Preparation and Luminescence characteristics of Na_2O-PbO-SiO_2 system long afterglow Luminescent glasses

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Abstract. In this paper, the Na_2O-PbO-SiO_2 system long afterglow luminescent glasses of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} were prepared. XRD analysis indicates the glass samples have the typical diffraction peaks of $SrAl_2O_4$: Eu^{2+}, Dy^{3+}. The emission spectra of the luminescent glass shows broad bands peaking at 510nm. The excitation spectra of the luminescent glass shows broad bands ranging from 300 to 480nm. The afterglow luminescence of the luminescent glasses which are excited by a 40W fluorescence lamp for 30min can be observed in the dark for more 10 hours with the naked eyes.

Introduction

In recent years, a new type of long afterglow phosphors have been synthesized[1], an example of these is $SrAl_2O_4$: Eu^{2+}, Dy^{3+} [2-3]. $SrAl_2O_4$: Eu^{2+}, Dy^{3+} is very different from previous sulfide phosphors and the brightness and afterglow time of this kind of phosphors are more than 10 times larger than the previous ones[4-6]. Furthermore, it has excellent properties such as highway, railway, airport, ferry, texture, watch and automobile [7].

But up to the present, the researches about long afterglow luminescence are focus on $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors [8-10] and there are only few literatures about luminescent glasses made of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors to our knowledge. In this paper, the Na_2O-PbO-SiO_2 system long afterglow luminescent glasses of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors have been prepared and there performances have been researched. The obtained luminescent glasses (LGs) have bright green phosphorescence for more than 10h after switching off the exciting source and applications widely in many fields.

Experimental

Preparation of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors. The powders of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors were prepared by calcining the mixture of $SrCO_3$, Al_2O_3, Eu_2O_3 and Dy_2O_3 according to the nominal composition of $SrCO_3 \cdot 0.1Eu_2O_3 \cdot 0.2Dy_2O_3$ in mol% at 1450℃ for 3h in a reducing atmosphere of H_2/N_2 mixed gas in a Al_2O_3 crucible. They were pulverized and sieved using a 200 mesh screen.

Preparation of matrix glasses. The glass systems of Na_2O-PbO-SiO_2 were used to prepare matrix glasses. The mixed 100g batches of H_3BO_3, SiO_2, PbO, Na_2CO_3, $SrCO_3$ and Sb_2O_5 were melted in a Pt crucible at 1250-1350℃ for 30min in a reducing atmosphere of H_2/N_2 mixed gas. The melted glass liquids were poured into a stainless steel container and quenched to the room temperature. The glass powers were obtained by pulverizing the quenched glass and sieving it by using a 200 mesh screen.

Preparation of luminescent glasses. The LGs were obtained by firing the mixture of matrix glasses with the proportions of l0wt%, 20wt%, 30wt%, 40wt%and 50wt% $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors at 600-900℃ for about 30min and cooled down to the room temperature in a reducing atmosphere of H2/N2 mixed gas.

Measurement of properties. The emission and excitation spectra of the glasses were measured by a fluorescence spectrofluorometer (Fluoromax SPEX) with 450W Xe lamp as a source of the excitation light. The intensity decay curves of the LGs were measured using a luminescence brightness instrument (USA 1980A) after LGs were illuminated with a 40w fluorescence lamp for 30min. XRD patterns of the samples were measured using a X-ray diffractometer (Rigaku，D/max-RB) using radiation through a nickel filter with 40kV, 30mA.

Results and Discussion

Fig.1 shows the decay curves of luminescent intensities with different measuring times for the LGs with different percentage contents of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors. The luminescent intensities increase with $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors contents ranging from 10wt% to 50wt%. The LG with more than 50wt% $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors shows rough surfaces because $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors cannot be encapsulated completely by the matrix glass for too much $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors particles during the firing stage. Therefore, the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors content in the LG should be less than 50wt%. Depending on the application requirements the contents of the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors can vary from 20wt% to 45wt%. In our experiment, the optimal percentage composition of the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors is 30wt% in the Na_2O-PbO-SiO_2 system long afterglow luminescent glasses. On one hand, the lifetime of afterglow meets for the equation $I(t) = I_0 t^{-n}$, where $I(t)$ is the intensity at the time t, I_0 is the initial intensity and n is a slope coefficient. On the other hand, the afterglow luminescent times of the LG can be seen in the dark for more 10 hours after switching of the excitation source light.

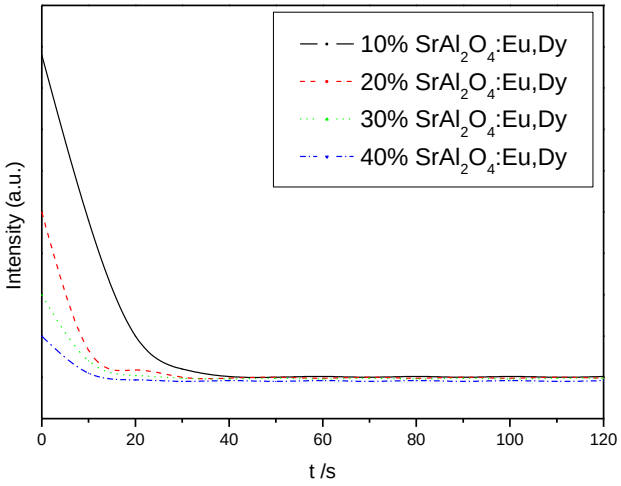

Figure. 1 Decay profiles of afterglow for the luminescent glass with various contents of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors

Fig.2 gives the decay profiles of afterglow for the LGs with 30wt% $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors at different firing temperature for 30min. The luminescent intensities decrease with increasing firing time duration and firing temperature. It is mainly because that the partial Eu^{2+} ions are oxidized forming Eu^{3+} ions, and it leads to luminescent intensities decreasing quickly. But the crystal phase is no change and is strontium aluminate crystal during the process of heating (Fig.3).

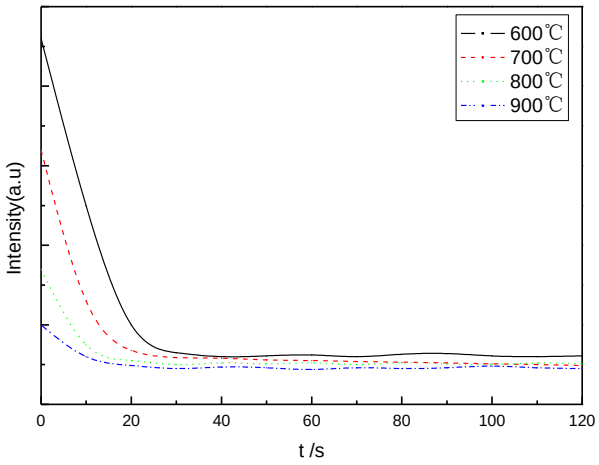

Figure. 2 Decay profiles of afterglow for the LGs with 30wt% $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors at different firing temperature for 30min

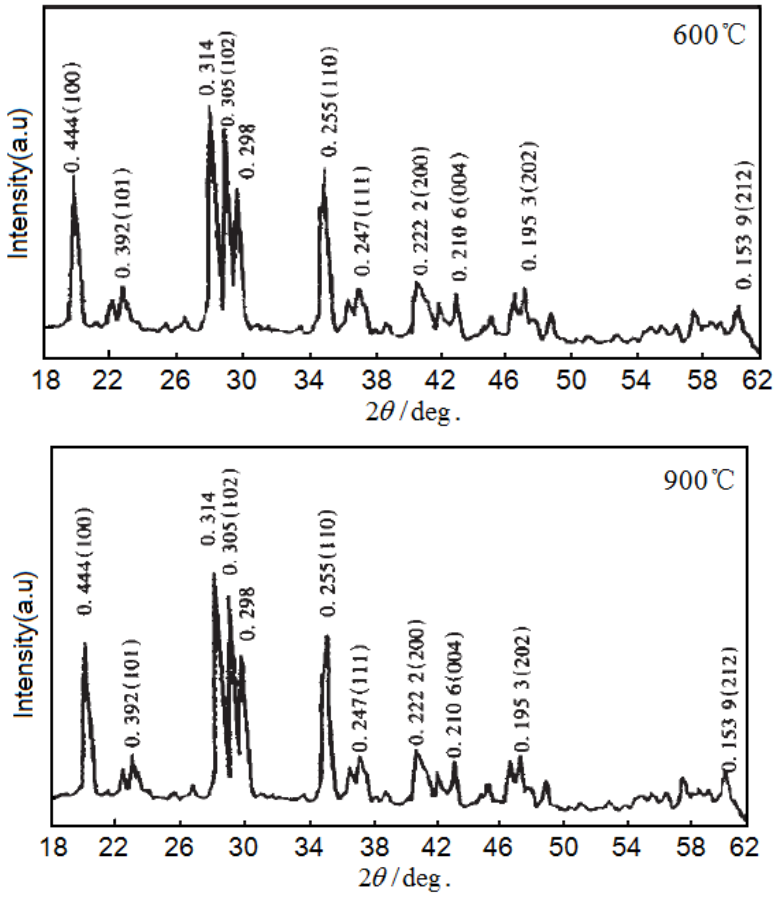

Figure. 3 XRD patterns of the LGs with 30wt% $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors after heat treatment

Fig.4 shows the excitation and the emission spectra respectively. The excitation and the emission spectra indicate the luminescence is originated from the 5d4f→4f transition of Eu^{2+} in the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors. The results indicate that the luminescence of the glasses is originated from the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors in the samples. The mechanism of the long lasting phosphorescence in

$SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors has been investigated[11]. In this study，we suggest that the mechanism of the luminescent glasses are the same as that of $SrAl_2O_4$: Eu^{2+}, Dy^{3+}. After irradiation by the fluorescent lamp，electrons and holes were formed in the luminescent glasses . A parts of electrons or holes are trapped by trapping centers. Since the trap depth is broadly distributed and shallow，the electrons or holes can be thermally released at room temperature and long lasting afterglow luminescence is brought about.

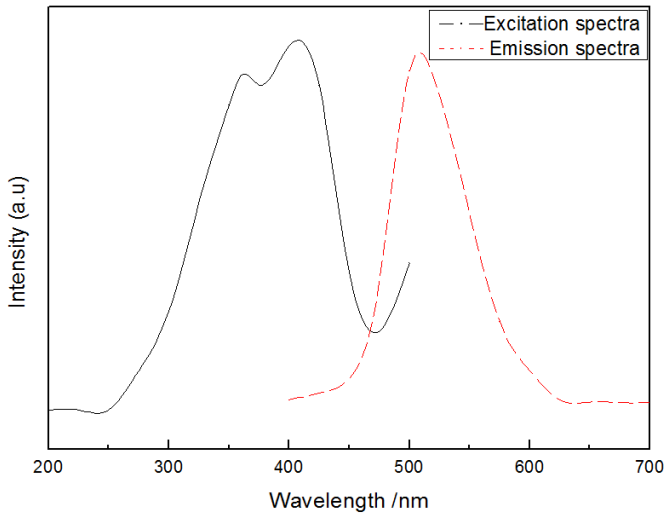

Figure. 4 Excitation spectra and Emission spectra of the LG with 30wt% $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors at 700℃ for 20min. The exciting wavelength is from 300 to 480nm and the emitting wavelength is 510nm.

Summary

Bright long afterglow LGs are prepared by firing the mixed $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors and matrix glasses together under an ambient atmosphere. It is found that the LGs show bright and long afterglow luminescence. What's more, the LGs can exhibit higher brightness and longer afterglow after firing at lower temperature and shorter time. The optimum content of the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors in the LGs are 30wt%.

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