Article ID: 1003-7837(2005)02,03-0599-05

Study on preparation and application performance of blue sky rare earth light storage and emission material

ZHOU Shao-hui(周绍辉), NI Hai-yong(倪海勇), HUANG Zhao-hui(黄朝辉),
LI Xu-bo(李许波), DING Jian-hong(丁建红), ZHANG Zhen(张 震)

(Guangzhou Research Institute of Non-ferrous Metals, Guangzhou 510651, China)

Abstract: Under reduction atmosphere, a blue sky rare earth silicate light storage and emission material was prepared by high temperature solid phase synthesis. The best constituent ratio of this material was determined through orthogonal experiment, and its excitation and emission spectra and X-ray diffraction patterns were measured. And a comparative study was conducted on its application properties.

Key words: rare earth; light storage and emission material; silicate

CLC number: O612.4 **Document code**: A

1 Introduction

In comparison with traditional zinc sulphide light storage and emission materials, rare-earth-activated light storage and emission materials are of advantages of higher luminance, longer afterglow time, safe and non-toxic and environmentally friendly. They have been widely applied in various transparent mediums, daily consumables, architecture decoration, transportation tools , military facilities and fire emergency system as well as arts and crafts.

Rare earth aluminate light storage and emission material is limited to some application fields due to its sole glow color, poor heat and water resistance. While silicate system, as another new type light storage and emission material, has more stable chemical performance than that of aluminate system, and can complement the aluminate system material in glow colors, moreover, in some industries like ceramics, it has better application effects than those of aluminate light storage and emission material, and is a very promising new type light storage and emission material.

In this paper, the best constituent ratio of sky blue rare earth silicate light storage and emission material was determined by high temperature solid phase synthesis using orthogonal experiment, the silicate light storage and emission material of above 10 hours' afterglow time was synthesized. And its water resistance and heat stability during its application were compared, the results show that its water resistance and heat stability are obviously superior to those of aluminate and zinc sulphide light storage and emission materials.

Received date: 2005-04-21

Biography: ZHOU Shao-hui(born in 1970), Female, Engineer, Bachelor

2 Experimental

2.1 Raw materials for preparation of luminescent materials

The raw materials adopted for this experiment mainly include MgO, SiO_2, $SrCO_3$, Eu_2O_3 and Dy_2O_3, among which MgO is analytical reagent, the others are high pure one.

2.2 Preparation of luminescent materials

Weigh appropriate amounts of SiO_2, $SrCO_3$, Eu_2O_3 and Dy_2O_3 according to a certain mole ratio, place them into a blending pot, finely grind and blend well, then place into an alumina crucible and burn in a high temperature oven-type furnace for 3 hours at 1300℃ under reduction atmosphere, after that, cool and finely grind, sieve through 200 meshes, the sample is then produced.

2.3 Performance test of sample

Performing an analysis of crystalline structure using D/MAX－Ⅲ X-Ray diffraction facility.

Measuring the excitation and emission spectra by MPF－4 spectrofluorophotometer (Hitachi, Japan).

Determining the brightness of sample using an ST－86LA brightness meter.

Brightness test conditions are: environmental temperature(20±3)℃, relative humidity≤70%, D65 standard light source, illumination intensity 1000±10 Lux, excitation time 20 minutes. Placing the sample in a total darkness for over 24 hours prior to conducting the test.

3 Results and discussion

3.1 Determination of the best ratio of luminescent materials components

On the basis of single factor experiment, an experiment was carried out using $L_9(3^4)$ orthogonal design. The assignment of experimental factors and levels are as follows:

Table 1 $L_9(3^4)$ orthogonal test and test results

No.	A Silicon dioxide /mol	B Magnesium oxide /mol	C Strontium carbonate /mol	D Eu_2O_3/Dy_2O_3 /Mole ratio	1min Luminance /(mcd·m^{-2})
1	1.96	0.98	1.96	1:5	301.2
2	1.96	1.0	2.0	1:10	565.0
3	1.96	1.02	2.04	1:15	539.8
4	2.0	0.98	2.0	1:15	482.6
5	2.0	1.0	2.04	1:5	503.9
6	2.0	1.02	1.96	1:10	546.1
7	2.04	0.98	2.04	1:10	560.2
8	2.04	1.0	1.96	1:15	469.5
9	2.04	1.02	2.0	1:5	570.6
Ⅰ	1406.0	1344.0	1316.8	1375.7	—
Ⅱ	1532.6	1538.4	1618.2	1671.3	—
Ⅲ	600.3	1656.5	1603.9	1491.9	—
K1	468.7	448.0	438.9	458.6	—
K2	510.9	512.8	539.4	557.1	—
K3	533.4	552.2	534.6	497.3	—
R	64.7	104.2	100.5	98.5	—

It can be seen from the ranges, the primary and secondary factors affecting luminance intensity among all components of material: magnesium oxide > strontium carbonate > Eu_2O_3/Dy_2O_3 (mole ratio) > silicon dioxide. It can be found from Table 1 that the designed optimum experimental conditions are strontium carbonate 2.0 mol, magnesium oxide 1.02 mol, silicon dioxide 2.04 mol, Eu_2O_3/Dy_2O_3 (mole ratio) 1:10, boric aid 0.04 mol.

An optimized experiment was performed according to above conditions, the experimental results are shown in Table 2.

Table 2 Test results

Name	1 min luminance /(mcd · m^{-2})	30 min luminance /(mcd · m^{-2})
Optimized formula	576.5	45.3
Stoichiometric ratio formula	550.3	43.6

Table 2 shows that under the same process conditions with ratios of matrix compositions of $Sr_2MgSi_2O_7$ changed, 1 min luminance is 576.5 mcd · m^{-2}, increased by 4.8% than the luminance in stoichiometric ratio formula. Thus it indicates that SiO_2 used for preparing $Sr_2MgSi_2O_7$ luminescent materials should be slightly overdosed, as it can make Sr^{2+} of $Sr_2MgSi_2O_7$ in a vacancy, a hole trap is thereby formed intensifying the luminance.

3.2 Crystal structure of samples

The X-ray powder diffraction pattern is shown in Fig. 1. After the comparison of as-obtained diffraction peak value with standard JCPDS card (No. 15−0016), it is found that the main phase of sample is $Sr_2MgSi_2O_7$.

3.3 Excitation and emission spectra

The excitation and emission spectra are shown in Fig. 2. From the excitation spectrum of sample, it can be seen that the primary excitation is a broad band in a wavelength range of 250−435 nm, within the range of ultraviolet and visible light, the main peak is located at 320 nm and 375 nm, and is the typical excitation spectrum of Eu^{2+}. Its emission spectrum is also a broad band spectrum, whose peak value is located at 469 nm, and the glow is caused due to the 4f−4d transition of Eu^{2+}, while no characteristic peak (610 nm) of Eu^{3+} appears in the figure.

3.4 Heat stability test

Place rare earth aluminate (AL−2), ZnS and sky blue rare earth silicate (Ts−2) in a muffle furnace set at 800°C for 30 minutes at the same time, then take them out and cool down, at last sampling to test its luminance. The test results are shown in Table 3.

From Table 3, it can be known that after 30 min of temperature holding under 800℃, the 1 min illuminance of AL−2 decreases by 49%, and 20 min illuminance decreases by 80%; the 1 min illuminance of ZnS decreases by 47%, and 20 min by 62%; the 1 min illuminance of Ts−2 decreases by 8%, and 20 min by 11%. Thereby, it indicates that the heat stability of rare-earth-activated silicate light emission materials is obviously superior to that of rare-earth-activated aluminate light emission and ZnS materials.

Table 3 Heat stability test /(mcd · m^{-2})

Time /min	Illuminance of AL−2		Illuminance of ZnS		Illuminance of Ts−2	
	Room temperatur	Holding 30 min at 800℃	Room temperatur	Holding 30 min at 800℃	Room temperatur	Holding 30 min at 800℃
1	2047	1037	235	124	317	291
5	643	207	37	17	122	110
10	—	89	15	6.6	70	62
20	179	35	5.9	2.25	37	32.5

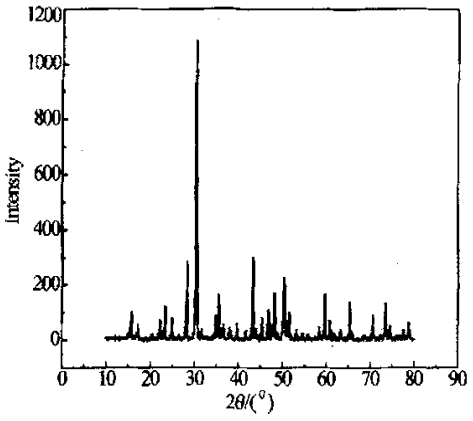

Fig. 1 X-ray diffraction pattern of sample

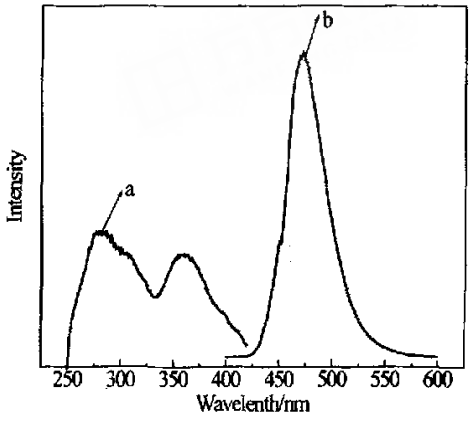

Fig. 2 Excitation and emission spectra of sample a-excitation spectrum; b-emission spectrum

3.5 Water resistance test

Place AL−2, ZnS and Ts−210 grams each at the same time into cups of 50 mL ion exchange water for the test. Observe the test appearances shown in Table 4. From the table, we can know that rare earth activated aluminate (AL−2) is of most inferior stability in the water, and has been completely hydrolyzed after 48 hours; while the stability of rare earth activated silicate (Ts−2) and zinc sulphide is good, there are no obvious changes after being put in the water for 90 days, their glow still can be clearly seen. Thereby, it can be seen that the stability of rare earth activated silicate (Ts−2) and zinc sulphide when in the water is obviously superior to that of rare earth activated aluminate light storage material, but the reason for zinc sulphide having better water resistance is just because a layer of compact organic matter encapsulated on its surface.

Table 4 Water resistance test

Time	Type	Aqueous solution	Glow effect after illumination
24 hours	AL−2	White and turbid, with small amounts of yellow-green particles	Faint glow
	ZnS	Crystal clear, the colors of particles have no change	Bright glow
	Ts−2	Crystal clear, the colors of particles have no change	Bright glow
48 hours	AL−2	White and turbid, with small amounts of yellow-green particles	No glow completely
	ZnS	Crystal clear, the colors of particles have no change	Bright glow
	Ts−2	Crystal clear, the colors of particles have no change	Bright glow
90 days	AL−2	White and turbid, with small amounts of yellow-green particles	No glow completely
	ZnS	Crystal clear, the colors of particles have no change	Bright glow
	Ts−2	Crystal clear, the colors of particles have no change	Bright glow

4 Conclusions

(1) The best ratio of sky blue rare earth light storage and emission material components has been determined using orthogonal design of experiment.

(2) The excitation spectrum of sky blue rare earth light storage and emission material displays a broad-band between 250 nm and 435 nm within the range of ultraviolet and visible light; the emission spectrum is a broad-band one with an emission peak at 469 nm, exhibiting characteristic emission of Eu^{2+}.

(3) The sky blue rare earth light storage and emission material shows excellent water resistance and heat stability, obviously superior to those of aluminate and zinc sulphide light storage and emission materials.

References

[1] 罗昔贤. 新型硅酸盐长余辉发光材料[J]. 发光学报,2003,(4):165－170.
Luo X X. New type silicate long afterglow phosphors[J]. Chinese Journal of Luminescence, 2003,(4):165－170.

[2] 王晓欣. Eu,Dy 共添加的 $Sr_2MgSi_2O_7$ 基长余辉发光材料[J]. 硅酸盐学报,2004,(30):216－219.
Wang X X. Eu and Dy Co-coped $Sr_2MgSi_2O_7$-based long afterglow photoluminescent materials[J]. Journal of the Chinese Ceramic Society, 2004,(30):216－219.

[3] 姜岭. 长余辉发光材料的研究进展[J]. 无机材料学报,2004,(19):268－274.
Jiang L. Progress in the research of long lasting phosphorescent materials[J]. Journal of Inorganic Materials, 2004,(19):268－274.

[4] 田华. 不同基质结构对长余辉发光材料发光光谱的影响[J]. 天津理工学院学报, 2003,(19):73－75.
Tian H. Effect of different matrix structure on luminescent properties of long afterglow phosphors[J]. Journal of Tianjin Institute of Technology, 2003,(19):73－75.

[5] 李成宇. 稀土元素掺杂长余辉发光材料研究的最新进展[J]. 发光学报,2003,(24):19－27.
Li C Y. Development of long-lasting phosphorescent materials doped by RE ions, Chinese Journal of Luminescence, 2003,(24):19－27.

[6] Xiao Z G, Xiao Z Q. Long afterglow silicate phosphor and its manufacturing method[P]. CN Patent: 1194292, 1998－09－30.

[7] Xiao Z G, Xiao Z Q. Long afterglow silicate luminescent material and its manufacturing method[P]. US Patent: 6093346,2000－06－25.