

DESIGN, SYNTHESIS, AND THERMAL STABILITY OF RARE EARTH LUMINESCENT MATERIALS

by

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As a new generation of luminescent materials, aluminate rare earth materials have the characteristics of long luminescent time, adjustable wavelength and high brightness. Aluminate rare earth luminescent materials were prepared by high temperature solid-state method, and the luminescent properties of the luminescent materials were studied. Firstly, the author synthesized magnesium aluminate, calcium aluminates, and zinc aluminate matrix by combustion method. Then aluminate rare earth luminescent materials were prepared by high temperature solid phase method through raw material distribution, raw material mixing, drying, calcination, and post-treatment. Finally, a fluorescence spectrophotometer was used to measure the excitation and emission spectra of the prepared sample material. The research results indicate that the excitation wavelength does not affect the relationship between the emission wavelength and light intensity, the emission spectra of $\text{MgAl}_2\text{O}_4:\text{Tb}^{3+}$ and $\text{CaAl}_2\text{O}_4:\text{Tb}^{3+}$ exhibit narrowband transition emission states; When the mass fraction of rare earth factor Eu^{3+} in the activator is 6% and the temperature is 1300 °C, the emission peak intensity of the luminescent material reaches its maximum value, and the luminescence intensity is the best.

Key words: excitation spectrum, luminescence, rare earth factor, light intensity, high temperature solid-phase method, aluminate rare earth

Introduction

Based on the research achievements of teachers, research-oriented experiments transform the forefront of subject development into teaching practice content, adopting a teaching model of teacher teaching, student practice, and teacher-student discussion, with a focus on cultivating students' innovative and practical abilities, so as to better match talent cultivation with social needs. They are widely used in w-LED, fluorescent lamps, flat panel displays, conversion luminescent materials, and coatings [1]. However, there are few reports on converting related research content into teaching resources [2, 3]. As is well known, white light w-LED are mercury free and pollution-free, with high electro-optic conversion efficiency. They are known as the most valuable green lighting sources and have received attention from the government and society. As a key component in assembling w-LED, luminescent materials have extremely important commercial value. In the context of the aforementioned social needs and cutting-edge scientific development, with the application of chemical technology in the energy-saving and environmental protection industry to promote sustainable social development as

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the starting point, a comprehensive experimental project titled *Preparation of Silicate Based Rare Earth Luminescent Materials* has been developed for undergraduate students majoring in chemistry, chemical engineering, materials, and other related fields. The experiment selected $\text{NaBa}_3\text{La}_3\text{Si}_6\text{O}_{20}$. In recent years, the research on rare earth doped inorganic nanoluminescent materials has attracted great attention, mainly because trivalent rare earth ions have long-lived multi-level energy levels, which can be effectively utilized by converting short wavelength ultraviolet light into visible light in different wavelength ranges through different rare earth doped inorganic fluorescent powders [4]. White LED, as a new type of lighting source, has advantages such as small size, high luminous efficiency, good reliability, energy conservation, long lifespan, and mercury free design. At present, there are two ways to synthesize white LED: one is to combine blue LED chips with yellow emitting phosphors to form white light, but there is a lack of red light in the emission spectrum of this white light, and the yellow light changes slower than the blue light under high current, resulting in poor color rendering performance and limitations in application [5, 6]. The other way is to use near ultraviolet (UV) InGaN chip to excite three primary phosphors and compound them to get white light. The disadvantage is that the phosphors have low near ultraviolet luminous efficiency and low color index. Given the aforementioned reasons, researching efficient and stable red fluorescent powders has become an important task. From an application perspective, blue and green long afterglow materials are relatively mature in application, while research on red long afterglow materials is relatively weak. Therefore, further research and development of red long afterglow luminescent materials is crucial. Inorganic luminescent materials mainly consist of a matrix material system and a small amount of activator ions doped into the matrix material. Due to the excellent thermal stability, strong mechanical properties, environmental friendliness, and various types of oxides such as Gd_2O_3 and La_2O_3 in matrix materials, they have become a focus of research on inorganic luminescence. Dry media reaction is a traditional method of powder preparation. Specifically, the solid raw materials required for synthesizing the powder are mixed and ground evenly, then placed in a crucible, placed in a high temperature furnace, calcined at a certain temperature, and then naturally cooled to room temperature. After crushing, the required fluorescent powder is obtained [7]. The advantages of this method are simple preparation process, simple operation, easy control of reaction conditions, high atomic utilization rate, mature anal technology, and easy industrialization. There are many reports on the preparation of up conversion inorganic luminescent materials by dry media reaction. Generally, it is a simple and effective method to prepare phosphors to study the up conversion luminescence mechanism. The preparation of aluminate rare earth luminescent materials by high temperature solid state method includes two parts: batching and calcination. In the batching preparation, the obtained reactants are fully mixed, the contact area of reactants is increased, the diffusion speed of molecules and ions in the reactants is improved, and the reaction speed is improved. The purpose of calcination is to cause a chemical reaction between reactants to obtain a matrix with a certain crystal structure, and to add activator rare earth ions to the matrix to form a luminescent center. The activator rare earth ions and matrix mixed powder are obtained as samples, and the luminescence characteristics of the sample material are analyzed. Aluminate rare earth luminescent material was prepared by high temperature solid state method and its luminescence properties were studied. First, magnesium aluminate, calcium aluminate, and zinc aluminate matrix were synthesized by combustion method, then aluminate was prepared by high temperature solid phase method by raw material distribution, mixing, drying, calcination and post-treatment, and the excitation and emission spectra of the prepared samples were determined by fluorescence spectrophotometer.

Preparation and luminescence of aluminate rare earth luminescent materials by high temperature solid state method

Combustion synthesis of aluminate matrix

Magnesium aluminate, calcium aluminates, and zinc aluminate matrices were obtained by combustion synthesis. Oxidants and reducing agents are the main components of raw materials used in combustion synthesis methods. Cationic nitrates are generally used as oxidants, which have excellent water solubility and meet the standards for preparing suitable solutions. The reason for using organic compounds as reducing agents is that they have the characteristics of simple structural composition and low carbon content, which can solve the problem of carbon residue pollution. Moreover, when reacting in high temperature environments, the gas produced is not toxic. In addition, the reducing agent should be easily soluble in water and have strong complexing ability with metal ions, which can effectively solve the problem of burning and volatilizing to produce crystals that break the overall uniformity. Aluminum nitrate, alkaline earth metal nitrate, and urea are the main raw materials for obtaining the matrix, in order to ensure the experimental effect of luminescent materials, high purity experimental materials were selected, as shown in tab. 1.

Table 1. Raw material names and parameters

Raw material name	Chemical formula	Purity [%]
Urea	H_2NCONH_2	A.R
Aluminum nitrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	A.R
Magnesium nitrate	$\text{Mg}(\text{NO}_3)_2$	A.R
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	A.R
Zinc nitrate	$\text{Zn}(\text{NO}_3)_2$	A.R
Concentrated nitric acid	HNO_3	A.R
Terbium oxide	Tb_2O_3	98.80
Europium oxide	Eu_2O_3	98.80
Cerium nitrates	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	98.80
Dysprosium(III) oxide	Dy_2O_3	98.80
Boric acid	H_3BO_3	A.R

The aluminate rare earth luminescent materials magnesium aluminate, calcium aluminates, and zinc aluminate matrix are obtained according to the aforementioned method, and the aluminate rare earth luminescent materials are continuously prepared by the high temperature solid state method.

Preparation of aluminate rare earth luminescent materials

The aluminate rare earth luminescent materials are prepared by high temperature solid phase method, and the temperature range is 1020~1500 °C. Contact, reaction, nucleation, and crystal growth reaction are the main steps of preparing aluminate rare earth luminescent materials by high temperature solid phase method, this method has the characteristics of simplicity, convenience, and high frequency of use. In order to obtain high quality aluminate rare earth luminescent materials, save research costs and simplify the preparation process, the design and preparation steps are:

Step 1: Raw material allocation. Select high quality experimental raw materials from the perspectives of manufacturer, production date, particle size, purity, *etc.* The quality of the raw materials is calculated based on the corresponding chemical formula, and high precision balance is used to weigh the raw materials. The quality of the raw materials is about 12 g.

Step 2: Mix the raw materials. Store the allocated raw materials in a ball milling tank, and pour a certain amount of agate balls and anhydrous ethanol. Mix the aforementioned raw materials in a ball milling process with a duration of 120 minutes and a speed of 320 rpm.

Step 3: Drying. Use an agate mortar to grind and mix the raw materials, and terminate when they meet the uniformity standard. Set the temperature of the drying oven to 65 °C and continue drying for 5 hours.

Step 4: Calcination. Grind and dry the powder material again, place it in an Al₂O₃ crucible, and then use a high temperature furnace for calcination at a temperature of 1020-1500 °C. Set the heating rate of the calciner to 4.5 °C per minute, continuously calcine for 4.2 hours, and the calciner will naturally cool down. Obtaining high valence rare earth ion luminescent materials by sintering directly in air. Low valent rare earth ion luminescent materials were obtained by calcination in a reducing atmosphere.

Step 5: Post processing. Grinding, powder selection, and powder washing are several methods of post-processing. The process of preparing aluminate rare earth luminescent materials by high temperature solid state method is shown in fig. 1.

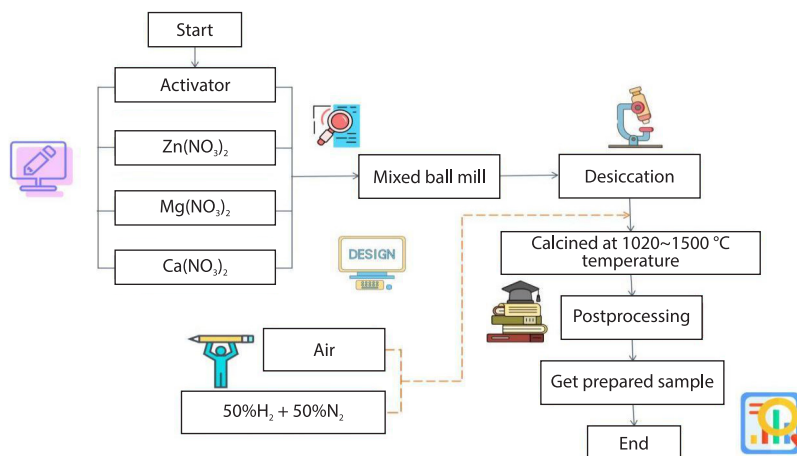


Figure 1. Process of preparing aluminate rare earth luminescent materials by high temperature solid state method

Electronic Analytical balance, with measurement accuracy of 0.001 g. Crucible, with a specification size of 100 mL. The SJG-16A high temperature resistance furnace, with a normal operating temperature of 1500 °C and a size of 500 mm × 300 mm × 17 mm. Diffractometer, the UV lamp, and low pressure mercury lamp. The emission spectrum refers to the intensity and energy arrangement of different wavelengths of light emitted by a certain wavelength excited luminescent material. Emission and excitation spectra are good indicators for describing the luminescent properties of luminescent materials. Studying the emission and excitation spectra of luminescent materials cannot only grasp the luminescent mechanism of luminescent materials, but also understand the luminescent properties of luminescent samples under different experimental environments.

Experimental results

Study on the luminescence of activator rare earth factor Tb_3 mixed with different substrates

A Tb^{3+} doped magnesium aluminate based luminescent powder sample was prepared by high temperature solid-state method. Observing the luminescent powder sample, it can be seen that the luminescent powder cannot emit light under natural light irradiation. Under the stimulation of ultraviolet light, the luminescent powder emits a yellow green color light. Using a fluorescence spectrophotometer to test the excitation and emission spectra of the sample, the luminescence of Tb^{3+} in magnesium aluminate matrix was studied. The effect of Tb^{3+} mass fraction on the luminescence performance of magnesium aluminate, tab. 2.

Table 2. Effect of Tb^{3+} mass fraction on the luminescence performance of magnesium aluminate

Tb^{3+} mass fraction 1%	Glow	Tb^{3+} mass fraction 1%	Glow
4.51	Not emitting light	7.01	Strong yellow green light
5.01	Not emitting light	7.51	Yellowish green light weakens
5.51	Weak yellow green light	8.01	Weak yellow green light
6.01	Weak yellow green light	8.51	Not emitting light
6.51	Weak yellow green light	9.01	Not emitting light

From tab. 2, it can be seen that when the mass fraction of Tb^{3+} is between 5.51-8.01%, the sample has a good luminescence effect, with the luminescence effect mainly being yellow green light. When the Tb^{3+} mass fraction is too low or too high, that is, below 5.51% or above 8.01%, the sample has poor luminescence effect and is almost in a non-luminescent state. The experimental results indicate that, when the mass fraction of Tb^{3+} is small, the amount of Tb^{3+} entering $MgAl_2O_4$ to form crystals and form luminescent centers in the sample is relatively small, resulting in no luminescence. When the mass fraction of Tb^{3+} is too high, the number of Tb^{3+} entering the $MgAl_2O_4$ crystal to form the luminescent center in the sample is high. Due to multiple Tb^{3+} being in the same crystal and the existence of ion repulsion between Tb^{3+} , the transition trend during crystal excitation is weakened, resulting in the sample not emitting light.

Study on the luminescence of Eu^{3+} and $ZnAl_2O_4$ mixtures as activators

The $ZnAl_2O_4:Eu^{3+}$ powder was used as the sample for studying the luminescence characteristics. The luminescence intensities of samples with different mass fractions of $ZnAl_2O_4:Eu^{3+}$ are shown in fig. 2, and the variation curve between the luminescence intensity of $ZnAl_2O_4:Eu^{3+}$ and the mass fraction of Eu^{3+} is shown in fig. 3.

From fig. 2, it can be seen that when the mass fraction of Eu^{3+} is 8%, the luminescence intensity of $ZnAl_2O_4:Eu^{3+}$ is the lowest. When the mass fraction of Eu^{3+} is 6%, the luminescence intensity of $ZnAl_2O_4:Eu^{3+}$ is the highest [8]. When the mass fraction of Eu^{3+} is 8% and the wavelength is 526 nm, the luminescence intensity of $ZnAl_2O_4:Eu^{3+}$ is the lowest, and the highest intensity is 31 a.u. When the mass fraction of Eu^{3+} is 6% and the wavelength is 534 nm, the highest luminescence intensity of $ZnAl_2O_4:Eu^{3+}$ is 98.1 a.u. Therefore, under different Eu^{3+} mass fractions, there is a significant change in the luminescence intensity of $ZnAl_2O_4:Eu^{3+}$. As the Eu^{3+} mass fraction increases, the luminescence intensity of $ZnAl_2O_4:Eu^{3+}$ shows a trend of first increasing and then decreasing. As the mass fraction continues to increase, the luminescence intensity of $ZnAl_2O_4:Eu^{3+}$ gradually decreases. From Curves 2, 4, and 3 in

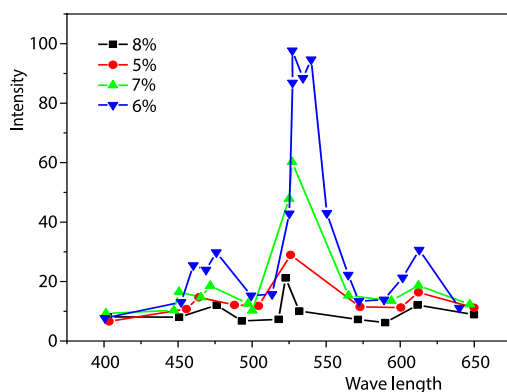


Figure 2. Luminescence intensities of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ samples with different mass fractions

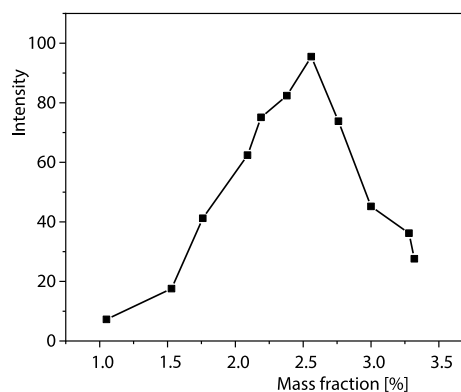


Figure 3. Variation curve of Eu^{3+} luminescence intensity and Eu^{3+} mass fraction in ZnAl_2O_4

fig. 2, it can be seen that as the mass fraction of Eu^{3+} in $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ increases, the emission peak intensity increases. When the mass fraction of activating agent Eu^{3+} is 6%, the emission peak intensity reaches its maximum value (Curves 1-4 of fig. 2 are 8%, 5%, 7%, and 6%, respectively). It can be seen from Curves 4, 3, 1, and 3 in fig. 2 that, when the mass fraction of Eu^{3+} in $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ exceeds 6%, the emission peak intensity decreases. When the mass fraction of Eu^{3+} in $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ exceeds 8%, the emission peak intensity quenches. The relationship between the critical transfer distance and the mass fraction of Eu^{3+} in $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ samples:

$$R_c \approx 2 \left[\frac{3V}{4\pi x_e N} \right]^{1/3} \quad (1)$$

where V is the powder crystal parameter, N – the number of crystals, X_e – the critical Eu^{3+} mass fraction and the value is 0.04. Substituting the aforementioned values into eq. (1), $R_c = 1.2506$ nm, while the critical distance of exchange interaction of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ sample is 0.5 nm. The value is much smaller than this value, indicating that concentration quenching is not caused by exchange interactions. According to Dexter theory, the relationship between the critical transfer distance and the mass fraction of Eu^{3+} in $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ powder crystals is the interaction between electric multipoles. When this interaction is enhanced, energy resonance phenomenon occurs. If a quenching channel is generated during the energy transfer process, this energy will be released in the quenching channel, causing $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ to not emit light. The luminescence and quenching of luminescent materials are competitive. If the mass fraction of Eu^{3+} is too high, the probability of excitation energy transfer in the luminescent center will be much better than the probability of conversion into luminescent transitions. The probability of encountering quenching channels during multiple energy transfers also increases, leading to a decrease in the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$.

The high temperature solid-phase temperature not only affects the crystal structure of the mixture, but also affects the luminescence properties of the mixture. The luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ powder and the emission spectrum intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ samples at different high temperature solid-phase temperatures are shown in figs. 4 and 5, respectively.

From fig. 4, it can be seen that when the high temperature solid phase temperature is 1200.9 °C, the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ is the lowest. When the high temperature solid phase temperature is 1300 °C, the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ is the high-

est [9, 10]. When the high temperature solid phase temperature is 1200 °C and the wavelength is 527 nm, the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ is the lowest, and the highest intensity is 23.4 a.u. When the high temperature solid phase temperature is 1300.9 °C and the wavelength is 536 nm, the highest luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ is 98.6 a.u. When the high temperature solid phase temperature is 1400 °C and the wavelength is 546 nm, the highest luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ is 58.1 a.u. When the high temperature solid phase temperature is 1500 °C and the wavelength is 436 nm, the highest luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ is 30.1 a.u. Therefore, there is a significant change in the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ under different high temperature solid phase temperatures. As the high temperature solid phase temperature increases, the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ shows a trend of first increasing and then decreasing, among them, when the high temperature solid phase temperature is 1300 °C, the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ is the highest. As the high temperature solid phase temperature increases to 1500 °C, the luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ gradually decreases [11]. From figs. 4 and 5, it can be seen that as the high temperature solid phase temperature increases from 1200-1300 °C, the emission spectral intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ powder gradually increases. As the high temperature solid phase temperature increases from 1300-1500 °C, the emission spectral intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ powder gradually decreases.

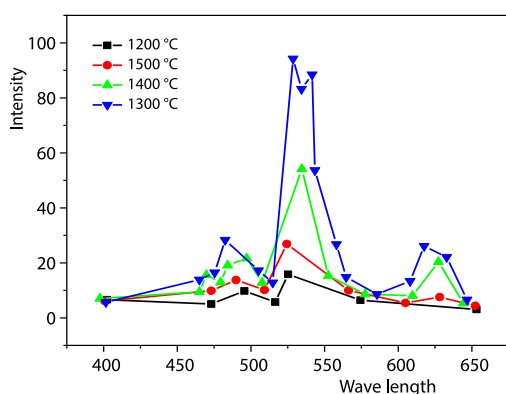


Figure 4. Luminescence intensity of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ powder at different high temperature solid phase temperatures

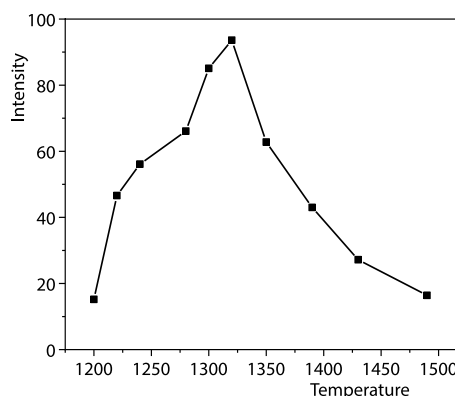


Figure 5. Temperature dependent emission spectral intensity curve of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ sample

Conclusion

The aluminate rare earth luminescent materials were prepared by high temperature solid state method, and the luminescent characteristics of the materials were studied in detail, in order to provide effective basis for mastering the luminescence mechanism of luminescent materials and understanding the factors affecting their luminescence performance. The research results indicate that the mass fraction of Eu^{3+} as an activator and the temperature both affect the luminescence characteristics of ZnAl_2O_4 rare earth luminescent materials. The Eu^{3+} mass fraction and temperature should be selected according to the actual research situation, and the two parameters have a non-linear relationship with the luminescence intensity of ZnAl_2O_4 rare earth luminescent materials. The preparation of aluminate rare earth luminescent materials by high temperature solid-state method has the advantages of simple process and low cost. However, compared to traditional methods, this method has longer calcination reaction time and higher

calcination temperature, in the future research on the preparation of luminescent materials, new preparation methods such as microwave method and hydrothermal method can be further used to improve the shortcomings and defects in the process of preparing aluminate rare earth luminescent materials by high temperature solid state method.

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