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Effect of Sb_2O_3 on Solarization of Photosensitive Glasses Containing Ag and CeO_2

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The relationship between the addition of Sb_2O_3 and the color difference by solarization in photosensitive glasses was investigated. Glasses containing CeO_2 and Sb_2O_3 simultaneously and glasses with only CeO_2 were changed reddish and yellowish respectively after exposing to ultra violet ray. Color difference between compositions was represented by dominant wavelength and purity. Since, in glasses containing CeO_2 and Sb_2O_3 simultaneously, Sb_2O_3 as reduction agent affected Ce^{3+} ions to increase in glass and more Ce^{4+} ions were induced than in glasses with only CeO_2 during UV irradiation, more electrons released by photo-ionization, which were color centers, were trapped by Ce^{4+}. In conclusion, the introduction of Sb_2O_3 to photosensitive glasses with CeO_2 resulted in the change of color center concentration in glasses and prevented the solarization of photosensitive glasses with CeO_2.

Key words: Solarization, Photosensitive glass, CeO_2, Sb_2O_3

I. Introduction

In 1947, Stookey invented glasses with a number of compositions in which photosensitive phenomenon could be intensified sufficiently so as to make photography possible. Photosensitive glasses containing Ag were obtained by Armistead.[1] It is known that the color of photosensitive glasses is developed by ultraviolet ray (UV) irradiation and heat treatment, and no color change is observed in photosensitive glass visually before heat treatment. The color by solarization is not deep in the glass but tint on extreme surface of the glass, and can be eliminated upon slight heating to 400-500°C.[1,2] Because two phenomena are caused by light, light sensitivity in photosensitive glasses seems to be confused with solarization on the surface of commercial glasses with polyvalent ions. There have been many studies about solarization phenomenon in soda lime silicate glass because of commercial problem, but there were few reports about it in case of photosensitive glasses.[3,4]

If redox active components such as As or Sb coexist with Ce or Mn in soda-lime-silicate glass, solarization occurs as following reaction.[2]

$$As^{5+} + n\ Me^{n+} + h\nu(\text{light}) \rightarrow nMe^{n+1} + As^{3+} \qquad (1)$$

where Me is a polyvalent element and n is constant.

In studies of solarization in commercial soda-lime-silicate containing Mn , Sb and Fe, only Sb affected the change of Mn^{2+} to Mn^{3+} for solarization, and Fe had no effect, because it was not reduced more easily than Sb during UV irradiation.[4]

In previous study about photosensitive glass ceramics, solarization phenomenon was found after exposure to UV and slight difference of colors between glasses with CeO_2 only and samples with CeO_2 and Sb_2O_3 simultaneously was found.[5] Because photosensitive glass had polyvalent element such as Ce and Ag and was exposed to UV, it was suggested that solarization characteristics appeared in photosensitive glasses as well as soda lime glasses with polyvalent ions. But it was not comprehended why two types of glasses with and without Sb_2O_3 had the different color after UV irradiation.

The objective of this study was to measure and quantify the color of photosensitive glass containing Ag, CeO_2 and Sb_2O_3 by solarization and to understand the relation between addition of Sb_2O_3 in photosensitive glasses and coloring by solarization.

II. Experiment

The glasses were composed of 78 SiO_2, 5 Al_2O_3, 13 Li_2O, 4 K_2O in wt% (71.15 SiO_2, 2.67 Al_2O_3, 23.84 Li_2O, 2.33 K_2O, mole%), and 0.02 Ag, 0.05~0.20 CeO_2, 0.20 Sb_2O_3 as additives. The composition and sample names are summarized in Table 1.The purity of SiO_2 is 99.99%, and $Al(OH)_3$, Li_2CO_3, K_2CO_3 and · additives were used with chemical

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Table 1. The Glasses Compositions(wt%) and Sample Names

		CeO_2	Sb_2O_3	Base Composition
CS-series	C5S	0.05	0.20	78 SiO_2
	C10S	0.10	0.20	5 Al_2O_3
C-series	C5	0.05	-	13 Li_2O
	C10	0.10	-	4 K_2O
	C20	0.20	-	0.02 Ag

grade.

Batches weighing 150 g were placed in Pt-5%Rh crucibles and heated at 1550°C for 4 hours. Samples were made in the form of plates with 3 mm thickness by pouring the melts into a preheated graphite mold and annealed at 470°C (about glass transition temperature, Tg) for 30 minutes. Fig. 1 shows the thermal expansion curve of glass without Sb_2O_3. Glasses were free from bubbles and were lapped and polished up to 20×20×1 mm in the form of plate. Polished samples were irradiated for various times (0~30 minutes) by metal halide lamp at a power of 1 kW at a distance of 50 cm.

UV absorption spectra and colors (tristimulus values: X, Y, Z) of UV irradiated samples were measured by UV spectrophotometer (Shimazu, UV2101PC, Japan). The standard observer angle for color was 2° and the illuminant was D65 because these glasses related to absorption in UV range. The dominant wavelength and excitation purity from tristimulus values were calculated according to a program suggested by Kim and Choi's report.[6] Fig. 2 explains the view directions for photograph of Fig. 3, exposure to UV, and the measurement of color.

III. Results

1. Appearance

It was difficult to distinguish the difference of colors between glasses with and without Sb after UV irradiation, because the depth of solarization was shallow by 1 mm and glasses had slight tinge and the thickness of polished samples was 1 mm. It was hard to classify glasses by appearance, because all looked like colorless (top view in Fig. 2).

But when glasses were observed horizontally (side view in Fig. 2), there a the difference of colors between glasses with and without Sb as Fig. 3. Glass simultaneously containing Sb_2O_3 0.20 wt% and CeO_2 0.10 wt%(C10S) was reddish as Fig. 3(b), and one with CeO_2 only (C5, C10, and C20) was yellowish as Fig. 3(c). Also, according to CeO_2 content, the extent of color was changed in the same system.

2. Color measurement and Transmission

The color changes of glasses exposed to UV were estimated by dominant wavelength and purity, and that is shown in Fig. 4 and 5. Dominant wavelength represents the central wavelength of the color of the object, and purity does for the depth of color. Dominant wavelength shifted to shorter wavelength, purity became higher and color became deeper with increasing exposure time regardless of the composition. These changes of glasses were consistent with color changes that were identified with naked eyes. Glasses containing Sb_2O_3 had slightly longer wavelength than the one without Sb_2O_3 after UV irradiation, and it means that the former became more reddish than the latter did. Mean-

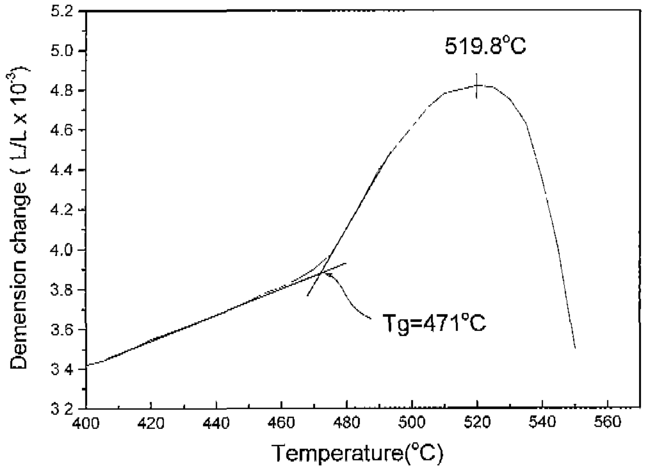

Fig. 1. The thermal expansion curve of Sb_2O_3 free glass.

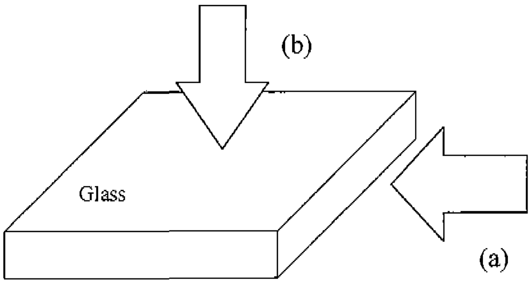

Fig. 2. The directions for (a) photograph of Fig. 3 (side view) and (b) exposure to UV and the measurement of color (top view).

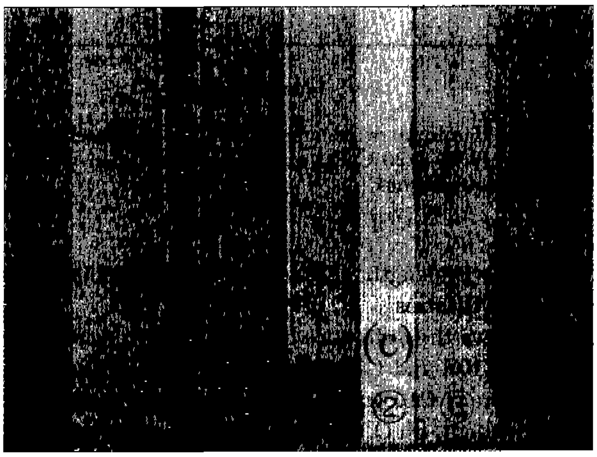

Fig. 3. The color of glasses observed horizontally after exposed to UV for 20 min. (a) glass unexposed to UV. (b) glasses with Sb_2O_3 0.20 and CeO_2 0.05, 0.10 wt%, (c) glasses with CeO_2 only 0.05, 0.10, 0.20 wt%.

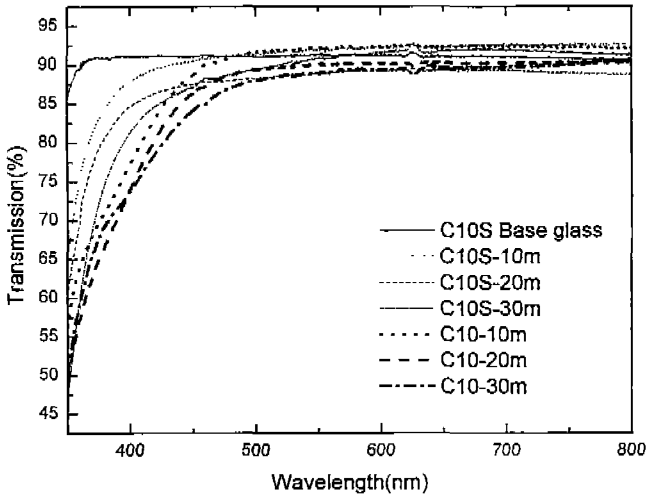

Fig. 4. Tansmission spectra of glasses C10S and C10 with increasing UV exposure times.

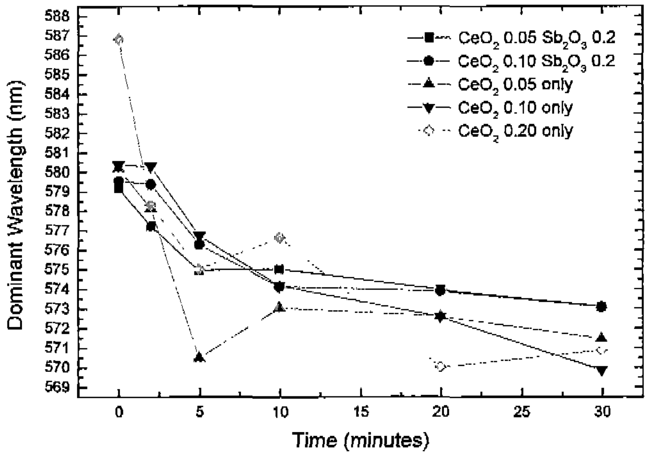

Fig. 5. The dominant wavelength changes of glasses containing 0.02 Ag, 0.05~0.20 CeO_2, and/or 0.20 Sb_2O_3 (in wt%) with various exposure times.

while, the wavelength of CS-series changes slightly less than that of C-series.

Fig. 6 shows the difference between transmission spectra of glasses C10S and C10. In the range from 350~450 nm, transmission of C10 was lower than C10S. It means that glasses without Sb_2O_3 contained more sources that can absorb short wavelength from UV to visible range than one with Sb_2O_3. With regard to coloring by solarization of photosensitive glasses with various additives, it was thought that the ionic states of polyvalent ion such as Ag or Ce, which acted as UV absorber and colorant in photosensitive glasses, were affected by adding Sb_2O_3 and any absorption change occurred in UV or near visible light range. To identify this assumption, the absorption of samples was measured in the range from 200 to 360 nm.

Though the purity of glasses increased as exposure time increased, it was hard to clarify the difference according to the glass composition (Fig. 5).

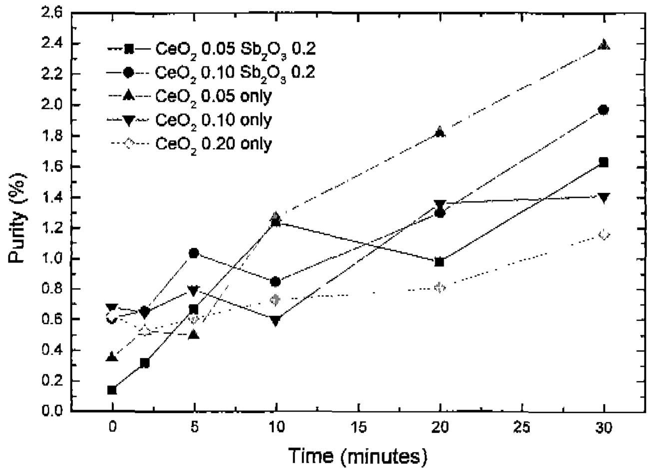

Fig. 6. The purity changes of glasses containing 0.02 Ag, 0.05~0.20 CeO_2, 0.20 and/or Sb_2O_3 (in wt%) with various exposure times.

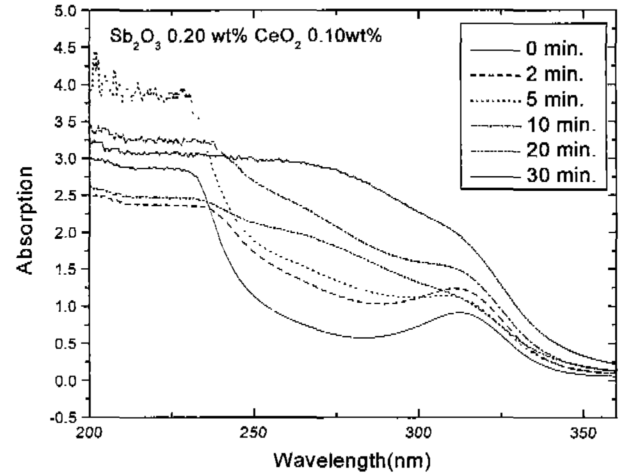

Fig. 7. The absorption spectra of glass containing Sb_2O_3 0.20 and CeO_2 0.10(wt%) simultaneously with various exposure times.

3. UV Absorption

Fig. 7 and 8 show absorption spectra in the range of 200 to 360 nm of samples C10S and C10 with various exposure times. In both figures, the change of the absolute amount of absorption through overall range with various exposure times is irregular. Because samples were lapped and polished manually, it was thought that irregularity of absorption curves with time resulted from parallelism of thin sample and the finishing condition of surface. Nevertheless, there was a difference of spectrum shape between two base glasses (C10S and C10); exposure time was 0 second. The C10S base glass had an absorption band around 320nm and no band in the range of 250~300 nm in Fig 4. But since slow slope appeared from 250 to 280 nm in C10 base glass, it is surmised that there was any band in this range.

An absorption band at 320 nm indicates the existence of Ce^{3-} and one at 270 nm does Ce^{4+}, but if two types of ions coexist in the glass, two bands overlap.[7-9] In proportion to

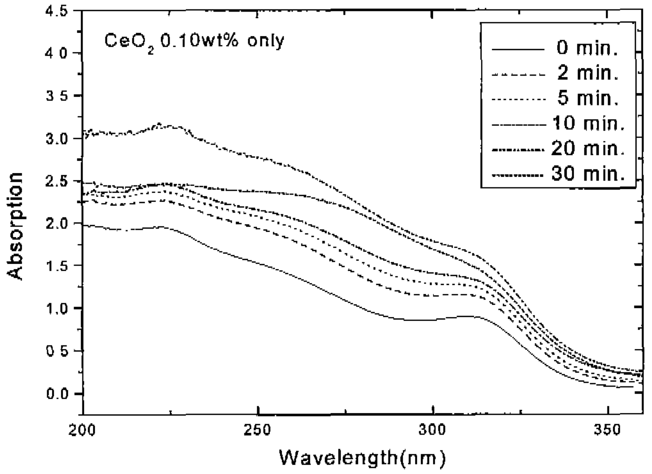

Fig. 8. The absorption spectra of glass containing CeO_2 0.10 wt% only with various exposure times.

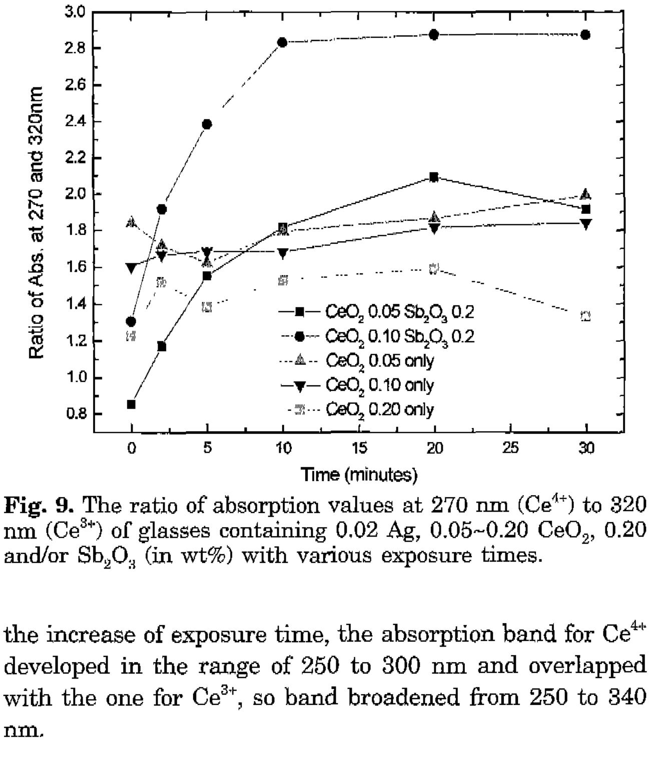

Fig. 9. The ratio of absorption values at 270 nm (Ce^{4+}) to 320 nm (Ce^{3+}) of glasses containing 0.02 Ag, 0.05~0.20 CeO_2, 0.20 and/or Sb_2O_3 (in wt%) with various exposure times.

the increase of exposure time, the absorption band for Ce^{4+} developed in the range of 250 to 300 nm and overlapped with the one for Ce^{3+}, so band broadened from 250 to 340 nm.

IV. Discussion

Generally, solarization has been explained by 1) interaction between polyvalent elements as Mn, Fe, Sb, As, Ce, Ag and so on[2,4] and[2] the development of color centers[3,8] in glass during UV exposure. It has been known that the interaction between polyvalent elements during solarization is related to the redox reaction as Eq. (1). However further studies revealed that defects intrinsic to the glass structure can absorb sub-band gap UV light and release electrons and/or holes that can be trapped at other sites to form color centers;[3,8] intrinsic defects are non-bridging oxygen, oxygen vacancy (Si-Si), and peroxy linkage (Si-O-O-Si), ubiquitous in silicate glasses.

First, the interaction between polyvalent elements during solarization was considered. In this study, elements, which are related to solarization coloring, are Sb, Ce, and Ag. Volf[2] described that glasses containing trivalent Ce ions show intense solarization which involves changes in the color of glasses on irradiation with sunlight. Glasses containing Ce^{3+} ions are sensitive to the photochemical effect of sunlight only when some polyvalent elements such as As, Sb, V, Bi, Cu or Ag are present. Eq. (1) can be represented by Ce as following;

$$2Ce^{3+}+Sb^{5+}+h\nu \rightarrow 2Ce^{4+}+Sb^{3+} \qquad (2)$$

Sb is the element for intense solarization of Ce^{3+} ion and is also electron acceptor, but it is not a colorant. It was also supposed that Ag^+ played a role in an electron acceptor and a colorant during solarization process, because there was Ag^+ in photosensitive glasses in this study. According to Weyl,[10] Ag atom in glass does not tinge and crystalline Ag only has yellow color. In this study, Ag ion seems to be able to be electron acceptor but not colorant. So, solarization coloring of two types of glasses, C-series and CS-series, was related to Ce^{4+} ions only. However, since the absorption bands of Ce^{3+} and Ce^{4+} coexist in UV range as prescribed, both Ce ions in glasses are not colorants but related to color generation. A mere interaction between redox couple could not explain the color generation of these glass system during solarization.

The fact that Ce helps to prevent solarization has been known for decades.[3] Stoud identified an absorption band peaking in the UV range but extending well into the visible which he assigned to an electron trap and showed that Ce^{3+} and Ce^{4+} ions can respectively trap holes and electrons that might otherwise be trapped elsewhere to form color centers.[8] Especially, electrons released by photo-ionised are trapped either by Ce^{4+} or other electron trap do not absorb strongly in visible.[8] So, it was thought that the color difference between CS-series and C-series glasses after exposing to UV resulted from the difference of the amount of photo-released electrons.

Generally, when Sb_2O_3 is added to glass, Sb ion becomes Sb^{5+} in melt and acts as reducer of polyvalent ions. Because CS-series glasses contained Sb_2O_3, it could be thought that more Ce ions were reduced to Ce^{3+} in melt than in C-series by following reaction.

$$Sb^{3+}+2Ce^{4+} \rightarrow Sb^{5+}+2Ce^{3+} \qquad (3)$$

That was the reason for difference between absorption curves of base glasses (Fig. 4 and 5).

Thus, the ratio of Ce^{4+}/Ce^{3+} during UV exposing was estimated by ratio of absorption value at 270 nm for Ce^{4+} to that at 320 nm for Ce^{3+} and it is shown in Fig. 9. This ratio in Fig. 9 is not a real ratio of Ce^{4+}/Ce^{3+} but a relative value and trend only, because any quantitative trend of curves with exposure times was not shown in absorption spectra due to thickness and surface condition as described above. But the shapes of curves and the absorption ratios at two wavelengths changed with UV irradiation times. There is little change of ratio in C-series, but the ratio increases in CS-series with exposure times for 20 minutes relatively in Fig. 9. This means that the amount of Ce^{4+} in CS-series became more and trapped more released electrons than C-series after exposing to UV. Thus, C-series had more released electrons, which form color center in visible range, and was more susceptible to solarization than CS-series.

Although it was thought that the difference between C5S and C10S in Fig. 9 resulted from the amount of Ce ions reduced by Sb_2O_3, more studies were needed.

V. Conclusion

The effect of Sb_2O_3 on solarization of glasses containing Ag and CeO_2 was investigated. Glasses with CeO_2 and Sb_2O_3 were reddish and glasses with CeO_2 only were yellowish after solarization. The color difference between CS-series and C-series glasses after exposing to UV resulted from the different amount of color centers, which were released electrons not being trapped by Ce^{4+} ions.

The introduction of Sb_2O_3 to photosensitive glass reduced Ce ions in melt, and increased the initial amount of Ce^{4+} which play a role as the trap of electrons from Ce^{3+} during exposure to UV, and supported CeO_2 to prevent solarizaton. In conclusion, Sb_2O_3 was found to be assistant of solarization restrainer as CeO_2 as well as a reduction agent in photosensitive glasses.

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