Ultraviolet-radiation-induced structure and long-lasting phosphorescence in Sn$^{2+}$–Cu$^{2+}$ co-doped silicate glass

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Abstract

We report the relaxation of ultraviolet-radiation-induced structure and long-lasting phosphorescence in Sn$^{2+}$–Cu$^{2+}$ co-doped glass with composition of 70SiO$_2$·20Na$_2$O·10CaO·0.05CuO·0.05SnO in mol ration. After irradiation by an ultraviolet lamp ($\lambda_{\text{max}} = 254$ nm) with a power density of 5 mW/cm$^2$ for 30 min, a visible light peaking at 510 nm could be observed with the naked eyes in the dark after the removal of the activating light. Thermostimulated luminescence glow curves and electron-spin-resonance spectra were measured. We suggest that the long-lasting phosphorescence in the Sn$^{2+}$–Cu$^{2+}$ co-doped glass samples resulted from the recombination of electrons and holes at shallow traps in the glass matrix that can be thermally released at room temperature.

Keywords: Long-lasting phosphorescence; Defect; Oxygen vacancy

1. Introduction

Silicate-based materials are widely employed in the field of microelectronics and UV optics. In these materials, point defects play an important role since they can change chemical and physical properties of the materials. In general, such point defects result in undesirable degradation of electrical and/or optical properties, but they can also be used to exhibit some specific features or applications. A variety of metastable defects in glasses have been observed under an excimer laser and a femtosecond laser induces a variety of metastable defects [1–3]. It is hence likely that some novel optical functions can be elicited if the characteristics and quantities of the defects can be controlled. In the case of photostimulated luminescence, defect centers (e.g. halogen ion deficit sites) act as electron trapping centers. The electron trapped in the F center, after X-ray irradiation, is released by excitation of a visible or an infrared laser, and subsequently recombines with a trapped hole, leading to emitted light whose intensity is proportional to the number of F centers, which in sample is proportional to the X-ray dose [4–6]. Photostimulated luminescent phosphors have been used as materials for two-dimensional X-ray sensors [4,5].

Long-lasting phosphorescence is also a radiation-induced defect-related phenomenon. Many researchers try to install certain defects into crystalline and glass materials to control the decay time of long-lasting phosphorescence. Numerous practical materials have been developed, which an emission is strong enough to be observed by naked eyes for a time period exceeding 8 h. So far, long-lasting phosphorescence phenomena have been observed in rare-earth ions doped polycrystalline [7,8] and glasses which were prepared under strong reduction environment [9–11] or were treated by an infrared femtosecond laser [12,13]. In this paper we report that a long-lasting phosphorescence phenomenon was observed in a Sn$^{2+}$–Cu$^{2+}$ co-doped silicate glass without any special treatment.

2. Experimental procedure

Glass composition of Cu and Sn ions co-doped silicate glass sample employed in this study was 70SiO$_2$·20Na$_2$O·10CaO·0.05CuO·0.05SnO in mol ration. Regent grade SiO$_2$, CaCO$_3$, Na$_2$CO$_3$, CuO, and SnO were used as starting materials. An about 40 g batch was mixed, and placed into a platinum crucible. Melting was carried out in an electronic
furnace at 1550 °C for 1 h under the ambient atmosphere. Glass sample was obtained by quenching the room temperature. The glass sample was cut, polished, and subjected to experiments.

Long-lasting phosphorescence was measured as functions temperature and time as follows. The sample was excited by UV-light (254 nm) for 15 min, and the measurement of the intensity of the phosphorescence started at 3 s after removal of the excitation light. Sample temperatures below and above room temperature were achieved by using a temperature controller.

The optical absorption spectra of the glass samples were measured in the wavelength range from 280 to 800 nm with a Hitachi U-3500 spectrophotometer. Electron spin resonance (ESR) measurement was carried out by a Bruker EMX EPR spectrophotometer. Phosphorescence spectra were measured by a Hitachi 2200 spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

The present glass co-doped with Cu$^{2+}$ and Sn$^{2+}$ was transparent and colorless. The long-lasting phosphorescence can be observed in the dark at about half an hour after the removal of the activating 254 nm UV light. The excitation and phosphorescence spectra of Sn$^{2+}$–Cu$^{2+}$ co-doped Na$_2$O–CaO–SiO$_2$ glass measured at room temperature are shown in Fig. 1. A very broad phosphorescence band at around 510 nm is observed in a sample removal the UV light and the sample was illuminated for 15 min with a 254 nm UV light. Fig. 2 shows the intensities of the phosphorescence for the Cu$^{2+}$–Sn$^{2+}$ co-doped glass integrated in the time range of 5–180 s plotted as a function of temperature. A maximal value for the phosphorescence intensity appeared at about 220 K, and the intensities increased in the range of 77–220 K and rapidly decreased above 220 K. This result is considered to be the reason for the long-lasting phosphorescence not very long (can be observed in the dark for about 30 min after the removal of the UV light) at room temperature.

Fig. 3 shows the decay curve of the phosphorescence at 510 nm in the glass sample doped with Sn$^{2+}$–Cu$^{2+}$ ion. The time dependence of the inverse of the intensity of the phosphorescence is also shown in Fig. 3, the intensity of the phosphorescence decreases in inverse proportional to the time, indicating the phosphorescence may be a decay process due to heat-helped tunneling effect.
In general, a long-lasting phosphorescence phenomenon is considered to be occurred when trapped electrons or holes in a solid are liberated by incident low-energy photons, and the recombination energies of electrons and holes are then released as phosphorescence. When the sample employed in present study was illuminated with 254 nm light, an almost symmetric ESR signal appeared at $g = 1.999$; as can be seen from Fig. 4. After removal of the activating UV light, the intensity of the signal due to a defect center decreases with time, which is expected for the decay of phosphorescence. The negative $g$ shift ($g - g_e$, where $g_e$ is the value for free electron, 2.0023) suggest the center to be of trapped electron type. Hosono et al. [14] found a photochromic phenomenon in a calcium aluminate glass melted under a reducing atmosphere. Two absorption bands at around 2 and 3.5 eV were observed with ultraviolet radiation, and disappeared after removal of UV light at the room temperature. They suggest that this ESR signal is probably due to an electron trapped at the oxygen vacancy site surrounded by Ca$^{2+}$ ions, similar to an F$^{-}$-like center of CaO. On the other hand, long-lasting phosphorescence could not be observed in the cupric ion singly doped glass. The role of Sn$^{2+}$ ion to the mechanism of long-lasting phosphorescence, therefore, cannot be neglected.

According to the above results, in the present case, a possible mechanism of the long-lasting phosphorescence may be interpreted as follows. The free electrons generated by UV illumination were excited from the ground state to the conduction band and then trapped at the oxygen vacancy site surrounding by Cu$^{2+}$ ion. The Sn$^{2+}$ ions act as hole traps, resulting in Sn$^{2+} + \text{hole} \rightarrow (\text{Sn}^{2+})^+$, where $(\text{Sn}^{2+})^+$ is a tin ion of unstable intermediate valency. The energy depth of electron trapping site is very shallow and be broadly distributed. It is hence probable that the electrons at the trapping site can be thermally released even at room temperature and recombine with the trapped holes. Thus, the released energies due to the recombination of electrons and holes then transfer to the Cu$^{2+}$ ions. Consequently, a long-lasting phosphorescence phenomenon takes place. Fig. 5 summarizes the mechanism of long-lasting phosphorescence in Sn$^{2+}$–Cu$^{2+}$ activated SiO$_2$–Na$_2$O–CaO glass.

4. Conclusion

Long-lasting phosphorescence spectra which centered around 510 nm was observed in a Sn$^{2+}$- and Cu$^{2+}$-doped Na$_2$O–CaO–SiO$_2$ glasses. We suggest that the long-lasting phosphorescence results from the thermal stimulated recombination of holes and electrons at trapping site induced by UV light illumination, which leave holes or electrons in a metastable excited state at room temperature. In this case, the oxygen vacancy sites surrounding by Ca$^{2+}$ ions act as electron trap centers, they trap the free electrons, which were generated by UV illumination and were excited from the ground state to the conduction band. The Sn$^{2+}$ ions were oxidized under illumination of UV light excitation, resulting in Sn$^{2+} + \text{hole} \rightarrow (\text{Sn}^{2+})^+$, and they act as hole traps. Due to the recombination of electrons and holes then transfer to the Cu$^{2+}$ ions at room temperature, a long-lasting phosphorescence phenomenon occurs.

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