Long-lasting Phosphorescence in Mn$^{2+}$ Doped GeO$_2$–B$_2$O$_3$–ZnO Glasses and Glass-Ceramics

Jianbei QIU, Hajime IGARASHI and Akio MAKISHIMA

Center for Nano Materials and Technology, Japan Advanced Institute of Science and Technology, Asahidai 1-1, Tsukuba, Ibaraki 305-8565, Japan

Mn$^{2+}$-doped GeO$_2$–B$_2$O$_3$–ZnO (GBZ) glasses were investigated and developed as efficient long-lasting phosphorescence host materials. Surface crystallization phenomenon occurred when the Mn$^{2+}$ doped 25GeO$_2$–25B$_2$O$_3$–50ZnO glasses were heat-treated at 706°C for 30 min. By X-ray diffraction measurement, it is clarified that Zn$_2$Ge$_2$O$_7$ crystallites with a diameter of about several μm are precipitated on the sample's surface after heat-treatment. A red long-lasting phosphorescence from Mn$^{2+}$ was observed in the 25GeO$_2$–25B$_2$O$_3$–50ZnO glass matrix, however, a very strong long-lasting green phosphorescence was observed in the phase of Zn$_2$Ge$_2$O$_7$ crystallites. This phenomenon is considered 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, which an emission is strong enough to be observed by naked eyes for a time period exceeding 8 h. So far, long-lasting phenomena have been observed in rare-earth doped polycrystals, such as alkali-earth aluminates, SrAl$_2$O$_3$:Eu$^{2+}$ + D$_{2}$$^{3+}$ (7–8) or glasses prepared under a strong reducing environment (9–10) or were treated by an infrared femtosecond laser. 11 In this paper, 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 in the glass-ceramics after heat-treatment, a possible mechanism of long-lasting phosphorescence in Mn$^{2+}$-doped 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 is 25GeO$_2$–25B$_2$O$_3$–50ZnO-0.2MnO 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 differential 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 seconds after removal of the excitation light. A translucent glass-ceramics was obtained by heat-treated the glass at 706°C for 30 min, X-ray diffraction measurements were carried out by using a Rigaku RINT 2100 X-ray diffractometer using Cu-Kα radiation.

The photoluminescence spectra and excitation spectra were measured in the wavelength range from 280 to 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

3.1. Phosphorescence properties of the Mn$^{2+}$ doped GBZ glass and glass ceramics

The present Mn$^{2+}$-doped glass was transparent and colorless. A long-lasting orange/yellow phosphorescence was observed in the dark for about 2 h after the removal of the activating 254 nm UV light for 3 min. As can be seen in Fig. 1, The emission spectrum show a broad emission band, the band has it maximum around 2 eV (590 nm) and is assigned to $^4T_1 \rightarrow ^2A_1$ transition within the 3 $d$ configuration of the Mn$^{2+}$. The orange/yellow emission from Mn$^{2+}$ has been observed in many materials and finds application in electroluminescent device.

On the other hand, a surface crystallized translucent glass-ceramics phase was obtained by annealing at 706°C for 30 min, the thickness of glass-ceramics phase is no more than 10

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μm, the phase expanded with increasing annealing time. Figure 2 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 diffractive peaks assigned to the polycrystalline phase of zinc germanate, i.e., GeZnO, by comparing the XRD data of the samples with JCPDS cards, was shown. The Tanabe-Sugano diagram for the Mn²⁺ ion shows that the ⁴T₁⁻→⁴A₁ transition in the Mn²⁺ ion strongly depends on the crystal field induced by host lattice. Therefore, it revealed that a GeZnO; Mn²⁺ solid solution was precipitated on the sample's surface by heat-treated at 706°C for 30 min, and the change of host lattice results in an increase of the Mn²⁺-related emission energy. As can be seen in Fig. 1, a very bright green phosphorescence (centered 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 Mn²⁺ may be changed from glass to crystal.

3.2 mechanism for long-lasting phosphorescence in Mn²⁺-doped GBZ glass

Figure 3 shows the decay curves of the phosphorescence, comparing to the sample before heat-treating, the long-lasting phosphorescence evidently became brighter and longer in the sample after heat-treatment. In commonly, the long-lasting phosphorescence processes is considered to be dominantly due to the electron-hole recombination through thermally assisted tunneling. Li et al. suggested that Mn²⁺ ions act as hole trapping centers in Mn²⁺-doped phosphorescent zinc silicate materials. Avouris and Morgan found that the phosphorescence of manganese activated zinc silicate decayed as the reciprocal of the time and interpreted it by the radiative recombination of trapped electrons and holes through tunneling. Delbecq et al. found a t⁻¹ decay law of the phosphorescence from the recombination of trapped holes and electrons in KCl: AgCl (TICl) by tunneling model. Figure 4 shows the time dependence of the inverse of the phosphorescence intensity, however, the decay time of phosphorescence do not obey a t⁻¹ law in the present work. This result implies that the mechanism of the Mn²⁺-related long-lasting phosphorescence is distinct from those described in Ref. 12.

In general, a long-lasting phosphorescence phenomenon is considered occurring 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 the present study was illuminated with 254 nm light, an almost symmetric ESR signal appeared at g = 1.998, as can be seen in Fig. 5. 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–gₑ, where gₑ is the value for free electron, 2.0023) suggest the center to be of trapped electron type. Since long-lasting phosphorescence could not observed in SiO₂–B₂O₃–
ZnO and ZnO$_2$–B$_2$O$_3$ glasses, and we also found that the ESR signal relates to Ge$_2$O$_3$ concentration, therefore, this signal may be due to an F$^-$ center, i.e., an electron trapped at the site of an oxygen vacancy coordinated by Ge$^{4+}$.

It is worth mentioning that a long-lasting phosphorescence was also observed in Mn$^{2+}$-free glass, though the phosphorescence is weaker than Mn$^{2+}$-doped glass, and the decay time was almost similar to the Mn$^{2+}$-doped glass. This result implies that a similar oxygen vacancy concerns to the mechanism for long-lasting phosphorescence both in Mn$^{2+}$-free glasses and Mn$^{2+}$-doped glasses.

According to the above results, a tentative model for the long-lasting phosphorescence in the Mn$^{2+}$-doped glass was proposed as follows: Ge$^{4+}$-relating F$^-$-like center in oxide glasses creates donor levels in the band gap. 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 irradiation, thermal excitation of trapped electrons from these donor levels to the conduction band occurs. Then the electrons from the F$^-$ center recombined with photo-oxidized luminescent ions, (Mn$^{2+}$)$^{2+}$, giving long-lasting phosphorescence after removal of UV illumination.

4. Conclusion
Mn$^{2+}$-doped GeO$_2$–B$_2$O$_3$–ZnO (GBZ) glasses were developed for efficient long-lasting phosphorescence host materials. A surface crystallized translucent glass-ceramics were obtained by heat-treating at the 706°C for 30 min. By X-ray diffraction measurement, it is clarified that Zn$_2$Ge$_4$O$_{13}$ crystals with a diameter of about several μm are precipitated on the surface after heat-treatment. A red long-lasting phosphorescence from Mn$^{2+}$ was observed in the 25GeO$_2$–25B$_2$O$_3$–50ZnO glass matrix, however, the phase of Zn$_2$Ge$_4$O$_{13}$ crystals shows green long-lasting phosphorescence with a very high efficiency. This phenomenon is considered 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 electrons thermally released from F$^-$ center recombine with photo-oxidized luminescent ions, (Mn$^{2+}$)$^{2+}$, giving phosphorescence after stopping of UV light illumination.

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References

Fig. 5. Typical ESR spectra of Mn$^{2+}$-free or Mn$^{2+}$-doped GeO$_2$–B$_2$O$_3$–ZnO glass induced by UV light irradiation ($\lambda_{\text{exc}}$ = 254 nm) and time dependence upon ESR signal intensity after stopping UV irradiation.