, the precursor contains a great amount of H₂O, CO₃²⁻ and NH₄⁺·Al³⁺ and Mg²⁺ may precipitate as ammonium dawsonite hydrate (NH₄Al(OH)₂CO₃·H₂O) and hydrotalcite (Mg₆Al₂(-CO₃)(OH)₁₆·4H₂O). This analysis is in agreement with the IR and XRD pattern of the powder precursor.
Highly dispersed powders are necessary to obtain transparent ceramics. The influence of pH value on the dispersing of powders was studied in this work. Fig. 4 shows the TEM photographs of the powders produced at different pH value and calcined at 1100 °C. The powder prepared at pH 11 shows good dispersion. The average size of nanocrystalline particles is about 30 nm (shown in Fig. 4(a)) and the result is similar to the XRD analysis. With the decreasing of pH value, the powder tends to agglomerate. When pH 8, the particle seriously agglomerates. So we think that the suitable pH value to obtain the well dispersed powders is 11.

To confirm the existence of tetrahedral Co²⁺ ions in the MgAl₂O₄ nanocrystals, the absorption spectrum of the nanocrystals was studied. A thin wafer was made from the as-prepared nanocrystalline powder heated at 900 °C and was used to measure the optical absorption spectrum, the result is shown in Fig. 5. The absorption spectrum is similar to that of Co²⁺ doped MgAl₂O₄ crystal [3]. The broad absorption band in the range of 1200–1600 nm is assigned to ⁴A₂ → ⁴T₁(⁴F) transition of the tetrahedrally coordinated Co²⁺ ion. This absorption band clearly indicated that Co²⁺ ions occupy tetrahedral sites in MgAl₂O₄ spinel nanocrystalline powders by substituting for tetrahedrally coordinated Mg²⁺ ions.

5. Conclusions

Pure and highly dispersed nanoscale powders of MgAl₂O₄ doped with Co²⁺ ions were prepared by co-precipitation method using AHC as precipitation. MgAl₂O₄ nanocrystals were formed above 800 °C and the particle size was about 10–30 nm in the temperature range of 800–1100 °C. When pH is 11, the powders have good dispersion. Co:MgAl₂O₄ nanocrystals exhibit broad absorption band in the wavelength range of 1200–1600 nm and have the potential as passive Q-switch for infrared lasers. The next work that we do is to prepare Co:MgAl₂O₄ transparent ceramics from the corresponding nanocrystalline powders.

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References