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Structural relaxation and long-lasting phosphorescence in sol–gel-derived GeO₂ glass after ultraviolet light irradiation

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Abstract

We report on the observation of a long-lasting phosphorescence phenomenon in GeO₂ and Er³⁺-doped GeO₂ glass samples fabricated by the sol–gel method. Absorption spectra showed that there were oxygen-deficient defects associated with Ge ions in the samples. Irradiation with ultraviolet light at 254 nm induced long-lasting phosphorescence with a peak at 465 nm for the GeO₂ glass sample. The intensity of the phosphorescence decreased with increasing temperature and in inverse proportion to the time after a quick decrease of the intensity. The long-lasting phosphorescence in these samples is considered to be due to the thermally activated electron–hole recombination at room temperature.

1. Introduction

In 1978, Hill *et al* [1] observed photosensitivity in GeO₂-doped silica glass. It was shown that the photosensitivity in GeO₂-doped silica glass is related to the oxygen deficiency associated with Ge ions [2]. The optical properties of oxygen-deficiency-related defects in GeO₂ and GeO₂-doped silica glass were investigated [3–6]. Usually, an absorption peak is observed at 5 eV (≈ 250 nm) in GeO₂ and GeO₂-doped silica glass [3–5]. The peak was first assigned to the transition due to a twofold-coordinated Ge atom [3–5]. Recently, it has been stated that the absorption peak at 5 eV is related to at least two oxygen deficiencies [4, 5]. Peroxy radicals (Si(Ge)–O–O[•] or O^{2•-}) may also have an absorption peak at about 5 eV [7]. The two oxygen deficiencies are the neutral oxygen monovacancy (NOMV: ₃OGe–GeO₃) and the

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neutral oxygen divacancy (NODV: $-\text{O}-\text{Ge}-\text{O}-$) associated with Ge ions [4]. NOMVs are readily changed to GeE' centres by illumination with an ultraviolet (UV) lamp emitting 5 eV light. On the other hand, the NODV emits luminescence at 3.3 eV (≈ 380 nm) and 4.3 eV (≈ 290 nm), but this type of defect is assumed to be insensitive to illumination with a UV lamp. Knowledge of the mechanism of the light-induced permanent refractive index change in GeO_2 -doped silica glasses is still vague, in spite of many investigations [8].

Luminescence and phosphorescence properties of silica glass have been investigated by Skuja *et al* [9,10]. A relaxation time of about 10 ms was observed at 2.7 eV (≈ 460 nm) due to the triplet-singlet luminescence of twofold-coordinated silicon atoms at room temperature [9, 10]. GeO_2 glass is isostructural with glassy SiO_2 . Therefore, we expect that similar phenomena should be observed in GeO_2 glass. Upconversion fluorescence and phosphorescence were observed in Er^{3+} -doped GeO_2 glass samples fabricated by the sol-gel method [11]. However, there are few reports on the structural relaxation and long-lasting phosphorescence in GeO_2 and rare-earth-doped GeO_2 glasses.

Studying the UV-light-induced structure change and structural relaxation in GeO_2 glass will help us to clarify the mechanism of the photoinduced refractive index change and other phenomena in GeO_2 -doped silica glasses. In this paper, we report on the observation of room-temperature structural relaxation and long-lasting phosphorescence in GeO_2 glass samples after irradiation with UV light at 254 nm. The temperature dependence of the phosphorescence is investigated and the mechanism of the phenomenon is also discussed.

2. Experimental details

GeO_2 and 3 mol% Er_2O_3 -doped GeO_2 glass samples were fabricated using a sol-gel method. H_2O and CH_3COOH were dissolved in butanol ($n\text{-C}_4\text{H}_9\text{OH}$) at room temperature. After sufficient stirring, the butanol solution was dissolved in tetraethoxy-germanium ($\text{Ge}(\text{OC}_2\text{H}_5)_4$) together with *tris*-acetylacetonato-erbium ($\text{Er}(\text{C}_5\text{H}_7\text{O}_2)_3 \cdot 3\text{H}_2\text{O}$). Then, the resulting solution was continuously stirred in a closed glass container for 90 min at room temperature. The final molar ratio $\text{Ge}(\text{OC}_2\text{H}_5)_4:n\text{-C}_4\text{H}_9\text{OH}:\text{H}_2\text{O}:\text{CH}_3\text{COOH}$ was 1:7:1:0.1. The solution, placed in an uncovered Teflon container, was kept at 70 °C for one week and then at 100 °C for another week to get a translucent dried gel. An amorphous transparent glass sample was obtained by heat treatment of the dried gel at 640 °C for 1 h under ambient atmosphere. The absorption spectra of the samples were measured by a spectrophotometer (JASCO V-570). The photoluminescence spectrum was measured during the UV light irradiation, while the phosphorescence spectrum was measured 10 s after the excitation was stopped. The photoluminescence spectra of the samples were measured by means of a fluorescence spectrophotometer (Shimadzu RF-5300PC, Tokyo, Japan) using 254 nm UV light from a xenon lamp as the excitation source after passing through a monochromator. For the measurement of the phosphorescence spectrum and the decay curve of the phosphorescence, glass samples were first irradiated with a UV lamp (Topcon PU-2, $\lambda_{\text{max}} = 254$ nm) for 30 s. A heating temperature stage provided sample temperatures between 20 and 400 °C. Electron spin-resonance (ESR) measurements were carried out at an X-band frequency (9.8 GHz) by an ESR spectrophotometer (JEOL-FE3X). The microwave power, time constant, modulation amplitude and sweep time were 1 mW, 0.03 s, 1×100 and 4 cm min^{-1} , respectively.

3. Results and discussion

Figure 1 shows the room-temperature absorption spectra of GeO_2 (a) and 3 mol% Er_2O_3 -doped GeO_2 (b) glass samples fabricated by the sol-gel method. An absorption peak was observed at 250 nm in glass samples. The absorption peak can be assigned to oxygen deficiencies

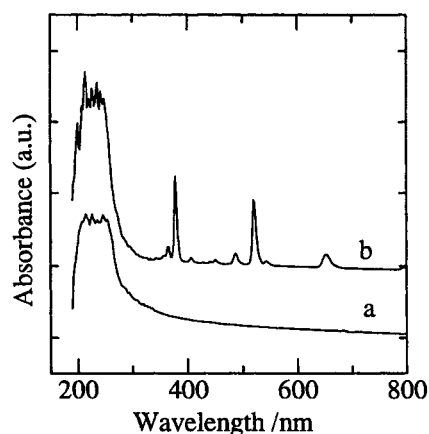


Figure 1. Absorption spectra of GeO₂ (a) and 3 mol% Er₂O₃-doped GeO₂ (b) glass samples.

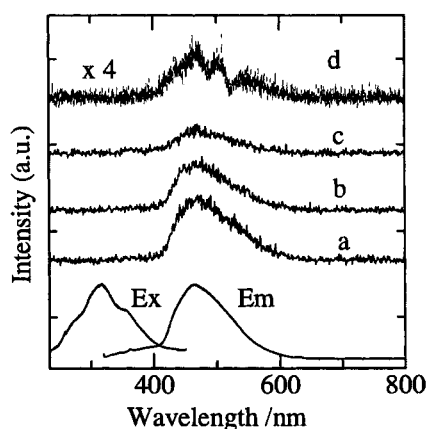


Figure 2. Photoluminescence (labelled 'Em'), excitation ('Ex') and phosphorescence (a–c) spectra of a GeO₂ glass sample at various temperatures (a: room temperature; b: 100 °C; c: 200 °C) and the phosphorescence (d) spectrum of a 3 mol% Er₂O₃-doped GeO₂ glass sample at room temperature. For the measurement of the excitation spectrum, the luminescence at 465 nm is monitored.

associated with Ge ions [4, 5]. Absorption peaks at 364, 380, 450, 490, 520, 550 and 650 nm observed in the 3 mol% Er³⁺-doped GeO₂ glass sample can be ascribed to the transitions between the ²G_{9/2}, ⁴G_{11/2}, ²H_{9/2}, ⁴F_{5/2}, ²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2} excited states and the ⁴I_{15/2} ground state of Er³⁺ [11].

After irradiation by the UV lamp ($\lambda_{max} = 254$ nm) with a power density of about 5 mW cm⁻², long-lasting phosphorescence was observed in both sol-gel-derived glass samples in the dark. In the case of a GeO₂ glass sample irradiated by UV light for 5 min, the phosphorescence can still be seen with the naked eye in the dark 10 min after the removal of the UV light.

Figure 2 shows the photoluminescence (labelled 'Em'), excitation ('Ex') spectra of a GeO₂ glass sample at room temperature, and phosphorescence spectra (a, b, c) of a GeO₂ glass sample at various temperatures, and the phosphorescence spectrum (d) of a 3 mol% Er₂O₃-doped GeO₂ glass sample at room temperature. As can be seen from the figure, the phosphorescence

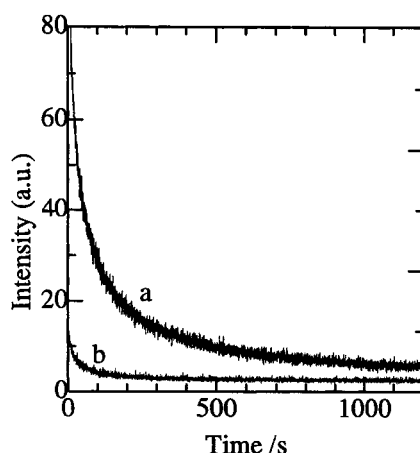


Figure 3. Decay curves of the phosphorescence at 465 nm in the GeO₂ (a) and 3 mol% Er₂O₃-doped GeO₂ glass (b) samples at room temperature.

spectrum induced by the UV light has the same appearance as the photoluminescence spectrum induced by the 254 nm UV light. The emission peak at 465 nm can be assigned to the triplet-to-singlet (T_1-S_0) transitions of the NODVs [10]. The red-shift of the emission peak from 3.3 eV (≈ 380 nm) may be due to the cross-relaxation among NODVs. Such a phenomenon has been observed in GeO₂-doped silica glasses fabricated by a vapour axial deposition method [6]. The intensity of the phosphorescence decreases with increase in the temperature. Two holes at 490 and 520 nm in the phosphorescence spectrum of the 3 mol% Er³⁺-doped GeO₂ glass sample can be assigned to the re-absorption due to the transitions between the $^4I_{15/2}$ and the $^4F_{5/2}$, $^2H_{11/2}$ states of Er³⁺. Weak photoluminescence at 465 nm was also observed in the translucent dried GeO₂ gel before heat treatment when excited by 254 nm UV light. This shows that there was oxygen deficiency even in the dried GeO₂ gel.

Figure 3 shows decay curves of the phosphorescence at 465 nm in the GeO₂ glass sample (a) and the 3 mol% Er₂O₃-doped GeO₂ glass sample after irradiation with UV light at 254 nm with a power density of 5 mW cm⁻² for 30 min. The intensity of the phosphorescence decreases quickly and then more slowly with the passage of time. The intensity of the phosphorescence of the 3 mol% Er₂O₃-doped GeO₂ glass sample is weak compared with that of the GeO₂ glass sample.

Figure 4 shows the temperature dependence of the phosphorescence in the GeO₂ glass sample at 465 nm after UV light irradiation with a power density of 0.5 mW cm⁻² for 5 min. We did not observe any linear correlation between the logarithm of the intensity of the phosphorescence and time. However, as shown in figure 5, the intensity of the phosphorescence seems to decrease in inverse proportion to the time in cases (a) and (b). This is a phenomenon typical of long-lasting phosphorescence due to the thermally excited recombination of holes and electrons [12–16]. The intensity of the phosphorescence decreases much faster at high temperature than at low temperature.

Figure 6 shows the ESR spectra of GeO₂ glass before and after UV light irradiation. The time shown in the figure is the time elapsed after removal of the activating light. Weak signals were observed in the unirradiated glass sample, while strong signals were detected after UV light irradiation. The induced signal decreases quickly at first and then slowly with the passage of time, which is similar to the decay of the UV-light-induced phosphorescence. We calculated the difference ESR spectrum for the GeO₂ glass sample—the difference between the spectra

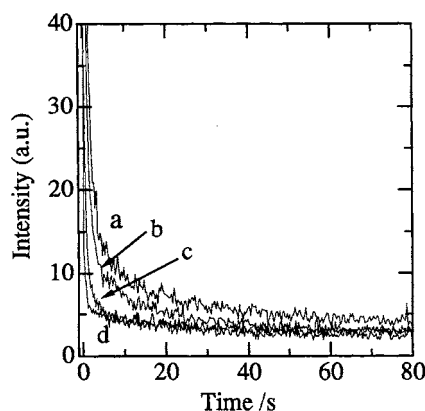


Figure 4. Decay curves of the phosphorescence at 465 nm in GeO₂ at various temperatures. a: room temperature; b: 100 °C; c: 200 °C; d: 300 °C.

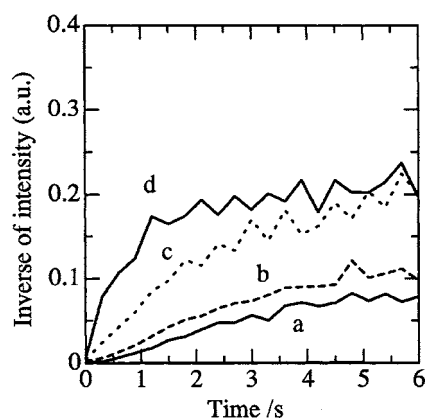


Figure 5. Correlation of the inverse of the intensity of the phosphorescence at 465 nm in GeO₂ and time at various temperatures. a: room temperature; b: 100 °C; c: 200 °C; d: 300 °C.

after and before the UV irradiation—and confirmed that no apparent change was observed in the signal at 3380 mT, while changes in the signals at 3390 and 3400 mT were observed. The g -values of the signals at 3390 and 3400 mT are 2.001 and 1.996, respectively, and these can be ascribed to the UV-light-induced defects, e.g. GeE', in the GeO₂ glass sample [5].

Long-lasting phosphorescence at room temperature is a phenomenon widely observed in crystals and glasses doped with rare-earth ions and transition metal ions [12–16]. The mechanism of the long-lasting phosphorescence has been suggested to be as follows. After the irradiation with the UV light, free electrons and holes were formed in the glass samples. The holes or electrons were temporarily trapped by defect centres, released by heat energy at room temperature, and recombined with electrons or holes trapped by other defect centres. The recombination of holes and electrons or the energy transfer due to the recombination of holes and electrons to the active ions, e.g. rare-earth and transition metal ions, results in the characteristic emissions of rare-earth ions and transition metal ions. Figure 7 shows the correlation between the intensity of the phosphorescence and the intensity of the ESR signal. The relative intensity of the ESR signal is calculated on the basis of the rough assumption that the signal intensity is proportional to the height of the signal. A linear correlation is

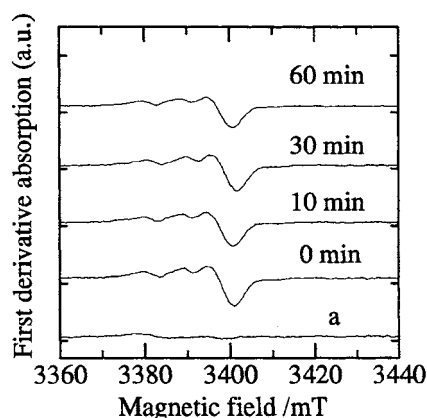


Figure 6. ESR spectra of the GeO₂ glass sample before and after the UV light (254 nm) irradiation. Spectrum a: before the UV light irradiation. The time shown in the figure is the time elapsed after removal of the activating light.

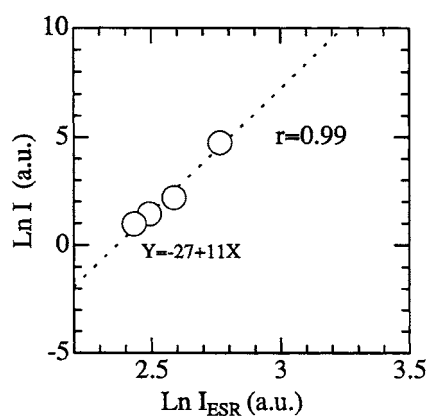


Figure 7. Correlation of the intensity of the phosphorescence and the ESR signal.

observed between the logarithm of the intensity of the phosphorescence and the logarithm of the induced ESR signal. We cannot explain the meaning of the parameters in the fitting equation at present. The phosphorescence and ESR signal due to the induced defects could not be simply related. However, the induced ESR signal due to UV-light-induced defects fades with time and is in agreement with the decay of the phosphorescence. The phosphorescence intensity of Er³⁺-doped GeO₂ glass is much weaker than that of undoped glass. This can be attributed to the direct absorption of 254 nm light by Er³⁺ ions, which does not result in the formation of free electrons and holes or phosphorescence. The other factor is the re-absorption of phosphorescence by Er³⁺ ions.

The time dependence of the intensity of the phosphorescence was not a simple exponential function. The decay curve of the phosphorescence in GeO₂ glass contains at least two components. One is the decay of the luminescence due to the radiative relaxation of the excited state of the NOMVs, which can be expressed as an exponential function. The other is due to the thermally excited recombination of trapped electrons and holes induced by UV light irradiation. The rate for electron escape from the trap can be expressed as $P = f \exp(-W_t/k_B T)$, where

W_t is the trap depth and the frequency factor f is given by the product of the density of states of the band into which the carriers are released, the carrier thermal velocity and the trap's capture cross-section. If we assume that the released carriers are captured by a fluorescent centre and are not recaptured by traps, the time dependence of the phosphorescence intensity after removal of the activating light can be expressed as $I(t) = \eta f P n(t) = n(0) \eta f P \exp(-Pt)$, where $n(t)$ is the number of trapped carriers at time t and η is the phosphorescence efficiency [17]. Therefore, the decay of the phosphorescence is strongly dependent on the trap depth as well as the temperature. The fast decay at higher temperature, as shown in figure 4, is due to the large P , i.e., the high rate of escape of trapped electrons from the traps.

The structural change of GeO₂-doped silica glasses after UV light irradiation has been investigated [3–5]. It was suggested that the photobleachable NOMVs converted to GeE' centres upon UV illumination. In the present case, the reaction can be represented as follows:



Some of the active electrons are temporarily trapped by some active sites, e.g. fourfold-coordinated Ge sites, and then released by the heat energy at room temperature, whereupon they recombine with the trapped holes, thus producing phosphorescence.

4. Conclusions

In conclusion, we have observed long-lasting phosphorescence in sol-gel-derived GeO₂ and Er³⁺-doped GeO₂ glass samples. The intensity of the phosphorescence decreased with increasing temperature and in inverse proportion to time. The decay of the phosphorescence agrees qualitatively with the decay in the ESR signals due to the UV-radiation-induced defects. We suggest that the long-lasting phosphorescence is due to the thermostimulated recombination of holes and electrons at traps at room temperature.

Acknowledgments

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