Long-lasting phosphorescence in Mn$^{2+}$: Zn$_2$GeO$_4$ crystallites precipitated in transparent GeO$_2$–B$_2$O$_3$–ZnO glass-ceramics

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Abstract

Mn$^{2+}$-doped GeO$_2$–B$_2$O$_3$–ZnO (GBZ) glasses were investigated and developed as long-lasting phosphorescence host materials. Transparent glass-ceramics were obtained after heat-treated at the first crystallization temperature for 20 min. By X-ray diffraction measurement and SEM observation, it is clarified that Zn$_2$GeO$_4$ crystallites with a diameter of about 1 μm precipitate on the sample’s surface after heat-treatment. An orange long-lasting phosphorescence from Mn$^{2+}$ was observed in the 25GeO$_2$–25B$_2$O$_3$–50ZnO glass matrix, however, a stronger long-lasting green phosphorescence was observed in the phase of Zn$_2$GeO$_4$ crystallites. This phenomenon is considered to be due to the different ligand field environment surrounding Mn$^{2+}$ ions in the glass and the glass-ceramics. A possible mechanism for the long-lasting phosphorescence in the Mn$^{2+}$-doped glass was discussed.

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1. Introduction

In recent years, it gains an understanding that point defects play important roles 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-dimension X-ray sensors [4,5].

Long-lasting phosphorescence is also a radiation-induced defect-related phenomenon. Many researches 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, their phosphorescence are strong enough to be observed by naked eyes for a time period exceeding 8 h. However, these ceramics materials are opaque and so far, long-lasting phenomena have been observed in rare-earth doped polycrystalline, such as alkaline-earth aluminate, SrAl$_2$O$_4$; Eu$^{2+}$+Dy$^{3+}$ [7,8] or glasses prepared under a strong reducing environment [9,10] or were treated under an extreme ambience, e.g. irradiated by an infrared femtosecond laser or under high pressure [11]. In this study, a strong long-lasting orange phosphorescence was observed in Mn$^{2+}$-doped GeO$_2$–B$_2$O$_3$–ZnO (GBZ) glasses without any special treatment, and the phosphorescence changed to greenish color in the glass-ceramics after heat-treatment, a possible mechanism of long-lasting phosphorescence in Mn$^{2+}$-doped GBZ glass was presumed.
2. Experiment procedure

Glasses were prepared according to a conventional melt-quenching method. Reagent grade GeO$_2$, B$_2$O$_3$, and ZnO were used as starting materials. Composition chosen in the present study are $x$GeO$_2$·25B$_2$O$_3$·(75−$x$)ZnO·0.2MnO ($x=20, 25, 30$) and $y$GeO$_2$·(50−$y$)B$_2$O$_3$·50ZnO·0.2MnO ($y=20, 25, 30$) in mol%. Accurately weighted 20 g batches were thoroughly mixed and placed into a platinum crucible. Melting was carried out in an electronic furnace at 1350 °C for 1 h under the ambient atmosphere. Glass samples were obtained by quenching at the room temperature. The obtained glasses were annealed at the respective glass-transition temperatures determined by thermal analysis. The glass samples were cut, polished, and subjected to experiments.

Long-lasting phosphorescence was measured as function temperature and time as follows. The samples were excited by UV-light (254 nm) for 3 min, and the measurement of intensity of the phosphorescence started at 3 s after the removal of the excitation light.

A translucent glass-ceramics was prepared by heat-treating the glass at the first crystallization temperature which was obtained by DSC measurements for 20 min, and X-ray diffraction measurements were carried out by using a Rigaku RINT 2100 X-ray diffractometer using Cu K$_\alpha$ radiation.

The photoluminescence spectra and excitation spectra were measured in the wavelength range of 280–800 nm with a Hitachi U-4500 fluorescence spectrophotometer. Electron spin resonance (ESR) measurements were carried out by a JES-RE3X, JEOL ESR spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

The precursor glasses, i.e. Mn$^{2+}$-free GeO$_2$–B$_2$O$_3$–ZnO system glasses was transparent and colorless and long-lasting orange/yellow phosphorescence was observed in the specimens in the dark for about 2 h after the removal of an UV-light for 3 min. Fig. 1 shows a typical phosphorescence spectrum and excitation spectrum of the specimens, and decay curve of long-lasting phosphorescence intensity measured after 3 min excitation with 365 nm light. On the other hand, very strong red phosphorescence was observed in Mn$^{2+}$-doped glasses under a 254 nm UV lamp excitation source. As can be seen in Fig. 2, the emission spectrum shows a broad emission band, which has its maximum around 2 eV (590 nm) and is assigned to $^4T_1 \to ^6A_1$ transition within the 3d$^5$ configuration of the Mn$^{2+}$. The red emission from Mn$^{2+}$ has been observed in many materials and finds application in electroluminescent device.

In general, a long-lasting phosphorescence phenomenon is considered to occur 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 specimen employed in the present study was illuminated with UV-light (365 nm), an almost symmetric ESR signal appeared at $g = 1.998$. As can be seen in Fig. 3, after removal of the activating UV-light, the intensity of the signal due to a defect center decreased with times, 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) suggests the center to be of trapped electron type. It is worth mentioning that a long-lasting phosphorescence can also be observed in Mn$^{2+}$-free glasses, though the phosphorescence intensity is quite weaker than Mn$^{2+}$-doped samples, and the decay time of long-lasting phosphorescence is almost similar to the Mn$^{2+}$-doped glasses. This result implies that the defect center, the dominate factor of decay time is same in Mn$^{2+}$-free and Mn$^{2+}$-doped glasses. It is well-known that point defects can be generated by quenching process in GeO$_2$.
glass melted in air or by pulling a GeO$_2$ containing silica fiber, which is connected to partially reduced Ge species, the so-called oxygen deficiency centers (ODCs), i.e. oxygen vacancies associated with Ge$^{4+}$ ions, Ge E$^0$ center, and Ge$^2+$ homoband [12]. In the present case, since we found that the decay time of long-lasting phosphorescence is related to the GeO$_2$ concentration, it is reasonable to consider that oxygen vacancies associated with Ge$^{4+}$ concern to the mechanism of long-lasting phosphorescence in Mn$^{2+}$-free and Mn$^{2+}$-doped GeO$_2$–B$_2$O$_3$–ZnO system glasses.

According to the above results, a tentative model for the long-lasting phosphorescence in the Mn$^{2+}$-doped glass was proposed as follows: the photo-oxidized reaction of Mn$^{2+}$ ions would occur with UV radiation, photo-oxidized Mn$^{2+}$ ions, (Mn$^{2+}$)$^+$, and excited electrons, e*, would be generated, and the e* would be trapped at the site of oxygen vacancies associated with Ge$^{4+}$. It is known that these electron centers are thermally unstable near room temperature, and are gradually converted into diamagnetic centers by thermally releasing an electron. After removal of UV-light radiation, thermal excitation of trapped electrons from these donor levels to the conduction band occurs. Then, the released e* would recombine with (Mn$^{2+}$)$^+$ to produce the excited state of Mn$^{2+}$ ions, Mn$^{2+*}$. Then, the 3d electrons on the excited states will finally relax to the ground state, and the red phosphorescence is due to the $^4T_1 \rightarrow ^6A_1$ transition.

As can be seen in Fig. 4, GeO$_2$–B$_2$O$_3$–ZnO system glasses employed in present work show two DSC curves, glass-transition temperature and the first crystallization temperature. Translucent glass-ceramics were obtained after heat-treatments at the first crystallization temperatures for 20 min. Fig. 5 shows the decay curves of the phosphorescence, compared to the sample before heat-treating, the long-lasting phosphorescence evidently became brighter and longer in the sample after heat-treatment. The first crystallization peak disappeared after heat-treatment; this result implies that a kind of component maybe precipitated from glass matrix. Fig. 6 shows the XRD patterns of the phases of glass and glass-ceramics. In the case of glass phase, a broad peak due to the amorphous structure was exhibited, whereas in the phase of glass-ceramics, sharp diffraction peaks assigned to the polycrystalline phase of zinc germanate, i.e. Zn$_2$GeO$_4$ by comparing the XRD data of the samples with JCPDS cards, was shown. SEM observation was also carried out; as can be seen in Fig. 7, rhombohedral crystals with diameter of about 1 μm were dispersed in the glass-ceramics.

The Tanabe–Sugano diagram for Mn$^{2+}$ ion shows that the $^4T_1 \rightarrow ^6A_1$ transition energy in the Mn$^{2+}$ ion strongly depends on the crystal field strength induced by host lattice. It is known that the coordination number of Mn$^{2+}$ ions in glass matrix is six, they emit red emission, and emit green emission when they are in four coordination number environment. Therefore, it is revealed that a GeZn$_2$O$_4$:Mn$^{2+}$ solid solution was precipitated and long-lasting phosphorescence was observed.
on the sample’s surface by heat-treatment at the first crystallization temperature, and the change of host lattice results in an increase in the Mn$^{2+}$-related emission energy. As can be seen in Fig. 4, a very bright green phosphorescence (centered at around 535 nm) was observed under UV-light in the sample after heat-treatment. Comparing the spectrum shape with glass, the spectrum of the glass-ceramics exhibits much more sharp; this result confirms that the coordination environment around Mn$^{2+}$ may be changed from glass to crystal. The reason why the decay time of long-lasting phosphorescence in glass-ceramics is longer than that in glasses before heat-treatment, unfortunately, has not been clarified in the present stage.

4. Conclusion

Mn$^{2+}$-doped glasses with GeO$_2$–B$_2$O$_3$–ZnO (GBZ) system were developed with very strong long-lasting phosphorescence host materials. A surface crystallized translucent glass-ceramics were obtained by heat-treatment at the first crystallization temperature of the specimens for 20 min. By X-ray diffraction measurement and SEM observation, it is clarified that Zn$_2$GeO$_4$ crystallites with a diameter of about 1 μm precipitates on the surface after heat-treatment. A red long-lasting phosphorescence from Mn$^{2+}$ was observed in the GeO$_2$–B$_2$O$_3$–ZnO glass matrix, however, the phase of Zn$_2$GeO$_4$ crystallites shows very strong green long-lasting phosphorescence. This phenomenon is considered to be due to the different ligand field environment surrounding Mn$^{2+}$ ions in the glass and the glass-ceramics. We assumed that the photo-excitation energy of the host glass can be temporarily stored in the trapping center, and then the energy transfers from the traps to the doping ions within reasonable long time period.

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