

Preparation of Rare Earth Doped Silicate Material with High Temperature Solid State Reaction Method and the Research on Luminescent Property

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It aims at giving analysis to the preparation of rare earth doped silicate material with high temperature solid state reaction method and the luminescent property. This paper mainly uses the high temperature solid state method in the preparation of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ fluorescent powder material, and it explores the relevant technological parameters of high temperature solid state method and the luminescent property. It is discovered from research that the best calcination temperature of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ fluorescent powder material is 11500C, doping contents of Eu^{3+} , Ce^{3+} and Tb^{3+} can affect the luminescent property, and the material is best to be warm white. High temperature solid state reaction method is a technological means of fluorescent powder preparation, which deserves applied research.

1. Introduction

In recent years, energy-saving and environment-friendly light source becomes the hot content researched by the people gradually. Rare earth ion Eu^{3+} is a more typical transition ion, which makes the object emitting red light and having certain application value in the aspect of display material and lighting equipment. Rare earth ion Ce^{3+} can absorb broadband and promote luminescent efficiency of luminescent material. Rare earth ion Tb^{3+} has some positive effect on the green luminescent material, and there is certain relevance between ion concentration and emission wavelength. As it may play a role in the luminescent material by doping some ion of rare earth in silicate material, many domestic and overseas scholars have researched and explored the ways of making luminescent material.

In this paper, high temperature solid state reaction method is mainly used in the preparation of luminescent material, and it gives research and analysis to luminescent property of the luminescent material prepared by rare earth doped silicate material. Moreover, it firstly explores raw materials, equipment construction conditions and construction technology of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ fluorescent powder prepared by rare earth doped silicate material; secondly, it gives research on the performance analysis method, and explores the luminescence property research technology and research method of the luminescence material of fluorescent powder; finally, it conducts research on the fluorescent powder material prepared by rare earth doped silicate material with high temperature solid state reaction method, analyzes luminescence property of the luminescence material, and researches and explores feasibility of the luminescent material preparation method.

2. Literature review

There are two kinds of luminescence spectra of rare earth ions in the crystal, one is the broadband spectrum, that is, the 4f-5d transition broadband spectrum, and the 5D energy level is higher. Therefore, the broadband spectrum of the 4f-5d transition is mainly concentrated in the vacuum ultraviolet region, but the Eu^{2+} , Ce^{3+} , Tb^{3+} plasma has the spectrum in the visible region, because its d electrons are easily affected by the crystal

field. The spectral intensity is large, the lifetime is short, and the spectral bandwidth can be used to scintillation. The other is the sharp linear spectrum, which comes from the interlevel transition in the 4f group, that is, the f-f transition, the typical rare earth ions are Eu^{3+} , Dy^{3+} , Sm^{3+} and so on. Their transition is almost unaffected by the crystal field of the base, so it is with the luminescence intensity Low, long life and sharp luminescent band. In 1993, Nakamura blue ray LED was first developed in Japan, and the emergence of blue ray LED promoted the development of white LED. After that, Nakamura and Schlotter package blue light tube and yellow phosphor and get white LED. In 1997, Japanese company invented the first commercial white LED, opening the first step of white LED manufacturing. After twenty-first Century, the white chip LED and white light were obtained by packaging the ultraviolet chip and three primary colors (red, green and blue). White light LED has long life, small size, energy saving and environmental protection. It is another generation of lighting source after incandescent lamp, fluorescent lamp and high-pressure gas discharge lamp. It has a bright future and wide application.

At present, the main ways to produce white LED include fluorescence conversion technology and three colour multi chip hybrid technology. The implementation of this technology mainly through the following ways: firstly, the blue light LED chip coated with blue light emitting yellow phosphor, LED chip fired blue light emitting yellow light after emitting blue light, blue light and yellow light compound to white light; secondly, blue light LED chip coated with blue light and green light phosphor, red light, red light, Blue light and green light are mixed together for white light, that is, the white light LED is emitted; thirdly, the red, green and blue light phosphors can be coated on the UV / purple LED chip which can be stimulated by ultraviolet light / violet light, and the white light is obtained after the combination of three kinds of light colours.

Zhai and others pointed out that the LED chip was coated with red, green and blue phosphors excited by ultraviolet / violet light, and the three kinds of light and color were combined to get white light. Three basic color multi chip hybrid technology is the combination of three kinds of LED chips, red, green and blue, and three kinds of light mixed with white light. This technology has the advantages of high luminous efficiency and adjustable color temperature. But because of the different light-emitting life of each LED, the light color is easily deviated from the color (Zhai et al., 2011). The production technology of blue light LED chip is mature and has been widely produced. The use of UV / violet light chip and three basic colour LED chip to produce white light has become the main development direction because of the advantages of high luminous efficiency and high colour temperature selectivity.

At present, the most widely used white LED is the form of blue LED chip and the phosphor that can be excited by it. In 1996, the YAG: Ce^{3+} phosphors found in Japan could be effectively excited by blue light LED chips, and the emission wavelengths ranged from 500nm to 750nm light, and blue light and yellow light were mixed into white light. Ding Jianhong and others Used Gd^{3+} to partially replace Y^{3+} , and the emission light has red shift phenomenon. Jiang and others found that the emission peak of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ under blue light is 535nm green light. Wang and others adopt high temperature solid state reaction method to synthesize phosphor $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$), which can be excited by near ultraviolet, the emission range is 550nm to 750nm, Eu^{2+} emission spectrum is red shift, $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ is a new type of red phosphor, and it is well used in the field of white LED. Yang and other $\text{SrZnO}_2:\text{Sm}^{3+}$ phosphors are synthesized by combustion method. The red light can be emitted from 600nm to 730nm by effective excitation in the purple light region. The main emission peaks are located at 607nm and 655nm, respectively (Wang et al., 2014).

Rare earth doped silica-based phosphors have been widely used in the research of phosphors. They are one of the main sources of phosphors for white LED. Liu and others synthesized red emitting M_2SiO_4 ($\text{M}=\text{Ba}, \text{Sr}$ and Ca): Eu^{3+} and Sm^{3+} Phosphors by solid state reaction. It can be seen from the emission spectrum and excitation spectrum that the phosphor emits strong red light when ultraviolet light at 395nm wavelength and blue light excited at 466nm. The charge compensation of R^+ ($\text{R}^+=\text{Li}^+, \text{Na}^+, \text{K}^+$) greatly enhanced the luminous intensity of $\text{M}_2\text{SiO}_4:\text{Eu}^{3+}$ and $\text{M}_2\text{SiO}_4:\text{Sm}^{3+}$ phosphors (Liu et al., 2012). The Tshabalala phosphor was synthesized by the high temperature solid state reaction method. When the sample was excited by the wavelength of 350nm excitation, the emission peaks of the $\text{Sr}_2\text{SiO}_4:\text{Dy}^{3+}$ phosphors were in 486nm, 575nm and 668nm respectively, corresponding to $(4\text{F}_9/2-6\text{H}15/2)$, $(4\text{F}_9/2-5\text{H}13/2)$ and $(4\text{F}_9/2-6\text{H}11/2)$ electron transition respectively. These emission light formed white light as we wanted (Tshabalala et al., 2014). Ju synthesized phosphor by the solid-phase reaction method, and the luminescence characteristics of the $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ were studied. The emission spectrum of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphors was wide-band and the emission range from blue to yellow, which made the $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphors a good luminescent material (Ju et al., 2013). Liu and others use high temperature solid state reaction to synthesize $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$, Sm^{3+} -series phosphor. The samples are excited by the excitation light of purple light 420nm, and the samples are emitted 558nm green light. The Sm^{3+} can improve the luminescence intensity of Eu^{2+} (Liu et al., 2012). Yellow emitting phosphors are also studied with $\text{CaSiO}_3:\text{Eu}^{2+}$, $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$ and so on.

Sun and others prepared three kinds of phosphors containing Eu^{3+} : $\text{Na}_2\text{Si}_{20}\text{O}_{41}\cdot 11\text{H}_2\text{O}$, $\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{Si}_8\text{O}_{17}\cdot 9\text{H}_2\text{O}$. It is found that the luminescence strength of the sample is influenced by the concentration of europium ions and the calcination temperature. In addition, the luminescence intensity of the sample will be

changed even if the concentration of the europium ions is the same. Therefore, the difference of the silicate type and the difference of the cation between the different layers of the same type will have a significant effect on the luminescence of the rare earth ions (Sun et al., 2012). Mandal and others through ion exchange, solution treatment and subsequent vulcanization to prepare two-dimensional ZnS nanoscale between Na-4 mica layer. This method first makes Zn^{2+} replace the mica interlayer Na^+ through ion exchange, and then a series of chemical reactions can be used to prepare the ZnS of nanoscale nodal structure through a series of chemical reactions (Mandal et al., 2012).

To sum up, the above research work mainly carries out LED white light luminescent materials for rare earth doped silicate luminescent materials, but the luminescence efficiency, luminescence spectrum and application performance need to be further improved. Therefore, based on the above research status, the preparation process and luminescence properties of the rare earth doped silicate luminescent materials are studied by selecting strontium silicate, and the luminescent materials are synthesized by high temperature solid state reaction and sol-gel method, and the structure and luminescence properties of the samples are studied.

3. Method

Calculate stoichiometric ratio of each raw material, give accurate weighing, dissolve Eu_2O_3 , Ce_2O_3 and Tb_4O_7 in appropriate nitric acid solution respectively to prepare $Eu(NO_3)_3$, $Ce(NO_3)_3$ and $Tb(NO_3)_3$ Solutions with certain concentration, and take constant volume with volumetric flask and set aside. Place the well-weighed powders of $Ca(NO_3)_2$, $Mg(NO_3)_2$ and $CO(NH_2)_2$ in a mortar, give grinding for 30 min to ensure uniform mixing, and obtain powder A; put a little ethyl alcohol in the well-weighed TEOS for hydrolysis, and obtain solution B; put the well-grinded powder A in the beaker with B, place the beaker on a magnetic stirrer, give stirring for 30min, and obtain the evenly mixed solution C. Heat up muffle furnace to a certain temperature in advance, and then push the material C to be sintered in crucible in the muffle furnace, close furnace door rapidly to start acute combustion, obtain fluffy luminescent material D after completing combustion, and cool it for use. The flow chart of $Ca_2MgSi_2O_7$ fluorescent powder preparation with solution-combustion method is as shown in the Figure 1 below.

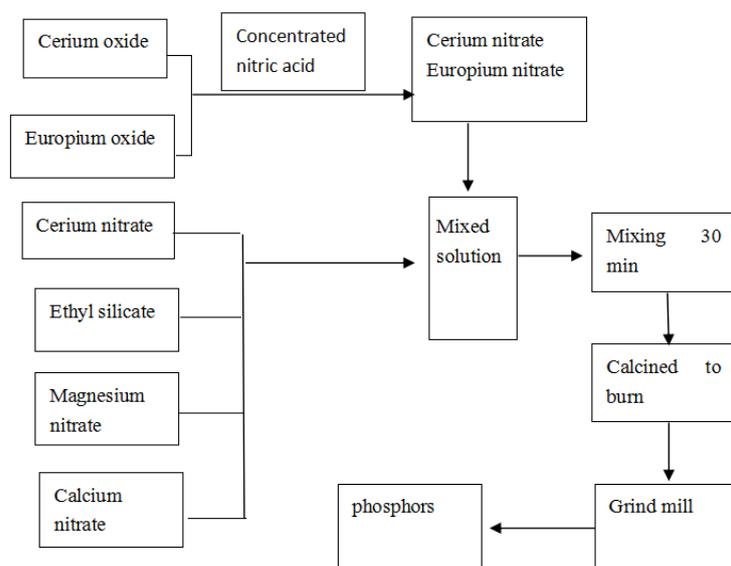


Figure 1: Preparation of a single matrix white led with fluorescent powder

Weigh and take the raw materials Ca_2CO_3 , $MgCO_3$, SiO_2 , Eu_2O_3 , Tb_4O_7 and Ce_2O_3 according to certain stoichiometric ratio, give ball-milling for 2 hours, and then load it in crucible. Put the uniform mixture after ball-milling in high temperature resistance furnace, give calcination for several hours, cool the sample together with furnace to the room temperature after finishing reaction, and then take out the sample, give fine grinding, and obtain the white sample. The flow chart of $Ca_2MgSi_2O_7$ fluorescent powder preparation with high temperature solid state method is as shown in the Figure 2 below.

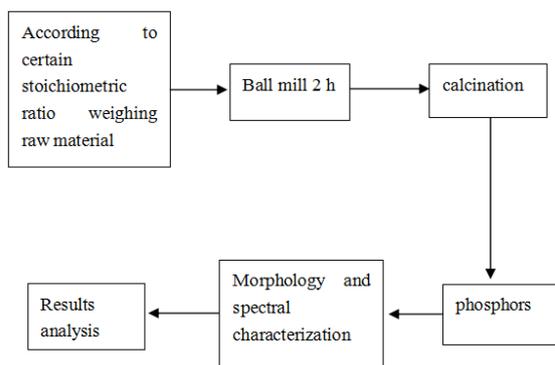


Figure 2: Preparation of a single matrix white LED with fluorescent powder

3.1 Characterization analysis method

Basic characteristic parameters of luminescent material include excitation spectrum, emission spectrum and brightness, and the common test instrument used in characterizing basic parameters of luminescence characteristics is fluorescence spectrophotometer. For the research on luminescent material, it usually needs to test crystal structure and microscopic morphology of the material, and the test instruments often used are scanning electron microscope and X-radial diffraction analysis, etc. These constitute the most common method for characterization and analysis of luminescent material.

Particle size and morphology of luminescent material have a very important influence on the fluorescence performance. The easiest and most effective way to observe morphology and structure of luminescent material is to use scanning electron microscope (SEM), with principle as follows: the electron images are generated for the relation between surface morphology and the quantity of secondary electron, back-scattered electron or absorbed electron produced by interaction of sample and the electron beam emitted by electron gun, and then they are expressed in the form of images through collection and conversion. SEM has the advantages of simple sample preparation method, deep and large field, stereoscopic image, easy identification and interpretation, large magnification change range, and higher resolution, etc.

In the research on luminescent material, fluorescence property index of luminescent material is the most important, and the spectrums characterizing fluorescence property most intuitively include excitation spectrum and emission spectrum as follows: excitation spectrum refers to the relation between a certain spectrum line and spectrum band intensity or luminescent efficiency and excitation wavelength of the luminescent material under the excitation of the light with different wavelength, and it represents a certain spectrum line or spectrum band of luminescent material can be excited by the light with which wavelength and how the excitation ability is; emission spectrum refers to intensity and energy distribution curve of the emitted light with different wavelength under the excitation of monitoring wavelength, namely the distribution of luminescent energy according to wavelength or frequency. Luminescence spectrum can be divided into linear spectrum, narrowband spectrum and broadband spectrum. The fluorescence spectrophotometer adopted in this experiment is RF-5301PC model manufactured by Shimadzu Corporation of Japan, and it is used in testing excitation spectrum and emission spectrum of the fluorescent material.

The lighting and display technology has very high requirements for color, while language cannot describe the color accurately, and it cannot explain the nuance of color. In accordance with the basic knowledge of colorimetry, the color can be expressed quantitatively with figure according to the human visual characteristics, and it can be measured with physical method by substituting the human eye, which is called CIE chromaticity diagram. Chromaticity coordinate is exactly color coordinate, a point can be identified on CIE chromaticity diagram via chromaticity coordinate, and this point can represent luminescent color of the luminescent material accurately, also color temperature is calculated via chromaticity coordinate. Energy transfer formula is as follows:



4. Results and Discussion

4.1 Analysis of the preparation technology with high temperature solid state method

The addition of ions Eu^{3+} , Ce^{3+} and Tb^{3+} does not affect the crystal structure of $\text{Ca}_2\text{MgSi}_2\text{O}_7$. Diffraction peak of the luminescent material prepared is more obvious, and it is relatively sharp when comparing with the standard

card. When the calcination temperature reaches 950 °C and 1050 °C, there shall be small miscellaneous peak, which indicates that the crystals are not completely generated for the low calcination temperature. Along with the promotion of calcination temperature, sharpness of the diffraction peak is improved. When the calcination temperature rises again, the diffraction peak obtained shall begin to diffuse, which indicates that the crystallinity starts to decline along with the rising of calcination temperature; When calcination temperature reaches 1150 °C, the diffraction peak shall be sharp obviously, and there is no miscellaneous peak; When calcination temperature reaches 1250 °C, there shall be a small miscellaneous peak, which indicates that crystal structure is destroyed and other impurity is generated for the excess temperature; Thus, the optimal calcination temperature determined in this experiment is 1150 °C, and the luminescent material prepared at this temperature shall be the best. (Schematic diagram of the crystallization of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ is as shown in Figure 3 below.)

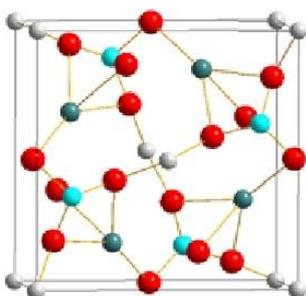


Figure 3: Schematic diagram of crystal structure of $\text{Ca}_2\text{MgSi}_2\text{O}_7$

Along with the rising of calcination temperature, particle size of the luminescent material shall increase gradually, morphology of crystal grain shall become more regular, grain diameter shall be more uniform, and agglomeration shall decrease gradually. When the calcination temperature reaches 1150 °C, the luminescent material prepared shall be optimal. If calcination temperature rises further, particles of the luminescent material shall show liquidation, and morphology of the particles shall be irregular, for the reason that high-temperature calcination mainly acts on the transport of internal ions of luminescent material and the growth of crystal grain. In the high temperature calcination process, the larger contact area of particles and the easy diffusion and transport are very beneficial to the growth of crystal grain, promotion of surface regularity and formation of the luminescent material needed. Finally, it is determined that the optimal luminescent material can be prepared when calcination temperature reaches 1150 °C. Luminescent intensity of fluorescent powder shall increase along with rising of calcination temperature with principle as follows: when promoting calcination temperature, chemical reaction among matrix components shall be more sufficient, activating agent can enter into the matrix easier, reaction speed can be quickened, crystallization capacity of the components can be promoted, and luminescent intensity of fluorescent powder can increase obviously. When the temperature rises to 1150 °C, fluorescent powder shall have the highest luminous intensity. If the calcination temperature rises further, emission peak intensity of the sample shall decline. Corresponding to the analysis results of scanning chart, the optimal calcination temperature shall be 1150 °C, and the luminescent material shall have the highest fluorescence intensity at this temperature. (Picture of the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ sample synthesized in 11500C is as shown in Figure 4 below.)

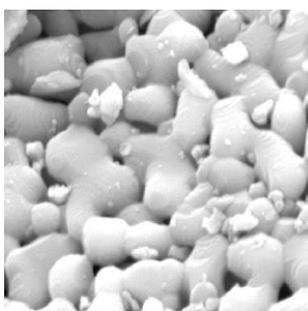


Figure 4: 1150 Temperature synthesis $\text{Ca}_2\text{MgSi}_2\text{O}_7$ the sample figure

4.2 Influence of the doping contents of Eu³⁺, Ce³⁺ and Tb³⁺ on luminescent property

After adding Ce³⁺ and Tb³⁺, emission peak position of Eu³⁺ shows no change, and the main emission peaks are in 588 nm and 618 nm respectively which are characteristic peaks of Eu³⁺ and correspond to ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ energy level transitions of Eu³⁺ respectively with red emitted light. However, the blue and green emission peaks appear respectively, the emission wavelength at the blue emission peak is 488 nm which corresponds to ⁵d₄→⁷F₄ energy level transitions of Ce³⁺, and that at the green emission peak is 542 nm which corresponds to ⁵D₄→⁷F₄ energy level transitions of Tb³⁺. Comparing with the double doping of Ce³⁺ and Tb³⁺, emission peak of Tb³⁺ enhances obviously, and luminescent intensity increases gradually along with increment of the Tb³⁺ ion concentration, which indicates that there is energy transfer between Ce³⁺ and Tb³⁺, and part of Ce³⁺ transfers energy to Tb³⁺ for being as sensitizer. The overall luminescent intensity reduces along with reduction of Ce³⁺ concentration, for emission peak declines during the reduction of the energy transfer of Ce³⁺ and other rare earth ion. Luminescent intensities of Tb³⁺ and Eu³⁺ increase along with increment of Ce³⁺ concentration, for Ce³⁺ acts as sensitizer of Tb³⁺ and Eu³⁺, transfers energy to them and makes their luminescent intensity increasing thereof. Thus, Ce³⁺ shall be more than the other two ions, and the optimal doping contents determined in this paper are 100:1 of metal ion/ Eu³⁺ and mole ratio 1:2:1 of Eu³⁺/Ce³⁺/Tb³⁺.

5. Conclusions

In this paper, it mainly gives research on the preparation of rare earth doped silicate material with high temperature solid state method and the luminescent property. During the preparation with high temperature solid state reaction method, it is discovered that the optimal calcination temperature of rare earth doped silicate material is 11500C. According to the research on preparation of fluorescent material, it is discovered that the optimal doping ratio of Eu³⁺, Ce³⁺ and Tb³⁺ of the rare earth doped silicate material is 1:2:1. As limited by the research time, solution-combustion method is not used in the preparation of luminescent material, and there are still some deficiencies existed in the research on luminescent property of rare earth doped silicate material. According to relevant research data, it can be known that the luminescent material produced with solution-combustion method can emit a warm white light with milder color and it is a better fluorescent powder material. Due to the limited research, the author mainly gives simple analysis to the high temperature solid state method and does not give in-depth research to the luminescent property of the high temperature solid state method. Moreover, as professional level and expression ability of the author are relatively insufficient, whether the research results are feasible still needs practice research.

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