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Long-lasting phosphorescence in Sn$^{2+}$–Cu$^{2+}$ codoped silicate glass and its high-pressure treatment effect

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Long-lasting phosphorescence was observed at 510 nm in a Sn$^{2+}$–Cu$^{2+}$ codoped Na$_2$O–CaO–SiO$_2$ glass at room temperature under UV illumination of 254 nm. When the glass was compressed under 3, 6, and 9 GPa, the phosphorescence shifted to 465 nm and its decay rate became shorter. The optical absorption spectra of the samples changed after compression, showing that the cupric ions were reduced to the cuprous ions. The high-pressure treatment also resulted in a lower-energy shift in the absorption edge. It was suggested that Sn$^{2+}$ ions act as hole trapping centers, while oxygen vacancies surrounding by Ca$^{2+}$ ions as well as active sites in the glass matrix, i.e., as electron trapping centers. © 2002 American Institute of Physics.

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nal appeared at $g = 1.999$, as can be seen from Fig. 2(a). This EPR signal is probably due to an electron trapped at the oxygen vacancy site surrounded by Ca\textsuperscript{2+} ions, similar to an $F^+$-like center of CaO.\textsuperscript{10–12} In the present case, a possible mechanism of the long-lasting phosphorescence can be interpreted as follows. The Sn\textsuperscript{2+} ions act as hole traps, resulting in Sn\textsuperscript{2+}+ hole→Sn\textsuperscript{3+}, where Sn\textsuperscript{3+} is a tin ion of unstable intermediate valency. 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 surrounded by Ca\textsuperscript{2+} ion. The energy depth of electron trapping site may be 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 transfers to the Cu\textsuperscript{2+} ions. Consequently, a long-lasting phosphorescence phenomenon takes place.

As can be seen from Fig. 1(b), it has been found that the phosphorescence peak shifted to a shorter wavelength after compression of the glass. The peak position of 465 nm was independent of the applied pressure. The color of long-lasting phosphorescence is blue green. As shown in the inset of Fig. 3, two absorption peaks at around 450 and 780 nm, which are due to Cu\textsuperscript{2+}, were observed in the optical absorption spectrum of the noncompressed glass samples. These two absorption peaks disappeared in the spectra of the high-pressure treated samples. Therefore, this result indicates that the cupric state, i.e., as Cu\textsuperscript{2+} ions were reduced to cuprous ion, Cu\textsuperscript{+}, under a high-pressure condition. The proposed mechanism of the long-lasting phosphorescence mentioned herein can also be applied to compressed samples. In this case, however, blue-green phosphorescence was observed, suggesting the released energy due to recombination of electrons and holes then transferred to the Cu\textsuperscript{+} ions.

As shown in Fig. 3, we also found that the optical absorption edge in the UV-visible (UV-VIS) region shifted to lower energies with increasing applied high pressure. In the densification of amorphous SiO\textsubscript{2} and GeS\textsubscript{2} glass similar phenomena have been observed in optical reflection bands.\textsuperscript{4,13} Xu and Ching\textsuperscript{14} have investigated the relationship between the optical reflection band and the Si—O bond length,
after high-pressure treatment is shown in Fig. 5. In particular, the long-lasting phosphorescence of the glass treated under 9 GPa was hardly observed even immediately after cessation of UV light illumination, while in the high-pressure treated glasses, the phosphorescence became faint. In noncompressed glass, the phosphorescence can be clearly observed by the naked eye even after the elapse of 30 min after cessation of UV light illumination. The intensity of this phosphorescence is inversely proportional to the depth of trapping potential $\varepsilon_T$. Thus, it is likely that the high-pressure treatment will facilitate the liberation of an electron from its trapping site, since the band gap between the valence band and the conduction band decreased with increasing applied pressure. This consideration was supported by the pressure dependence of the decay rate in Fig. 4. In noncompressed glass, the phosphorescence can be clearly observed by the naked eye even after the elapse of 30 min after cessation of UV light illumination, while in the high-pressure treated glasses, the phosphorescence became faint. In particular, the long-lasting phosphorescence of the glass treated under 9 GPa was hardly observed even immediately after the cessation of the UV light illumination. A possible mechanism of the long-lasting phosphorescence before and after high-pressure treatment is shown in Fig. 5.

In addition, an additional EPR signal around $g = 2.067$ was evidently observed after high-pressure treatment, as shown in Fig. 2(b). The EPR signal at $g = 1.999$, which is attributed to an F$^+$-like center associated with Ca$^{2+}$ ions was induced by illumination UV light, and its intensity greatly changed by the cessation of UV light. The intensity of this additional EPR signal, however, remained unchanged even after UV light illumination. We therefore suggest that a new hole center is permanently induced by high pressure. Unfortunately, the relationship between the new induced structure and the long-lasting phosphorescence mechanism has not been clarified in the present stage. Further investigation is necessary to make it clear.

In summary, we observed long-lasting phosphorescence in a Sn$^{2+}$- and Cu$^{2+}$-doped Na$_2$O–CaO–SiO$_2$ glass. We suggest that the long-lasting phosphorescence results from the thermal stimulated recombination of holes and electrons at trapping site induced by UV illumination, which leave holes or electrons in a metastable excited state at room temperature. We also suggest that the change in the optical band gap with the applied high pressure explains the reason why the decay rate of the phosphorescence increases with increasing applied high pressure. We observed that the reduction from cupric ion to cuprous ion by high pressure treatment results in a blueshift of phosphorescence. Furthermore, we observed the appearance of an additional paramagnetic defect after high-pressure treatment. Therefore, we suppose that the appearance of defects may be released by applying other energies, e.g., laser-light illumination. The present phenomena can be used in the fabrication of optical memory devices.