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Fabrication and luminescent properties of artificial luminous gem

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Abstract

Based on the matrix of alkali-earth-aluminate, the luminous gem is artificially manufactured, doped with Eu^{2+} as activator and Dy^{3+} as hole trap. The morphology and crystal structure of the luminous gem are analyzed by scan electron microscopy (SEM) and X-ray diffraction (XRD). The excitation and emission spectra of the gem are broad band, and the main emission band is around 514 nm. The decay times of the artificial luminous gem and the long afterglow phosphor are measured. The results indicate that the artificial luminous gem has high initial luminescent brightness and slow decay process. The gem could glow continuously for over 25 h in the darkness after absorbs natural light. They have high degree of hardness and no radioactivity just like ''night shinning jewel''. This product can have great potential applications in jewelry industry.

Keywords: Artificial luminous gem; Long afterglow; Phosphor; Night shinning jewel

1. Introduction

There are some natural luminescent materials in nature. In ancient times, these materials were called ''night shinning jewels'', which have peculiar luminescent properties and could glitter and emit translucent sheen in the darkness. They are considered as treasure because of the rarity of these materials.

Long afterglow phosphor is a kind of material that has attracted numerous attentions since more than ten years ago. After exposure in the sunlight or lamp light for a short time, it can absorb light and radiate in the darkness for more than 12 h. This absorbing-emitting process can be repeated forever, and thus it has similar properties to ''night shinning jewel''. Luminous gem can be fabricated by agglomerating long afterglow phosphor, and various shapes of luminous gem can be obtained through cutting, sanding and polishing, etc. The luminous gem obtained is highly bright, non-toxicant, harmless and nonradioactive, and is similar to the natural jewel in texture, appearance and properties.

However, up to now there are only a few studies on fabricating the luminous gem. Yamazaki et al. [1] prepared the long luminescent zinc borosilicate glasses $60ZnO–20B_2O_3–20SiO_2$ doped with 0.2 mol% Tb_2O_3 by melting the raw materials at 1300 °C for 3 h in an ambient atmosphere. The glass exhibited phosphorescence for up to 1 h after exciting with 254 nm light. Qiu et al. [2] found that the Eu^{2+} and Dy^{3+} co-doped $40SrO–30A1_2O_3–30SiO_2$ glass, after re-melted at 1550 °C for 1 h, showed bright and long lasting phosphorescence. They suggested that the long lasting phosphorescence resulted from the recombination of electrons and holes at shallow traps in the glass matrix which can be thermally released at room temperature. In Patent ZL200410029960.7 [3], in the process of luminous gem fabrication, the additive was added, which increases the cost and influences the brightness and afterglow time of the gem. In Patent ZL01120005.7 [4], the luminous gem obtained has loose inner structure due to the absence of compression moulding, and thus will not be anticipated outstanding behaviors in the process of cutting, sanding and polishing.

In this study, the luminous gem was fabricated by sintering long afterglow phosphors at high temperature in weak reductive atmosphere. The crystal structure and morphology of luminous gem was analyzed systematically with XRD and SEM measurements. The decay times and luminescent properties

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were also measured. The results show that the luminous gem is compact, highly bright and has long afterglow. Besides, the technology concerned is safe and low in cost, which endows the luminous gem with broad application prospect.

2. Experimental

First, the long afterglow phosphor was synthesized. The starting materials include the following chemicals: $SrCO_3$ (4350 g), Al_2O_3 (3060 g), Dy_2O_3 (140 g), Eu_2O_3 (53 g). 180 g H_3BO_3 were used as a flux. Powders were weighed and milled thoroughly for 6 h. The milled powders were pre-fired at 900 °C in the air for 2 h, then pulverized and ground to pass through a 20 μm screen. The pre-fired powders were calcined at 1350 °C in a weak reductive atmosphere of flowing 1.5% H_2 + 98.5% N_2 gas for 3 h to obtain $SrAl_2O_4$: Eu, Dy phosphors.

Second, the luminous gem was fabricated. 98 wt% long afterglow phosphor was mixed with 2 wt% SiO_2. Then the body was formed through isostatic compaction of mixture without using agglomerant. Finally, the luminous gem was prepared by the traditional ceramic synthesis method at 1350 °C for 3 h in weak reductive atmosphere of flowing 1.5% H_2 + 98.5% N_2 gas.

The XRD pattern is recorded in the 2 θ range of 15–70° with a RegakuD/Max B using Cu Kα radiation (1.5418 Å) at 40 kV. Scanning electron microscope (SEM) image is recorded with a Hitachi S-450 scanning electron microscope operating at 200 kV. The decay curves of luminous gem and long afterglow phosphor were measured by the PR-305 brightness meter, and the samples were irradiated by the standard Xe lamp for 10 min. A Hitachi F-4500 Fluorescence Spectrophotometer was used to detect the excitation and emission spectra of products.

3. Results and discussion

Fig. 1 shows the SEM image of the luminous gem. The upper half of the image shows the cross-section of the luminous gem obtained through natural fracture. The lower half of the image shows the cross-section obtained through cutting artificially. From the SEM image, it can be seen that there are no holes in the luminous gem. The results indicate that the structure of the luminous gem is compact, and the luminous gem has beautiful appearance as that of natural ''night shinning jewel''. A typical X-ray diffraction pattern of the luminous gem is shown in Fig. 2. As can be seen, the monoclinic phase diffraction peaks of $SrAl_2O_4$ are predominant in the XRD pattern, which is in agreement with the earlier results [5,6]. The luminous phosphor exhibits similar XRD pattern with the luminous gem, but presents much lower crystallinity. The good crystallinity of the luminescent gem favors the improvement of the luminescent properties.

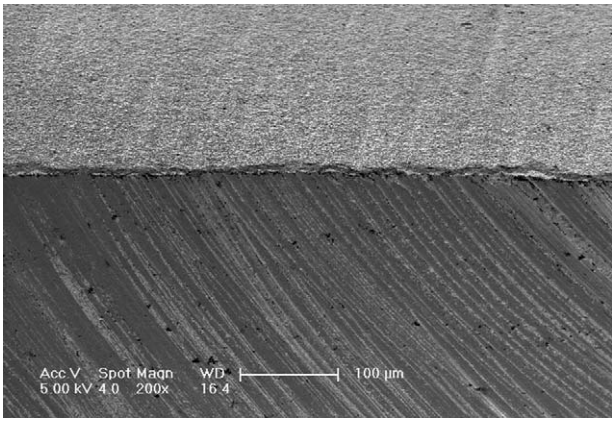

Fig. 1. The SEM image of the artificial luminous gem.

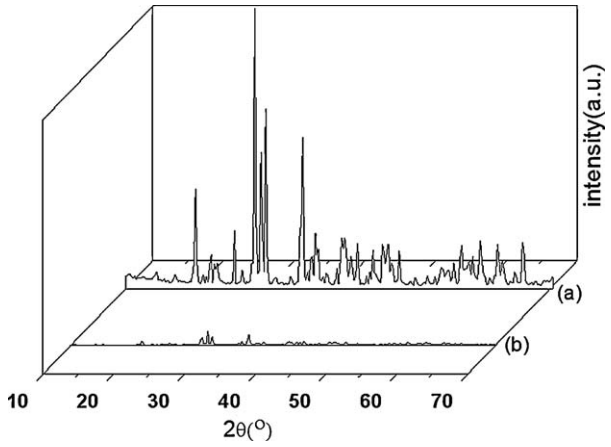

Fig. 2. The XRD patterns of the artificial luminous gem (a) and luminous phosphor (b).

$SrAl_2O_4$ host composes a three-dimensional framework of corner-sharing AlO_4 tetrahedra [7]. Each tetrahedron has one net negative charge that is balanced by Sr^{2+} cations occupying interstitial sites within the tetrahedral framework. It is generally considered that the Eu^{2+} and Dy^{3+} ions entered the Sr^{2+} sites in the $SrAl_2O_4$ hosts. Little amounts of co-doped rare-earth ions have almost no effects on the $SrAl_2O_4$ phase structure. Hence, the XRD patterns of the luminous gem and powder do not exhibit the presence of any Eu or Dy compounds.

The excitation and emission spectra of luminous gem at room temperature are shown in Fig. 3. The excitation spectra show a broad band, and there are two main excitation peaks at 365 and 423 nm. The doped Eu^{2+} ions in the luminous gem give rise to a green emission under UV excitation. The main emission spectrum is a symmetrical band at 514 nm, which is ascribed to the typical $4f^65d^1$-$4f^7$ transition of Eu^{2+}. They are in good agreement with the results of Lu et al., who synthesized the $SrAl_2O_4$: Eu, Dy phosphor by sol–gel route [8]. There is no special emission of Dy^{3+} and Eu^{3+} in the spectra, which implies that Eu^{3+} ions have been changed to Eu^{2+} completely. The phosphorescence spectrum of the luminous gem is very similar to the emission spectrum as shown in Fig. 3, indicating that the phosphorescence is originated from the slow emission of Eu^{2+} ion.

The decay curves of the artificial luminous gem and the long afterglow phosphors are shown in Fig. 4. It can be seen from the curves that the long afterglow phosphors show long persistence when the powders are effectively activated by the standard Xe lamp for 10 min. The afterglow time which allowed to be

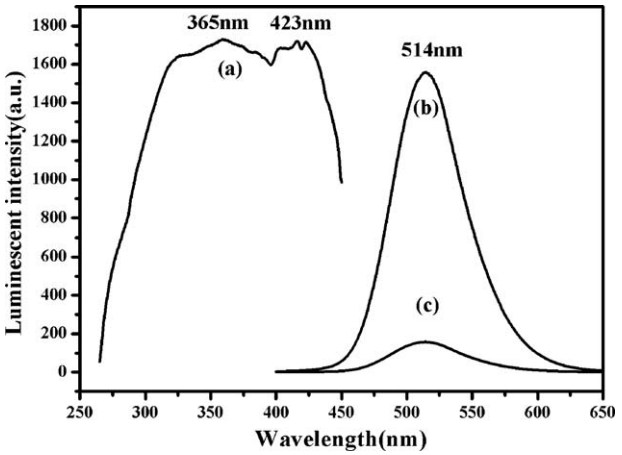

Fig. 3. Photoluminescent properties of the artificial luminous gem. (a) The excitation spectrum obtained by monitoring emission at 514 nm, (b) the emission spectrum excited by 365 nm and (c) the phosphorescence spectrum after the 365 nm excitation is removed.

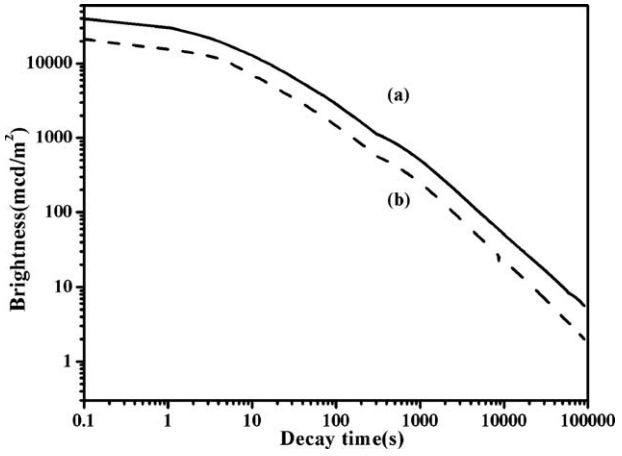

Fig. 4. The decay curves of (a) the artificial luminous gem and (b) the long afterglow phosphors.

visually recognized ($\geq$0.32 mcd m^{-2}) can last over 25 h in the darkness after removal of the irradiation light source.

As for the luminescent mechanism of luminous gem, the co-doped Dy^{3+} ions play an important role. In the earlier reports about strontium aluminates (such as $SrAl_2O_4$: Eu, Dy phosphors) [6], it was thought that the co-doped Dy^{3+} ion played the role of hole traps and prolonged the afterglow. And thus, in the luminous gem, from the results of decay curves and luminescent spectra, we think that the Dy^{3+} ions also act as the hole traps. The traps capture the holes from the valence band of the matrix, and then release them by the thermal disturbing. The capturing-releasing process prolongs the lifetime of the photo-generated holes effectively and thus results in the long afterglow phosphorescence.

In Fig. 4, it can be seen that the luminous gem shows a slow decay and high brightness, which is obviously higher than that of long afterglow phosphor. The enhanced brightness and longer afterglow time are probably caused by the improved crystallinity and density of the luminous gem in comparison with the long afterglow phosphor. The massive luminous gem has better crystallinity than pulverous long afterglow phosphor, causing less defects in the luminous gem. Thus quenching effect of defects on the luminescence decreases in the luminous gem compared with phosphors.

The Mons' hardness of the luminous gem is 6.5, the density is 3.57 g/cm^3 and the refractive index is 1.65, indicating that the luminous gem has the similar physical properties with some natural jades. The artificial luminous gem has potential applications in jewelry industry, e.g. being used to make necklaces, bracelets, earrings and rings, and playing a role in the indoor decoration.

4. Conclusions

The $SrAl_2O_4$: Eu, Dy luminous gem has been artificially manufactured, which shows the long afterglow properties. The main excitation peaking at 365 and 423 nm and the main emission peaking at 514 nm are all ascribed to typical $4f^65d^1$-$4f^7$ transitions of Eu^{2+} in the matrix. The artificial luminous gem has high initial luminescent brightness and slow decay process. The artificial luminous gem could glow for over 25 h continuously after it absorbs light. Regarding the luminescent mechanism of luminous gem, the co-doped Dy^{3+} ions play an important role, which act as the hole trap and capture the free holes, and thus prolong the duration. This product can have great potential applications in jewelry industry.

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References

[1] M. Yamazaki, Y. Yamamoto, H. Nosono, N. Sawanobori, M. Mizuguchi, H. Hosono, Long luminescent glass: Tb^{3+} activated $ZnO–B_2O_3–SiO_2$ glass, J. Non-Cryst. Solids 241 (1998) 71–73.
[2] J. Qiu, M. Kawasaki, K. Tanaka, Y. Shimizugawa, K. Hirao, Phenomenon and mechanism of long-lasting phosphorescence in Eu^{2+}-doped aluminosilicate glasses, J. Phys. Chem. Solids 59 (1998) 1521–1525.
[3] X.H. Wang, CN Patent, No. 200410029960.7 (2004).
[4] Q.L. Hao, CN Patent, No. 01120005.7 (2003).
[5] L.K. Kurihara, S.L. Suib, Sol–gel synthesis of ternary metal oxides. 1. Synthesis and characterization of $MA1_2O_4$ (M = Mg, Ni, Co, Cu, Fe, Zn, Mn, Cd, Ca, Hg, Sr, and Ba) and $Pb_2A1_2O_5$, Chem. Mater. 5 (1993) 609–613.
[6] Y.H. Lin, Z.T. Zhang, Z.L. Tang, J.Y. Zhang, Z.S. Zheng, X. Lv, The characterization and mechanism of long afterglow in alkaline earth aluminates phosphors co-doped by Eu_2O_3 and Dy_2O_3, Mater. Chem. Phys. 70 (2001) 156–159.
[7] V.A.-R. Schulze, H.M. Buschbaum, Zur Struktur von monoklinem $SrAl_2O_4$, Z. Anorg. Allg. Chem. 475 (1981) 205–210.
[8] Y.Q. Lu, Y.X. Li, Y.H. Xiong, D. Wang, Q.R. Yin, $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors derived from a new sol–gel route, Microelectron. J. 35 (2004) 379–382.