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Analysis of the Research Status of Red Luminescent Materials with Different Base Types

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Abstract: *According to the type of base materials, red luminescent materials can be divided into sulfide system, oxide and sulfur oxide system, nitride system, aluminate system, silicate system, tungstomolybdate system, etc. In this paper, the research status of different systems of red luminescent materials is analyzed. Sulfide system have been studied for the longest time, but have the disadvantage of being susceptible to deterioration and deliquescence when exposed to air. The oxide and sulfur oxide system has excellent properties and is a very good base materials, but the cost is high because all raw materials are high-purity rare earth oxides. Nitride system make up for the deficiencies of sulfide system and have broader excitation and emission wavelengths than sulfide or oxide system. The aluminate system has the characteristics of superior luminescent performance and low cost, which is worthy of further study. The physical and luminescence properties of silicate system are poor, and need to be further explored. The stable structure of tungstomolybdate system has good absorption of ultraviolet excitation light, which is beneficial to increase the emission efficiency and the excitation and emission energy of the luminescent center. The doping of* Eu^{3+} *makes it have better luminescence properties.*

Keywords: *base type; red; luminescent material; the research status*

1. Introduction

At present, the synthesis technology and process of green and blue luminescent materials are very mature and have been widely used in production and life. In contrast, the development of red luminescent materials is far from mature, and there are still some performance defects. The current red luminescent materials generally have low luminous efficiency. According to the three primary color principle, almost any color can be obtained by synthesizing red, green and blue in different proportions. That is to say, if these three luminescent materials are mixed in different proportions, light of any color can be obtained[1]. Therefore, it is of great significance to study red luminescent materials with superior performance. According to the type of base materials, red luminescent materials are mainly divided into: sulfide system, oxide and sulfur oxide system, nitride system, aluminate system, silicate system, tungstomolybdate system, etc.

2. The Research Status of Red Luminescent Materials with Different Base Types

2.1. Sulfide System Luminescent Materials

The luminescent materials of sulfide system is the earliest red luminescent materials with the longest research time at home and abroad. Most of the sulfide systems use alkaline earth metal sulfides as the base. However, the shortcomings of the sulfide system are obvious, due to the fact that the physical and chemical properties of sulfide are very unstable, sensitive to carbon dioxide and water, and will deteriorate when exposed to the air for a long time, and it is also easy to deliquescence, resulting in a decrease in the luminescence properties of the powder. It also releases gases that are harmful to the human body. In order to increase the stability of the powder, surface coating is usually used to prevent deliquescence and deterioration[2]. Xiyan Zhang[3] et al. adopted the coating method to improve the water resistance of CaS:Eu,Sm powder, and also found that although the peak shape and peak position of the luminescent spectrum of the samples before and after coating did not change, the luminescent intensity after coating decreases. In order to satisfy both water resistance and luminescence properties, researchers have done a lot of work, but have not achieved good results, which hinders the popularization and application of luminescent materials of this system[1].

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2.2. Oxide and Sulfur Oxide System Luminescent Materials

The oxide system is a good base material because of its relatively stable chemical properties, good thermal stability and simple preparation process. At present, the red luminescent materials of Eu^{3+} doped Gd_2O_3, Y_2O_3, La_2O_3 are mostly used in this system. Due to its excellent properties, $Y_2O_3:Eu^{3+}$ red luminescent materials is currently the only red luminescent materials that can meet the requirements of commercial level. Shiying Zhang[4] et al. synthesized $Y_2O_3:Eu^{3+}$ red luminescent materials with relatively high luminous intensity under the optimal synthesis conditions and adding an appropriate amount of flux. The surface defects were eliminated through the coating process, and the luminescence properties were improved.

Using sulfur oxide system as a base has more significant advantages than sulfide system, its chemical stability is better, it is not easy to absorb water and deliquescence, it has good oxidation resistance in air, high melting point and high luminous efficiency. At present, there have been a lot of researches on the sulfur oxide system activated by rare earth ions, and $Y_2O_2S:Eu^{3+}$ with better luminescent performance has been widely used in many aspects of life. Yang Geng[5] et al. used Eu_2O_3 as raw material, first synthesized $Y_2O_3:Eu^{3+}$ by combustion method, and then obtained nano-scale $Y_2O_2S:Eu^{3+}$ red luminescent materials by vulcanization under high temperature burning. The obtained sample particles are fine and uniform and have high luminescent intensity. In general, oxide and sulfur oxide systems are widely used in daily life due to their strong luminescent intensity and good stability. The biggest problem with the luminescent materials of these two systems is their high cost, because their raw materials are all high-purity materials of rare earth oxides[1].

2.3. Nitride System Luminescent Materials

Due to the lack of red light components, the color rendering performance of white LEDs is poor, and it is improved by doping the matrix with red powder. As mentioned above, the chemical properties of sulfide system luminescent materials are unstable, and it is easy to deliquesce and deteriorate when absorb water. The discovery of nitride system red luminescent materials makes up for the defects of sulfide system. Therefore, it is necessary to study the efficient and stable preparation method of nitride system red luminescent materials. H.T.Hintzen[6-10] et al. in the Netherlands have done a lot of research on nitrogen-containing red luminescent materials, and have successfully prepared $M_2Si_5N_8$ (M=Ca, Sr, Ba):Eu^{2+} red luminescent materials, which can be effectively excited by blue light and UV light. The influence of europium doping concentration on the luminescence properties of the luminescent materials was also analyzed. At the same time, $M_2Si_5N_8$(M=Ca,Sr,Ba):Mn^{2+} red luminescent materials was prepared, and its luminescence properties were analyzed, and it was concluded that the crystal field intensity of nitrogen ions was relatively strong and the electronegativity was relatively high. It was found that this material could emit orange to deep red emission light under the strong crystal field. Nitride system luminescent materials have wider excitation and emission wavelengths than sulfide or oxide systems, which is mainly due to the strong crystal field effect and high electronegativity of nitrogen ions in nitride system, which enhanced the splitting of doped Eu^{2+} ion at its own 5d energy level.

2.4. Aluminate System Luminescent Materials

The aluminate system has the characteristics of good stability, high quantum efficiency, and no deliquescence and deterioration when placed in the air. In recent years, it has received extensive attention and development research by researchers. The blue-green and yellow-green luminescent materials of aluminate system are relatively mature, and the research on red luminescent materials is still in the initial stage of exploration and development. Katsumata[11] et al. tested the luminescence properties of $Sr_3Al_2O_6:Eu^{2+},Dy^{3+}$ red luminescent materials synthesized by high temperature solid-phase method, and obtained five broad band-shaped emission peaks, which correspond to the characteristic transitions of Eu^{2+} and Dy^{3+}[1]. Matsuzawa[12] et al. obtained $MAl_2O_4:Eu^{2+},Dy^{3+}$ (M=Sr, Mg,Ba) series long afterglow luminescent materials with good afterglow properties by co-doping rare earth ions, but the chemical stability of luminescent materials based on MAl_2O_4(M=Sr, Mg,Ba) is not good, especially in a humid environment, the material is easily decomposed, and the luminescence properties are greatly affected[13]. The red luminescent materials of the aluminate system has excellent luminescent performance, good thermal stability, no harmful substances, and has a large content of aluminum resources and low cost. It is worthy of in-depth research in terms of energy utilization and the structure of the material itself.

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2.5. Silicate System Luminescent Materials

Silicate system luminescent materials have the advantages of stable chemical properties, good thermal stability, especially good water resistance, wide excitation wavelength range, high luminous efficiency, high color rendering, cheap raw materials, and low production costs. It occupies an important position in LED luminescent materials. The disadvantage of silicate system red luminescent materials is that the afterglow time is not long, and the synthesis process and luminescence properties need to be further improved. At present, blue-green luminescent materials are mostly reported in silicate system, while the research on red silicate luminescent materials is just at the beginning stage. Yang Wu[14] et al. synthesized spherical $Zn_2SiO_4:Eu^{3+}$ red luminescent material by sol-gel method, and found that the luminescent material had a strong red emission peak at 615nm under excitation light detection of 393nm. This paper mainly studies the control of powder size, and the effects of annealing temperature and co-doping of Eu^{3+} and Li^{+} on the luminescence properties of the samples were studied. Compared with the red luminescent materials of other base, the current research results of silicate system red luminescent materials are still a big gap between physical properties and luminescence properties. It is yet to be systematically and deeply explored by researchers from the three aspects of base and activator ions and subsequent treatment of powder.

2.6. Tungstomolybdate System Luminescent Materials

Tungstomolybdate system luminescent materials has better chemical stability, good photoelectric properties, low price, simple preparation and excellent luminescence properties. It is a very excellent luminescent materials and has important applications in production and life. W and Mo are structurally similar elements of the same family. MoO_4^{2-} and WO_4^{2-} in tungstomolybdate have special properties. They are not only structurally stable, but also have a strong charge transfer broadband from O^{2-} to Mo^{6+} or W^{6+} ions in the near-ultraviolet region. The electrons will undergo charge transfer transition, so that the tungstomolybdate base can absorb the energy of ultraviolet excitation light well, and transfer the absorbed energy to the luminescent center of the luminescent materials, thereby increasing the emission efficiency and the excitation and emission energy of the luminescent center[15]. Eu^{3+} doped tungstomolybdate luminescent material has better luminescent advantages, the base transfers the absorbed energy to Eu^{3+} ions, making it have good luminescence properties, which makes the choice of tungstomolybdate as the base and Eu^{3+} ion as the activator ions of the red luminescent materials can be better matched with the LED chip. An Xie[16] et al. prepared $LiEu_{1-x}Y_x(WO4)_{0.5}(MoO4)_{1.5}$ series luminescent materials by high-temperature solid-phase method. The crystallinity and particle size of the particles were controlled by the addition of flux. And the effects of cosolvent on luminescence properties of luminescent materials was analyzed. Xiuhua Cong[17] et al. prepared $KCa(MoO_4)_3:Eu^{3+}$ luminescent materials by high-temperature solid-phase method. By Characterization the powder, it was found that this luminescent materials can be effectively excited by near-ultraviolet light and blue light, and may become a red luminescent materials for white LED.

3. Conclusions

According to the three primary color principle, light of any color can be obtained by mixing the light emitted by the three color luminescent materials of red, green and blue in different proportions. At present, the synthesis technology and process of green and blue luminescent materials are very mature, and it is of great significance to study red luminescent materials with superior performance. According to the type of base materials, red luminescent materials can be divided into sulfide system, oxide and sulfur oxide system, nitride system, aluminate system, silicate system, tungstomolybdate system, etc. In this paper, the research status of different systems of red luminescent materials is analyzed. Sulfide system luminescent materials are the earliest and longest red luminescent materials, but they have the disadvantages of easy deterioration and deliquescence when exposed to air for a long time. The oxide and sulfur oxide system luminescent materials has excellent properties and is a very good base materials. And $Y_2O_3:Eu^{3+}$ is currently the only red luminescent materials that can meet the requirements of commercial levels. The all raw materials of oxide and sulfur oxide system luminescent materials are high-purity rare earth oxides, which makes it expensive. Nitride system luminescent materials make up for the defects of sulfide system and have wider excitation wavelength and emission wavelength than sulfide or oxide system. The aluminate system luminescent materials has the characteristics of superior luminescent performance and low cost, which is worthy of further study. The physical and luminescence properties of silicate system luminescent materials are poor, and it needs to be explored and studied from the three aspects of base and activator ions and subsequent treatment of powder. The tungstomolybdate system luminescent materials is a very superior luminescent material. The stable structure of the tungstomolybdate system has a good absorption of ultraviolet excitation light energy, which is beneficial to increase the emission efficiency and the excitation and emission energy of the luminescent center. Eu^{3+} doping tungstomolybdate luminescent materials have better luminescence properties.

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