A Study on the Thermal, Structural and Dielectric Properties of Photo Machinable Glass-Ceramics

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Abstract

The photomachinable glass-ceramics of Ag and CeO2 doped Li2O-Al2O3-SiO2 (LAS) glass system was investigated as a function of UV irradiation time. After the exposed and the non-exposed samples were heated, they went under crystalline phase with DTA, SEM, TEM and XRD of normal/high temperature. In this work, crystalline phases, microstructure and dielectric properties were studied under the various time of UV irradiation and heat treatment.

I. Introduction

Photosensitivity of glass generally means a state of glass when an appropriate wavelength of light grows during the development of metallic particles in the irradiated region of glass. R.H. Dalton discovered that certain glasses containing a small amount of copper, produced under reducing conditions, would remain colourless if cooled rapidly.[1] On the subsequent heat treatment these glasses would become ruby coloured due to the precipitation of fine metallic copper particles in the glass.

When the same glasses were subjected to UV radiation, this colour appeared at lower temperature and in shorter time. As it is well known, UV irradiation to light - sensitive glasses frees photoelectrons from cerium ion.[2)3)] The electrons localized at trapping centers give rise to a latent image and they are recombine with silver ions during subsequent heat treatment.[4)5)] As a result, the neutral silver atoms come to aggregate and the colloidal coloring of the glass occurs. Under the subsequent heat treatment, the silver particles in glasses of the lithium aluminosilicate system become the segregation centers of the crystalline phase-lithium metasilicate.[4)5)6)]

In this work, we examined the interrelation between UV irradiation and the resulted crystallization in the LAS system-glass composed of specific elements.

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This study focused on the phenomenon of UV irradiation which had an effect on the direction of crystallization. The relationship between crystallization and dielectric properties was investigated.

II. Experiment

In this work, lithium silicate glass was sensitized by silver and cerium ions. The sample used in this experiment were composed of 72.8% SiO_2, 1.4% Al_2O_3, 23% Li_2O, 3% K_2O, 0.0008% Ag and 0.006% CeO_2 (mole%), respectively. The glasses were melted in a Al_2O_3 crucible at 1450℃ for 3hrs and poured to a graphite plate. Alumina crucibles were used instead of platinum (Pt) ones because Pt would be dissolved into a form of Pt^{3+} and this would cause a conflict with the absorption edge of the original censitizer.[7] Differential thermal analysis (DTA) was performed on various samples using by Rigaku TAS-100 . At this time the DTA was measured by a Pt pan under normal atmosphere with raising temperature by 10℃/min. The effects of UV exposure and heat treatment were investigated. The polished samples were subjected to the UV irradiation (λ = 362 nm, average power 1KW). Each sample was irradiated for 0 ~ 5 minnutes, at 5 cm far from the light source. The heat treatment condition of all specimens was same ; for example, at 525℃ for 2hrs for the formation of silver colloids and then at 630℃ for 3hrs for the formation of lithium metasilicates.

XRD was performed on UV irradiated samples, and various crystalline phases of heat treated samples were investigated. Specimens were cut into the size of 50 × 50

× 1.5 mm and then polished. Also the sample irradiated for g60 sec. was investigated using XRD (Siemens D-5000) with high temperature chamber. At each temperature a scan from $2\theta = 10^{\circ}$ to 60° was performed. The stepwidth was set to 0.02° and the measuring time per step was 1 second. The measureme
nts were performed as the following Fig 1.

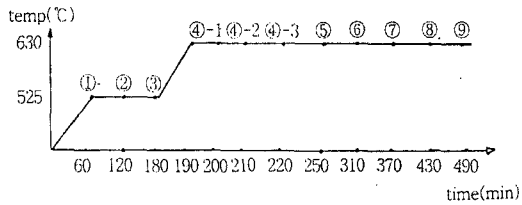

Fig. 1. Procedure of heat treatment.

The dielectric constant was measured by Impedance Analyzer (Hewlett packard 4292A) at the ranges between 1 Khz and 100 Khz in the temperature range 23 ~ 120℃. The dielectric constants were then calculated from these measurements.

The exposed portion and non-exposed one of SEM and TEM photographs were investigated and compared with $Li_2O \cdot SiO_2$ and $Li_2O \cdot 2SiO_2$.

III. Results and Discussion

1. Nucleation and Crystallization

Fig. 2 shows the (1/Tp - $1/Tp_o$) plot for nucleation temperatures validated by Marotta method.[8)9)] From the results of DTA, the crystallization temperature was marked at 630 ℃ for 3 hrs, while the nucleation temperature was at 525℃.

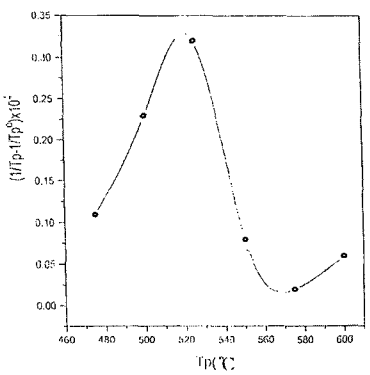

Fig. 2. Plot of (1/Tp - 1/Tpo) for nucleation temperature.

Fig. 3 shows the DTA traces of various samples. The curves of base glass, UV 5 minute exposed and UV non heat treated samples were similar, but UV 5 minute exposed and heat treatment glass were different. This exothermic peak was resulted from UV irradiation caused by lithium metasilicate phase.

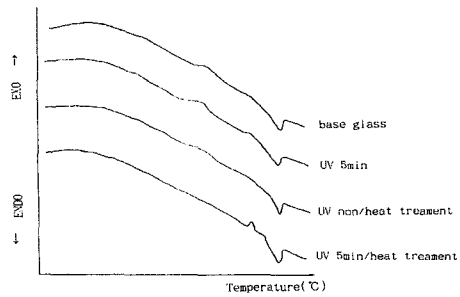

Fig. 3. DTA curves of samples according to UV irradiation and heat treatment.

UV and photo reaction mechanism is as follows;[3)4)5)]

$Ag^{+} + Ce^{3+} + h\nu \rightarrow Ag^{0} + Ce^{4+}$

(Ag ion reduction to Ag atom by photoelectron)

$Ag^{0} + heat \rightarrow nAg^{0}$

(agglomeration of Ag atoms to metal particles of colloidal dimension)

$nAg^{0} + heat \rightarrow Ag^{0}n$

(growth of Ag metal particles to critical size microcrystals)

$Ag^{0}n + heat \rightarrow$ major phase crystal nucleation (homogeneous nucleation) and growth

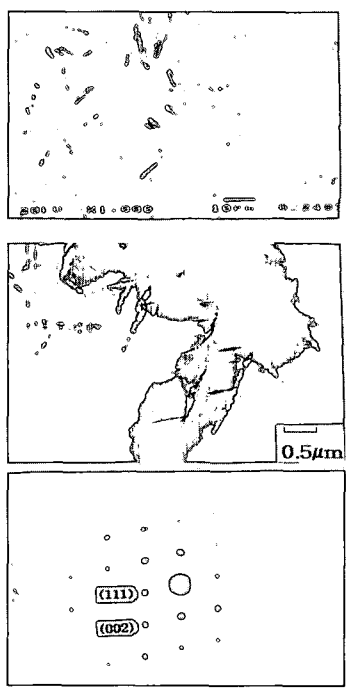

Fig. 4. SEM/TEM photographs of Li2O · SiO2 crystal. (a) SEM of Li2O · SiO2 crystal (b) TEM of Li2O · SiO2 crystal (c) Dark field image of Li2O · SiO2 crystal.

. As shown in Fig. 4, the photographs of SEM and TEM demonstrate that UV irradiated sample has crystalline phases. The crystal habits of $Li_2O \cdot SiO_2$ were lath-like and/or dendrite type and the crystal sizes were about 0.5 - 2.5 μm. Crystallized $Li_2O \cdot SiO_2$ phase was oriented [002] and [111] direction, and these data agreed well with the XRD one.

2. Structural review

During heating the sample get more milky colour. At 630℃ there is mainly $Li_2O.SiO_2(Li_2SiO_3)$. The temperature scans performed according to the temperature profile are shown in Fig. 5. The last measurement at 630℃ shows strong peaks of $Li_2SiO_3(L \cdot S)$ and $Li_2Si_2O_5(L \cdot 2S)$. Crystalline of $L \cdot S$ is generated at 525 ℃-nucleation temperature and $L \cdot 2S$ crystalline starts to grow up, reaching 630℃-crystallization temperature through the ctystallization process. However, the measurement at room temperature on the ground sample is dominated by amorphous background (Fig. 6) This indicates, that the crystallization during heating starts at the sample surface, whereas the bulk material is still amorphous at 630℃.

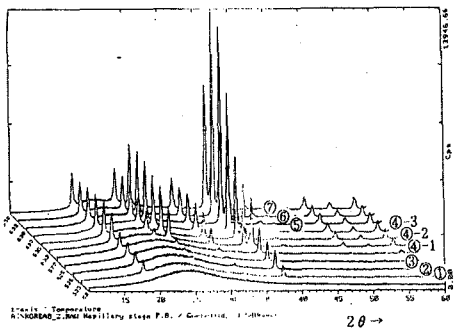

Fig. 5. XRD patterns of sequencial heat treatment.

At lower temperature up to 630℃, only the phase $Li_2SiO_3(L \cdot S)$ is occuring and identified by Siemense 5000D XRD measurements. (concerning sample in Fig. 6)

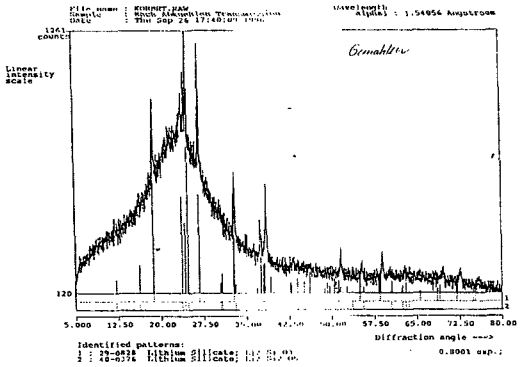

Fig. 6. XRD patterns of ground sample.

Fig. 7 shows the crystal phase is seperated out of the specimens by XRD. The process of two crystalline phases, $Li_2O \cdot SiO_2$ and $Li_2O \cdot 2SiO_2$ according to the UV irradiation time is able to describe as follows ; [002] direction of $Li_2O \cdot SiO_2$ phase is increased with irradiation time but [111] direction of $Li_2O \cdot SiO_2$ is not changed. It may be considered that only specific direction of $Li_2O \cdot SiO_2$ grows up with UV irradiation time and the optimum irradiation time with 362nm, 1kW of UV average power is 60 sec.

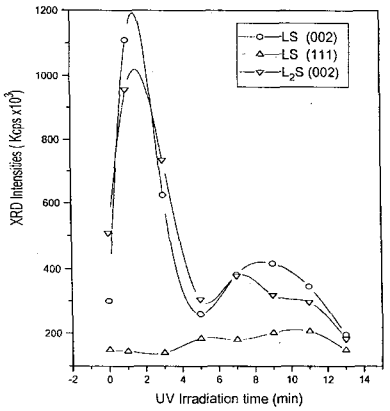

Fig. 7. XRD intensities of samples various UV irradiation time.

3. Dielectric constant

According to Bunag and Koenig[10], and Rigterink[11], the dielectric properties of matrix composed of fine crystalline particles and glass matrix are mainly dependent on the four factors.[12] There are many kinds of crystalline phases, composition of glassy matrix, pores and grain size of crystals. Among those four factors, the crystal phase in the specimens has the most strong effect on the dilectric constant.[13][14][15] It can be seen from Fig. 8 to Fig. 10 that the dielectric constant is changed with increasing UV irradiation time. There are variations in dielectric constant with frequencies as the crystallization proceed continuously after UV irradiation. A low value of dielectric constant might be due to the formation of [002] direction of $Li_2O \cdot SiO_2$ and this assumption can be supported by the XRD data. It seems to be resulted from that the $Li_2O \cdot SiO_2$ crystal grows toward [002], the shortest direction in the orthorhombic structure. As a result, dielectric constants with the changes of frequencies decrease as the volume of polarization decreases. At the room temperature, the UV irradiation deviation typically caused by frequencies can be reduced by the structurally stablized environment.. It is due to the increasement of the polarization, caused by the increase of thermal energy. It was found that UV irradiation had an effect on the growth of crystalline phase in the specific direction, which affected the dielectric constant.

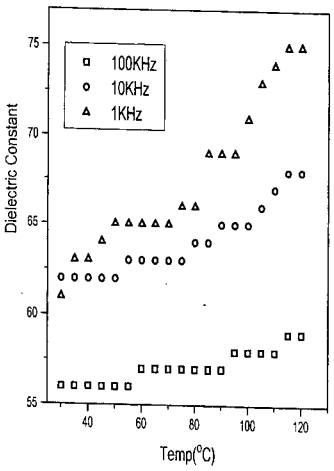

Fig. 8. Dielectric constant of UV non sample various frequency.

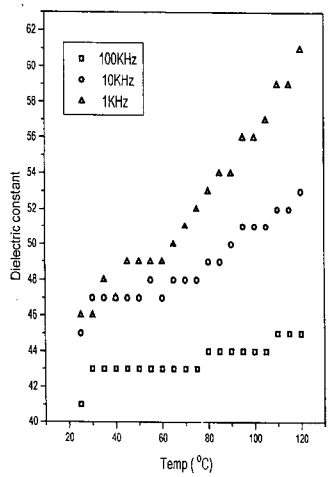

Fig. 9. Dielectric constant of UV 1 min.sample various frequency.

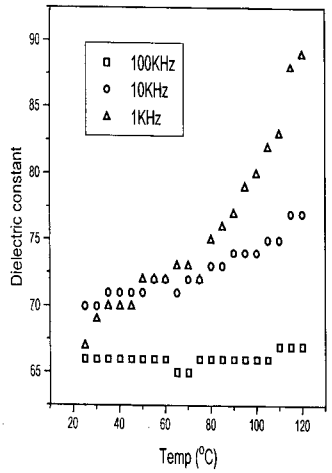

Fig. 10. Dielectric constant of UV 3 min. sample various frequency.

IV. Conclusion

The results of $3K_2O \cdot 1.4Al_2O_3 \cdot 23Li_2O \cdot 72.8SiO_2$ glass are expressed briefly as follows;

1. Optimum nucleation temperature is 525 ℃ and the phases of $Li_2O \cdot SiO_2$ habit are lath-like and/or dendrite type.
2. The [002] direction of $Li_2O \cdot SiO_2$ and $Li_2O \cdot 2SiO_2$ phases is changed by the UV irradiation time.
3. After verifying the lithium silicate crystalline phase growth depending on the UV irradiation time with XRD, the optimum irradiation time with 362nm, 1kW of UV irradiation was 60 sec.
4. Various dielectric constants may be due to the growth of $Li_2O \cdot SiO_2$ crystal mainly in the [002] direction which is the shortest in the orthorombic structure.

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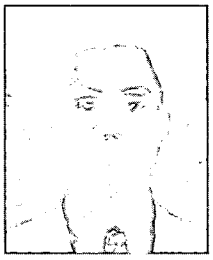

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