Title
Effects of Gold Colloid and K₂O on the Formation of Lithium Metasilicate Crystallites in Photosensitive Opal Glass

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Citation

Issue Date
1966-02-28

URL
http://hdl.handle.net/2433/76074

Type
Departmental Bulletin Paper
Effects of Gold Colloid and K₂O on the Formation of Lithium Metasilicate Crystallites in Photosensitive Opal Glass

Naohiro Soga and Megumi Tashiro

Received September 30, 1965

Normally, from chemically mashinable photosensitive opal glasses lithium metasilicate crystal but not lithium disilicate crystal is separated out upon reheating. In order to investigate its cause, lithium silicate glasses with small amounts of gold and K₂O have been prepared, and their crystallization temperatures have been measured by DTA technique. The crystals separated out from the glasses upon reheating have also been identified by X-ray diffraction technique. The results obtained are summarized as follows:

1. The crystallization temperature for the lithium silicate glasses rises proportionately with the increase of the K₂O/Li₂O (by mol.%) ratio of the glasses.
2. The crystallization temperature for the glasses is much lowered by the addition of 0.005 mol.% gold colloids.
3. The lithium metasilicate crystals are separated out upon reheating even from the glasses whose ratio of Li₂O/SiO₂ is less than 1/2, if the glasses contain K₂O higher than 1 mol.% together with gold of 0.005 mol.%. The explanations from the above mentioned phenomena have been drawn on the basis of the concept that (a) the Si-O bonds in the Li-Si-O groups are weakened by the polarizable single bonded oxygens associated with Li⁺ ions, and (b) the polarizable single-bonded oxygens are absorbed at the surface of gold colloids together with the Li⁺ ions.

INTRODUCTION

From lithium silicate glasses bearing of Li₂O·2 to 4SiO₂ composition lithium disilicate crystals (Li₂Si₂O₅) ordinarily precipitate upon their reheating. Rindone ¹ has studied the nucleating effects of platinum on the crystallization of a glass of Li₂O·4SiO₂ composition and determined the rate of formation of Li₂Si₂O₅ crystals from the glass as a function of platinum concentration at 600°C and 650°C. Matveev and Velya² have investigated the homogeneous crystallization of lithium silicate glasses having various compositions from Li₂O·2SiO₂ to Li₂O·6SiO₂, and found that solid solutions of silica in lithium disilicate separates out from the glasses of Li₂O·3 to 6SiO₂ compositions. Sakka and Tashiro³ have studied the effect of addition of various oxides on the crystallization of a lithium silicate glass and showed that their addition retards the precipitation of Li₂Si₂O₅ crystals from the glass in proportion to the polarizing power of the cations in the oxides added.

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Cases are known, however, in which lithium metasilicate crystals (Li2SiO3) separate out from the glasses containing less Li2O than that of the Li2O·2SiO2 composition. For example, Stookey has discovered the formation of Li2SiO3 crystals in lithium silicate photosensitive glasses added with minor amount of potassium oxide (70~80SiO2, 9~15Li2O, 0~8Na2O or K2O, 0.001~0.03Au and 0~0,05 wt. per cent CeO2) when nucleated by photographic precipitation of metallic colloids of gold, silver or copper. Stookey had ever once stated in his report on the crystallization of glass that generally, in the process of heterogeneous crystallization of glasses, a crystal whose crystal structure and lattice parameter are similar to those of the nucleating catalyst first precipitates on the surface of the catalyst. This statement, however, can not be applied to the peculiar phenomenon above mentioned, because, if so, there must have been a possibility of formation of Li2SiO3 crystals also in the lithium silicate glasses containing platinum colloids whose lattice parameter is almost similar to that of gold: The experimental results obtained by Rindone etc. showed no formation of the Li2SiO3 crystals as described above.

This fact has led the authors to consider if there might be some other more potent factors which determine the type of crystal formed in the photosensitive glass, and further to assume that the K2O component in the presence of gold colloid would be one of the factors. In order to ensure this assumption, in the present study, the photosensitive glasses containing both gold and K2O in various amounts have been prepared and their crystallization temperatures and the crystalline phases separated out from the glasses have been determined by the DTA and X-ray diffraction technique.

EXPERIMENTAL

1) Preparation of Glass

Reagent grade Li2CO3, K2CO3 and SiO2 were used for preparing the glasses, those batches of compositions were shown in Table 1. Photosensitive ingredients, Au and CeO2, were added to the batches as HAuCl solution and CeO2, respectively. After mixing thoroughly the batches were melted in sintered alumina crucibles with a capacity of 30 cc at 1320-1420°C for 2 hours in an electric furnace with silicon-carbide heating elements. This glass was poured directly on a steel plate and subsequently annealed at 500°C. Certain glasses of high alkali contents had a tendency to separate gold colloids upon cooling. For such glasses, a part of Li2CO3 in their batches was substituted by LiNO3 to create oxidizing atmosphere during melting.

2) Formation of Gold Metal Nuclei

Ultraviolet exposure and subsequent heat-treatment are the necessary procedures for the development of colloid gold nuclei in photosensitive glasses. According to the experimental results of Maurer, the number of gold nuclei to be precipitated can be adjusted by the total dose of U.V. ray, i.e., the intensity of U.V. ray and duration of its exposure, but not by subsequent heat-
### Table 1. Chemical composition and melting conditions of the glasses used.

<table>
<thead>
<tr>
<th>Glass composition (mole %)</th>
<th>Melting condition</th>
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<th></th>
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<tr>
<td></td>
<td>Li₂O</td>
<td>SiO₂</td>
<td>K₂O</td>
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<tr>
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<tr>
<td>32</td>
<td>33</td>
<td>67</td>
<td>3</td>
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</table>

Furthermore, according to Mie's theory, the glasses containing gold colloids of the same size and of the same number show the same light-absorption spectrum. In order to precipitate gold colloids of the same size and of the same number in all of the glass specimens prepared, in the present experiment, the glass specimens were exposed to the U.V. ray of constant intensity for such suitable time that after being subjected to the subsequent heat treatment, they will show the same light-absorption spectrum.

In practice, the following procedures were undertaken to find out the most suitable exposure time for each specimen. Several pieces of a glass were placed at a distance of 6 cm from a U.V. source (a 500 watts high pressure mercury... (438)
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lamp) and exposed for various periods from 30 to 1000 min. All the exposed glasses were then heated at a rate of 5°C per minute from 200°C to the development temperature near 500°C in a regular furnace with automatic temperature control equipments and held at that temperature for 30 min. After cooling, all the specimens were subjected to the absorption spectrum analysis so that only the specimens whose absorption spectra were close to the one shown Fig. 1 were selected for further experiments. The ultraviolet exposure conditions for such specimens are listed in Table 2.

3) Determination of Crystallization Temperature

The precipitation of a crystal phase from its parent glass is usually accom-

![Absorption spectrum of the glasses coloured by gold colloid.](image)

Table 2. U. V. exposure and development conditions for separating out gold colloid in each glass.

<table>
<thead>
<tr>
<th>Glass composition No.</th>
<th>U. V. Exposure time (min.)</th>
<th>Development condition</th>
<th>Temperature (°C)</th>
<th>Time (min.)</th>
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<tbody>
<tr>
<td>17</td>
<td>100</td>
<td>520</td>
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Fig. 2. Differential thermal analysis curves (1).

Fig. 3. Differential thermal analysis curves (2).

Fig. 4. Differential thermal analysis curves (3).

Fig. 5. Differential thermal analysis curves (4).
Gold Colloid and K₂O in Photosensitive Opal Glass

Fig. 6. Differential thermal analysis curves (5).

Fig. 7. Differential thermal analysis curves (6).

Fig. 8. Differential thermal analysis curves (7).

Fig. 9. Differential thermal analysis curves (8).
panied by the evolution of heat and, therefore, the differential thermal analysis (DTA) can be applied to the determination of its crystallization temperature. It should be mentioned, however, that the crystallization temperature obtained differs depending on the shape of the sample used: When the glass sample is in the powder form the crystallization temperature obtained is much lower than that obtained for the glass in a block, because the crystallization commences much faster at the glass surface than in the glass body. The crystallization temperature to be determined in the present study is of the body of the glass but not of its surface. Therefore, the glasses were formed into a slab 3×5×10 mm in dimension and used as specimens for DTA. For measuring the temperature of specimens, a small hole was made in each specimen, in which a chromel alumel thermocouple was inserted. Alumina powders, as a reference material in DTA, that previously fired up to 1400°C were used. The heating rate was in all cases 5°C per minute.

The results of DTA for all glasses are shown in Fig. 2 to 9. Furthermore, in order to compare the crystallization tendency of all the glasses, the temperature at which the first exothermal peak appears in the DTA curve was designated as the “crystallization temperature”.

The effects of gold colloids, Li₂O and K₂O content in the glass on the crystallization temperature can be seen more clearly in Fig. 10 where the crystallization temperature is plotted against the Li₂O content with various K₂O contents. It is obvious that the crystallization temperature is greatly influenced by both K₂O and Li₂O content. For the same amount of K₂O, the crystallization temperature rises as the Li₂O content decreases with an exception of the glasses containing no K₂O. The effect of K₂O is more apparent in the glasses without gold colloid than in those with gold colloids.

When the glass contains both gold colloids and K₂O, especially in large amount, three exothermal peaks appeared in the DTA curve. X-ray diffraction analysis of this glass revealed that the first exothermal peak is due to the pre-
Gold Colloid and K$_2$O in Photosensitive Opal Glass

cipitation of Li$_2$SiO$_3$, the second to the transformation from Li$_2$SiO$_3$ to Li$_2$Si$_2$O$_5$ and the third to the precipitation of SiO$_2$ phase.

4) Determination of Crystal Phases

The glass specimens were heated at a rate of 5°C/min. from room temperature up to the temperatures 10°C higher than their crystallization temperatures shown in Fig. 10 and kept for 30 min.. After cooled to room temperature they were subjected to X-ray diffraction analysis using a Shimazu diffractometer RX-2A utilizing Cu-K$\alpha$ radiation. The results are summarized in Table 3. The weight proportion of Li$_2$SiO$_3$ to Li$_2$Si$_2$O$_5$ in Table 3 was estimated from the intensities of diffraction peaks due to Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$. When only the peaks

Table 3. Crystalline phases separated out primarily from the glasses used.

<table>
<thead>
<tr>
<th>Glass composition No.</th>
<th>Catalyst</th>
<th>Heat-treatment Temp. (°C)</th>
<th>Relative amount of crystallite</th>
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(445)
of Li$_2$SiO$_3$ were observed, a value of 100 was given to Li$_2$SiO$_3$ and 0 to Li$_2$Si$_2$O$_5$. Fig. 11 shows typical examples which were designated as the proportion of Li$_2$SiO$_3$ to Li$_2$Si$_2$O$_5$ being 0 to 100, 50 to 50 and 100 to 0, respectively. From Table 3 it is evident that Li$_2$SiO$_3$ precipitates only from the glass containing both gold colloids and K$_2$O whereas Li$_2$Si$_2$O$_5$ precipitates primarily from the glass containing either gold colloids or K$_2$O. The proportion of Li$_2$SiO$_3$ to Li$_2$Si$_2$O$_5$ increases as K$_2$O content increases and reaches 100% when K$_2$O content becomes 3 mole%.

![Fig. 11. X-ray diffraction patterns of the crystallized lithium silicate glasses containing K$_2$O and gold colloid.](image)

**DISCUSSION**

1) The Effect of K$_2$O on the Crystallization of Lithium Silicate Glasses

Fig. 10 indicates that the addition of K$_2$O to lithium silicate glasses retards their crystallization irrespective of the presence of gold colloid nuclei. Its reasoning has already been presented in the paper by Sakka and Tashiro$^{31}$, which is based on the concept that the O-Si bonds in the Li-O-Si groups are strengthened by the introduction of single bonded oxygen ions associated with kalium ions: For the crystallization of lithium silicate glasses, the breaking of the Si-O bond in the Li-O-Si groups is the first requirement. When the single bonded oxygens associated with the K$^{+1}$ ions are brought near to the Li$^{+1}$ ions, the attraction of the oxygens toward the Li$^{+1}$ ions in the Li-O-Si groups is weakened because the Li$^{+1}$ ions are well screened by the oxygen associated with the K$^{+1}$ ions, and consequently the O-Si bonds in the Li-O-Si groups are strengthened, resulting in the
delay of crystallization of glasses.

If this concept accepted, each Li\textsuperscript{+} ions would receive more screening effect with increasing \(K_2O/Li_2O\) ratio in the compositions of glasses, and consequently the crystallization temperature of the glasses would increase with increasing their \(K_2O/Li_2O\) ratios. This expectation is actually found in Fig. 10: For instance, the two glasses of the compositions, \(2K_2O\cdot 20Li_2O\cdot 80SiO_2\) and \(3K_2O\cdot 30Li_2O\cdot 70SiO_2\), have the same crystallization temperature (640°C).

2) The Effect of Gold Colloids on the Crystallization of Lithium Silicate Glasses

The effect of gold colloid in decreasing the crystallization temperature of the glasses is obvious from Fig. 10 shown. Another interesting phenomenon is that the \(Li_2SiO_3\) crystal separates out from the glasses which contain both gold colloids and \(K_2O\). These two phenomena could be explained if the gold colloids have following two effects; an effect of lowering the activation energy for nucleation and of attracting lithium oxides on its surface.

a) An effect of lowering the activation energy for nucleation. According to the report resulted by Turnbull\textsuperscript{81}, the rate of formation of nuclei on the surface of a catalyst is represented by the formula,

\[
J_c = A \exp\left(-\frac{\Delta F f(\theta) + q}{kT}\right)
\]

in which \(F\) is the maximum free energy for formation of a nucleus on the surface of a catalyst, \(q\) being the activation free energy for diffusion of molecules across the phase boundary, \(f(\theta)\) the function representing the reduction of the interfacial energy due to wetting of the catalyst surface by the crystals precipitated on it where \(\theta\) is the contact angle between the surface of catalyst and the crystals precipitated on it.

As already mentioned by Stookey\textsuperscript{82} a lattice parameter of gold metal (4.070Å) is fairly close to one of those of \(Li_2SiO_3\) crystal (4.66Å), it can be expected that the value of \(f(\theta)\) in the above equation be low enough so that the crystallization commences from fairly low temperatures.

b) An effect of gold colloid in attracting lithium oxides. For the explanation of the formation of \(Li_2SiO_3\) crystal, it has been proposed by the authors with introducing the concept that the gold colloid tends to attract the \(Li_2O\), especially the polarizable oxygen ions associated with the \(Li^{+1}\) ions, towards its surface for its screening: The surface of the metal colloids has high surface free energy especially when their size is small, and consequently requires to be surrounded by polarizable ions such as single bonded oxygen ions. This concept has first been proposed by Weyl\textsuperscript{83} and later used by Rindone\textsuperscript{11} for explanation of the formation of \(Li_2SiO_3\) crystal on the surface of platinum colloids. By this adsorption process the \(Li_2O\) concentration near the surface of gold colloids increases, resulting in the precipitation of the \(Li_2SiO_3\) crystal whose \(Li_2O\) content is much higher than that of the original glass composition.

3) Schematic Representation of the Role of Gold Colloid and \(K_2O\)

Assuming the two effects described above, the role of gold colloid and \(K_2O\)
Fig. 12. Schematic representations of the crystallization temperatures of lithium silicate glasses containing no or small amounts of K$_2$O and gold colloids.

in lowering the crystallization temperature of the glasses and also in forming the Li$_2$SiO$_3$ crystal could be represented schematically as follows: The solid lines in Fig. 12 represent the relation between the Li$_2$O content of the glasses containing no gold nuclei and their crystallization temperature, which are drawn on the basis of the assumption that the crystallization temperature increases in proportion to the K$_2$O/Li$_2$O ratio as described above. If one further assumes that the catalyst which is capable of making $f(\theta) = 0$ in the above equation exist in the glasses, the total energy barrier for crystallization will decrease and consequently the shifts of crystallization temperature would occur from the solid lines to the dotted lines, each corresponding to the same K$_2$O contents.

If one makes one more assumption that the composition of the glass near the surface of gold colloids become richer in the Li$_2$O content because of the screening demand of the surface, the crystallization temperature of the glasses would shift still more to that represented by the chain lines: For instance, the crystallization temperature of the 3K$_2$O·20Li$_2$O·80SiO$_2$ glass with gold colloids would be represented by a point C in Fig. 12 if only the wetting effect of gold colloid be admitted. If one further admit the change of its composition toward the K$_2$O-rich region such as represented by a point B, the crystallization of the glass would take place at lower temperature as represented by a point A (the same temperature as represented by B). By considering the same way, the dotted line, C-B, could be shifted to the place represented by a chain line, A-D. The composition of the crystal formed at the point A should be Li$_2$SiO$_3$ but not Li$_2$Si$_2$O$_5$, because it is separated out from the glass near the surface of gold colloids whose Li$_2$O content is higher than that of the Li$_2$SiO$_3$ composition. The same shift could also be expected for the crystallization temperature lines of
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the glasses containing none and 2 mol K₂O respectively. In these two cases, however, the K₂O content of the glass at the surface of gold colloid would not exceed that of the Li₂Si₂O₅ composition as indicated by a point, B', and thus the composition of the crystal to be separated out would be Li₂Si₂O₅. The fact that the Li₂SiO₃ crystal is separated out only when the K₂O content of the glass is high could thus be explained.

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