Preparation and fluorescence properties of MgAl$_2$O$_4$: Tb$^{3+}$ nanorod-like phosphors

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Abstract

A series of MgAl$_2$O$_4$: x% Tb$^{3+}$ (x = 1.0–6.0) phosphors was prepared by a hydrothermal-assisted light burning method. The crystal structure, morphology and fluorescence properties of the samples were investigated. The results indicated that when the thermal and light burning temperatures were determined to be 120 °C and 1100 °C, respectively, the crystallinity for Mg$_4$Al$_2$(OH)$_{14}$ and NH$_4$Al(OH)$_3$CO$_3$ biphasic precursors is the best, conducive to generating pure phase MgAl$_2$O$_4$ nanorod-like phosphors. The entry of Tb$^{3+}$ into the MgAl$_2$O$_4$ lattice can cause lattice distortion, but the main structure of the spinel does not change. The main emission peaks for the series of phosphors are located in the green light region of 546 nm. The MgAl$_2$O$_4$: 4.0% Tb$^{3+}$ phosphor has the highest fluorescence intensity and shows the best colour quality. Its CIE coordinates (x, y), CCT and colour purity are determined to be (0.3171, 0.5290), 5845 K and 53.50%, respectively. The series of MgAl$_2$O$_4$: Tb$^{3+}$ phosphors exhibits typical cold green light emission and have good application prospects in solid-state display devices.

1. Introduction

Rare earth-doped aluminate phosphors have attracted extensive attention due to their excellent performance in chemical stability, luminous efficiency and long afterglow, and their applications have covered pigments, light storage and luminescence devices [1–3]. Facing many similar products in the field of luminescent materials, aluminate-based phosphors need to be comprehensively considered in terms of host materials, preparation processes, economic benefits and environmental protection. Compared with the same family of Sr and Ba aluminate materials, spinel-type Mg$_4$Al$_2$O$_7$ is an important aluminate with abundant raw material resources, low price and less pollution. In particular, MgAl$_2$O$_4$ not only has excellent performance in melting point, strength and stability, but also has a low phonon energy (~670 cm$^{-1}$), and is expected to be an ideal host material for new phosphors.

The preparation methods for MgAl$_2$O$_4$ phosphors can be divided into three main categories: solid-phase, combustion and liquid-phase methods. The solid-phase method has a simple operation, but there are some problems, such as high calcination temperature, high energy consumption and poor crystallinity for the product. The combustion method utilizes the instantaneous heat released by the rapid combustion of urea, amino acids and other fuels, so that the reaction can be completed in a short time, which has the effect of energy savings. However, it is easy to cause local uneven combustion and temperature gradients, resulting in uneven dispersion for the final product [4]. The liquid-phase method includes coprecipitation, sol-gel, hydrothermal and other synthesis technologies [5–7]. Among these technologies, the sol-gel method has unique advantages in the preparation of nanosized MgAl$_2$O$_4$ phosphor, but there are also problems such as irregular agglomeration for the nanosized powders and harmful alkoxide raw materials endangering human health [8–10]. In this context, the hydrothermal method has achieved good results as a pollution-free green synthesis technology in the regulation of special morphology [7, 11]. In addition, to meet the functional characteristics for phosphors,
the preparation method may no longer be limited to a single technology but a combination of two or even more technologies. For example, the hydrothermal-assisted light burning method has been applied to the preparation of MgAl$_2$O$_4$ phosphors, showing promising applications [12, 13].

Tb$^{3+}$ has a large absorption cross section at wide pump wavelength and is easily excited. Many scholars have used Tb$^{3+}$ widely in various fluorescent materials to obtain ideal green luminescence [14]. As a promising fluorescent material, MgAl$_2$O$_4$: Tb$^{3+}$ is expected to be used in various light-emitting devices and full-colour displays [15]. In recent years, some research results have been achieved on MgAl$_2$O$_4$: Tb$^{3+}$ phosphors, but these results are still relatively few. Gugliotti [16] and Motloung et al [17] studied the luminescence behaviour for low amounts of Tb$^{3+}$ (≤2 mol%) doped MgAl$_2$O$_4$ phosphors. The MgAl$_2$O$_4$: 2% Tb$^{3+}$ phosphor presented the highest luminescence intensity, and the colour could be tuned by changing the Tb$^{3+}$ content (≤2 mol%). For the first time, Valiev et al [18, 19] presented structural and spectroscopic investigations of MgAl$_2$O$_4$ ceramics doped with different concentrations of Tb$^{3+}$ ions (0.1, 1 and 5 wt%) fabricated by spark plasma sintering (SPS). However, there are still the few reports on the luminescence regularity of MgAl$_2$O$_4$ doped with higher concentrations of Tb$^{3+}$ ions. The formation of nonagglomerated powders is important to obtain high luminescence efficiency, especially the fluorescence intensity of nanorod-like phosphors with good dispersibility, which is significantly higher than the fluorescence intensity of other morphologies such as sphere-like, flower-like and tetrahedron morphologies [20, 21]. However, there are still few reports on nanorod-like MgAl$_2$O$_4$: Tb$^{3+}$ phosphors. Relevant studies have shown that nanorod-like phosphors with good dispersibility have more application advantages in light-emitting diode (LED) packaging materials [22, 23].

In view of these results, nanorod-like MgAl$_2$O$_4$: x% Tb$^{3+}$ (x = 1.0–6.0) phosphors were prepared by a hydrothermal-assisted light burning method. Under the excitation of 245 nm ultraviolet light, the fluorescence spectrum of phosphors was regulated by changing the doping amount of Tb$^{3+}$, and the chromaticity performance was characterized and analysed by CIE colour coordinates.

2. Experimental

2.1. Raw materials

Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and CO(NH$_2$)$_2$ are analytical pure reagents (99.50%) and purchased from Tianjin Damao Chemical Reagent Co. Ltd, Tb(NO$_3$)$_3$·6H$_2$O is a high purity reagent (99.99%) and purchased from Energy Chemical Co. Ltd The experimental water is pure water made by laboratory equipment, and absolute ethanol is analytical pure reagent.

2.2. Synthesis of MgAl$_2$O$_4$: Tb$^{3+}$ phosphors

Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Tb(NO$_3$)$_3$·6H$_2$O were weighed in stoichiometric amounts of MgAl$_2$O$_4$: x % (x/n) Tb$^{3+}$ (x = 1.0, 2.0, 3.0, 4.0, 5.0, 6.0) and mixed with a certain amount of pure water to maintain the Mg$^{2+}$ ion concentration in the nitrate solution at 0.05 mol·L$^{-1}$. Urea precipitants were added to the above nitrate solutions according to the ratio of n Mg$^{2+}$ : n Tb$^{3+}$ : n CO(NH$_2$)$_2$ = 1 : 2 : 30. All mixing was carried out at room temperature and stirring was continued for at least 30 min. The mixture was poured into a stainless-steel autoclave, and approximately 70% filling was maintained. The autoclave was placed in a drying oven at a certain temperature for 12 h. The hydrothermal products were washed several times alternately with pure water and absolute ethanol, and then dried at 80 °C for 6 h. The precursors were lightly burned in a muffle furnace at a certain temperature for 3 h to obtain the final phosphors.

2.3. Characterization

The crystal structure was characterized by x-ray diffraction (XRD) analysis (Empyrean X, Eindhoven, The Netherlands) equipped with Cu Ka radiation at the rate of 1° min$^{-1}$ in a 2θ range of 10° to 80°. The sample morphology was investigated by a field-emission scanning electron microscope (Supra 55, Zeiss, Oberkochen, Germany) with a working voltage of 5.0 kV. The emission spectra were recorded by using an F-7000 fluorescent spectra photometer equipped with a 150 W Xe lamp (Hitachi Limited, Tokyo, Japan).

3. Results and discussion

3.1. Structural characterization

The XRD patterns for precursors and light burning end-products at different hydrothermal temperatures are shown in figures 1(a) and (b), respectively. The hydrothermal products obtained at 100 °C–120 °C are biphasic precursors composed of Mg$_4$Al$_2$(OH)$_{14}$ (PDF No. 35-0964) and NH$_4$Al(OH)$_2$CO$_3$ (PDF No. 42-0250), from equations (1)–(2) [24]. As the hydrothermal temperature reaches 160 °C, the precursor phase of Mg$_4$Al$_2$(OH)$_{14}$ disappears, and the AlOOH (PDF No. 21-1307) phase appears. Because in an alkaline high-temperature
hydrothermal environment, Al$^{3+}$ will be transformed into relatively stable AlOOH instead of easily decomposed Mg$_4$Al$_2$(OH)$_{14}$. In addition, when the hydrothermal temperature is 120 °C, the light burning end-product has the best pure phase structure of MgAl$_2$O$_4$ (PDF No. 21-1152) (figure 1(b)). The amorphous MgAl$_2$O$_4$ solid solution and Al$_2$O$_3$ resulting from the thermal decomposition of Mg$_4$Al$_2$(OH)$_{14}$ and NH$_4$Al(OH)$_2$CO$_3$ were suggested to facilitate the formation of MgAl$_2$O$_4$ spinel [25]. Furthermore, the biphasic precursors at 120 °C have stronger peaks with better crystallinity (figure 1(a)). Therefore, the decomposition of the biphasic precursors with better crystallinity promotes the formation of amorphous products, which is important to obtain the final pure phase spinel phosphors.

$$2\text{Al}^{3+} + 4\text{Mg}^{2+} + 14\text{OH}^- \rightarrow \text{Mg}_4\text{Al}_2(\text{OH})_{14}$$  \hspace{1cm} (1)

$$\text{Al}^{3+} + \text{NH}_4^+ + 3\text{OH}^- + \text{HCO}_3^- \rightarrow \text{NH}_4\text{Al}($$\text{OH})$_2$CO$_3$ $\downarrow + \text{H}_2\text{O}$ \hspace{1cm} (2)

When the hydrothermal temperature was determined to be 120 °C, the XRD patterns of MgAl$_2$O$_4$: 1.0% Tb$^{3+}$ samples prepared by light calcination at different temperatures for 3 h are shown in figure 2. The diffraction peaks for the phosphors match the crystal planes of the standard MgAl$_2$O$_4$ structure. With increasing calcination temperature, the intensity of the diffraction peak increases and the peak width narrows. The results show that the crystallinity of the samples increases with increasing of light burning temperature.

From the above results, the hydrothermal and light burning temperatures were determined to be 120 °C and 1100 °C, respectively. The XRD patterns for MgAl$_2$O$_4$: x% Tb$^{3+}$ (x = 1.0–6.0) phosphors are shown in figure 3. The diffraction characteristic peaks of each sample can be well matched with the MgAl$_2$O$_4$ (PDF No.21–1152) without any impurity characteristics, indicating that the rare earth Tb$^{3+}$ ions can effectively enter the MgAl$_2$O$_4$.
lattice without affecting the spinel structure. Although the ionic radius for Tb\(^{3+}\) (0.92 Å) is larger than the ionic radius of Mg\(^{2+}\) (0.57 Å) and Al\(^{3+}\) (0.54 Å), when rare earth ions replace the Mg\(^{2+}\) sites in the spinel structure, the structures are more stable in energy and configuration [26]. Therefore, a larger Tb\(^{3+}\) ion occupying the Mg\(^{2+}\) site will lead to lattice expansion and increase the crystal plane spacing, resulting in a gradual shift of diffraction peaks to lower angles [27], as shown in figure 3(b). Furthermore, the cell parameters and volumes gradually increase with the Tb\(^{3+}\) ion doping content (table 1), which further confirms that Tb\(^{3+}\) ions effectively incorporate into the MgAl\(_2\)O\(_4\) host by occupying the Mg\(^{2+}\) sites. However, the occupation of Mg\(^{2+}\) sites by Tb\(^{3+}\) ions is a nonequivalent substitutional behaviour. To maintain charge balance, some Mg\(^{2+}\) and Al\(^{3+}\) ions may be inverted to form an inverse spinel structure, and some oxygen vacancies (V\(^0\), V\(^{2+}\)) may both compensate for positive charge defects [13].

### 3.2. Morphological characterization

Figure 4 shows the SEM images for MgAl\(_2\)O\(_4\): 1.0% Tb\(^{3+}\) phosphors prepared at different hydrothermal temperatures (100°C–160°C). The microscopic morphology for the phosphors changes with increasing of the hydrothermal temperature. When the hydrothermal temperature is 100°C, the phosphors exhibit an uneven rod-like morphology with some agglomerates (figure 4(a)). When the hydrothermal temperature is 120°C, the phosphors exhibit a uniform nanorod-like morphology under the action of the biphasic precursors with good crystallinity (figure 4(b)). As the hydrothermal temperature reaches 140°C, the rods increase in size and become micron-scale rods with good dispersion (figure 4(c)), but the phase analysis at this temperature is not satisfactory due to the inclusion of a small amount of MgO and amorphous Al\(_2\)O\(_3\) impurities (figure 1(b)). Continuing to raise the hydrothermal temperature to 160°C, the products are seen to be almost completely turned into flocculent aggregates (figure 4(d)), possibly caused by the high temperature hydrothermal generation of the boehmite AIOOH precursor (figure 1(a)). The bond energy of AlOOH is relatively strong, and AIOOH easily causes local gelatinous agglomeration, which is unfavourable for the formation of spinel [28].

SEM images of MgAl\(_2\)O\(_4\): 1.0% Tb\(^{3+}\) phosphors prepared at different light burning temperatures are shown in figures 5(a)–(c). The microscopic morphologies of the phosphors change with increasing calcination temperature. When the temperature is 900°C, the prepared phosphors exhibit irregular microscopic morphology due to poor crystallinity. When the temperature is 1000°C, nanorods appear, but there are still a small number of agglomerates. Continuing to raise the temperature to 1100°C, the phosphors are regular.

![Figure 3](image-url) (a) XRD patterns for the MgAl\(_2\)O\(_4\): x% Tb\(^{3+}\) (x = 1.0–6.0) samples; (b) Amplified diffraction peaks of (311) plane.

![Table 1](image-url)

| Tb\(^{3+}\) doping content (x%) | Cell parameter (Å) | Cell vol (Å\(^3\)) |
|---------------------------------|--------------------|--------------------|
| 1.0                             | 8.0252             | 516.8519           |
| 2.0                             | 8.0188             | 515.6114           |
| 3.0                             | 8.0429             | 520.2736           |
| 4.0                             | 8.0478             | 521.2400           |
| 5.0                             | 8.0717             | 525.8985           |
| 6.0                             | 8.0720             | 525.9264           |
nanorods with uniform appearance and excellent dispersion, and the diameter of the rod is approximately 200 nm (figure 5(c)). With an increasing Tb$^{3+}$ ion doping amount, the main nanorod structure for the phosphor does not change significantly, but the surface for the rod is smooth at 1.0% Tb$^{3+}$ doping, while the surface
becomes rough at 5.0% (figure 5(d)). According to the XRD experimental results (figure 3(a)), the diffraction peak intensity of the 1.0% Tb³⁺-doped sample is significantly higher than the diffraction peak intensity of 5%. Generally, the decrease in the peak intensity as Tb³⁺ mol% is increased can be explained by the destruction of the crystalline quality during the growth of MgAl₂O₄ crystals [17]. The more rare earth ions enter the host lattice, the easier it is to cause lattice distortion, resulting in a decrease in crystallinity and a rough surface morphology.

3.3. Fluorescence properties

The excitation spectrum for the MgAl₂O₄: 1% Tb³⁺ phosphor was measured at 545 nm (figure 6(a)). The sample has a broad excitation band between 220–270 nm in the UV region with a peak at 245 nm. This broad band is attributed to the matrix absorption band and the 4f⁸ → 4f⁷5d¹ transition for Tb³⁺. Figure 6(b) shows the emission spectra measured for MgAl₂O₄: x% Tb³⁺ (x = 1.0–6.0) samples under 245 nm light excitation. The series of phosphors can be effectively excited by ultraviolet light, and the characteristic emission peaks are located at 492, 546, 588 and 624 nm, which are attributed to the 5D₄ → 7F₃ (J = 6, 5, 4, 3) transition of Tb³⁺, respectively. The strongest emission peaks for all samples are located at 546 nm and change regularly with increasing Tb³⁺ doping amount. With increasing the Tb³⁺ doping amount to 4.0%, the fluorescence intensity reaches the maximum value. Continuing to increase the doping amount of Tb³⁺ weakens the luminescence intensity due to concentration quenching.

To better understand the fluorescence mechanism, a energy level diagram for the MgAl₂O₄: Tb³⁺ phosphor transition was drawn, as shown in figure 7. Under irradiation with λₑₓ = 245 nm UV light, electrons are directly excited from the valence band of the host to the conduction band. Then, through the energy transfer (ET) process, the electrons complete the population at the 4f⁷5d¹ level of Tb³⁺. The electrons undergo nonradiative relaxation (NR) to the 5D₄ excited state energy level, and finally complete the 5D₄ → 7F₃ (J = 6, 5, 4, 3) transition in the form of radiation, releasing 492, 546, 588 and 624 nm emission light, respectively.

The colour performance for MgAl₂O₄: x% Tb³⁺ (x = 1.0–6.0) phosphor application is evaluated by the CIE chromaticity diagram and coordinates (x, y), as shown in figure 8. The emission range for the series of phosphors is mainly in the green spectral region. The correlated colour temperature (CCT) and colour purity values for phosphor were calculated in table 2 using the obtained CIE coordinates (x, y) data as follows:

| Tb³⁺ doping amount (x) | CIE coordinate (x, y) | CCT (K) | Colour purity (%) |
|------------------------|-----------------------|---------|-------------------|
| 1.0                    | (0.2773, 0.4402)      | 7188    | 32.48             |
| 2.0                    | (0.2810, 0.4445)      | 7036    | 33.41             |
| 3.0                    | (0.3082, 0.4899)      | 6070    | 43.31             |
| 4.0                    | (0.3171, 0.5290)      | 5845    | 53.30             |
| 5.0                    | (0.3073, 0.5087)      | 6087    | 48.00             |
| 6.0                    | (0.3019, 0.4841)      | 6271    | 41.95             |
when the doping amount of Tb$^{3+}$ is 4.0%, the coordinate reaches the maximum value $(0.3171, 0.5290)$, indicating that the green luminescence purity is the best at this time. The CCT values for these phosphors are all greater than 5000 K, showing typical cold light emission and good application prospects in solid-state display devices [30]. Among the phosphors, MgAl$_2$O$_4$: 4.0% Tb$^{3+}$ has the highest colour purity value of 53.50%, showing the best luminous colour quality. Compared with the same concentration of Tb$^{3+}$-doped aluminosilicate and zirconate phosphors, the MgAl$_2$O$_4$: Tb$^{3+}$ series has a greater advantage in green colour purity [30, 31].

$$\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5541.31 \quad (3)$$

$$\text{colourpurity} = \frac{[(x - x_0)^2 + (y - y_0)^2]^{\frac{1}{2}}}{[(x_e - x_0)^2 + (y_e - y_0)^2]^{\frac{1}{2}}} \quad (4)$$

where $n = (x-x_c)/(y-y_c)$ was defined, $(x, y)$ is the CIE coordinate for the prepared samples, $(x_c, y_c)$ is the coordinate of the centre point that can be identified as $(0.3320, 0.1858)$, $(x_0, y_0)$ is the coordinate of the white
illuminant point (0.33, 0.33), and \((x_g, y_g)\) is the coordinate of the dominant green wavelength for the prepared samples.

4. Conclusions

Nanorod-like \(\text{MgAl}_2\text{O}_4: \text{Tb}^{3+}\) phosphors were obtained by a hydrothermal-assisted light burning method. When the the hydrothermal and light burning temperatures were determined to be 120 °C and 1100 °C, respectively, the crystallinity for \(\text{Mg}_4\text{Al}_2(\text{OH})_6\text{O}_4\) and \(\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3\) biphase precursors is the best, which is conducive to generating pure phase \(\text{MgAl}_2\text{O}_4\) rod-like phosphors with a diameter of 200 nm. In the \(\text{MgAl}_2\text{O}_4: x \% \text{Tb}^{3+}\) \((x = 1.0–6.0)\) phosphors, \(\text{Tb}^{3+}\) can enter the \(\text{MgAl}_2\text{O}_4\) lattice without changing the spinel structure, but it will cause lattice distortion and reduce the surface quality of the rods. The main emission peaks for series of phosphors are located in the green light region of 546 nm. The \(\text{MgAl}_2\text{O}_4: 4.0\% \text{Tb}^{3+}\) phosphor has the highest fluorescence intensity and shows the best colour quality. Its CIE coordinates \((x, y)\), CCT and colour purity are determined to be (0.3171, 0.5290), 5845 K and 53.50%, respectively. The series of phosphors exhibit a typical cold green light emission and has good application prospects in solid-state display devices.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare that they have no conflict of interest.

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