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<td>Author(s)</td>
<td>Sakka, Sumio</td>
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Kyoto University
Formation of Tungsten Bronze and Other Electrically Conducting Crystals by Crystallization of Glasses Containing Alkali and Tungsten Oxide

Sumio Sakka*

Received August 10, 1970

An experimental study has been made to explore a new method for preparing electrically conducting glass-ceramics. Glasses of selected compositions in the systems Na₂O-WO₃-P₂O₅, K₂O-WO₃-P₂O₅, Li₂O-WO₃-P₂O₅ and Na₂O-WO₃-B₂O₅ were crystallized in hydrogen atmosphere. Most of the resultant crystallized glasses (glass-ceramics) were conducting at the surface or in the bulk. Some of the glasses have changed to glass-ceramics with sodium tungsten bronze layer at the surface, which showed surface electrical resistivities of the order of magnitude of 0.1–1Ω for 1 cm distance between two electrodes 1 cm long.

I. INTRODUCTION

There are a number of tungsten oxide compounds, such as β-tungsten (β-W), lower tungsten oxides and alkali tungsten bronzes, which are electrical conductors. A series of alkali tungsten bronzes are non-stoichiometric compounds having a general formula, RXWO₃, where R is Li, Na or K and x is less than unity. They are metallic conductors and some of them are reported to be superconductors. The present work has been started in order to see if we can obtain electrically conducting glass-ceramics by crystallization of glasses containing tungsten oxide. Especially, precipitation of alkali tungsten bronzes was aimed at, since they have many interesting properties besides metallic conductivity. For this purpose glasses have been heated in hydrogen atmosphere. This method of precipitating tungsten bronzes would be applicable for many other compounds called "bronze". In the present paper preliminary results on glass formation and crystallization of glasses in the systems Na₂O-WO₃-P₂O₅, K₂O-WO₃-P₂O₅, Li₂O-WO₃-P₂O₅ and Na₂O-WO₃-B₂O₅ have been reported.

II. EXPERIMENTAL

Preparation of Glasses

Reagent grade chemicals of alkali carbonates, alkali metaphosphates, fused boric oxide and tungsten trioxide were used as raw materials for glass melting. Phosphoric oxide component was given by various alkali metaphosphates. Except Li₂O-WO₃-P₂O₅ compositions, batches of about 20 grams consisting of appropriate mixtures of materials were melted in 20 cc silica glass crucibles at 1,000–1,100°C for 10–20 minutes. Melting and forming of Li₂O-WO₃-P₂O₅ glasses will be described later. An electric furnace with silicon carbide heating element was used for melting.

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glasses, with no control of melting atmosphere. The melts were quenched by pouring on an aluminum plate and pressing with a pressing iron.

Whether a melt became clear glass without devitrification or not depended upon the quenching rate which in turn was mainly determined by the thickness of the sample plates formed by pressing operation. The melts were pressed to 0.4-0.5 mm thick sheets quickly except for Li2O-WO3-P2O5 melts.

**Crystallization of Glasses**

Glasses were heated in hydrogen atmosphere to 500–550°C and held there for 4–5 hours. The heating-up rate was kept constant at 5 deg./min. Some of the glasses were heated in air in order to make comparison of crystallization behavior in different atmospheres.

**Examination of the Crystallized Glasses**

Crystal phases found in crystallized samples were identified by the x-ray powder diffraction using CuKα radiation. In order to differentiate the crystal phases precipitated at the surface of crystallized glasses from those found in the interior, surface layer of the samples was ground away gradually and x-rays diffracted from new surfaces were analysed. Microscopic examination of cross sections of the crystallized samples were also made. The samples were embedded in epoxy resin, and ground and polished with 3 μ ceria powder. A metallurgical microscope was used to observe the cross sections under reflected light.

**Measurement of Electrical Conductivity**

The surface conductivity and bulk conductivity were measured on the samples coated with conducting silver electrodes. A General Radio type 1650-A impedance bridge was used.

**III. RESULTS**

**Na2O-WO3-P2O5 System**

Compositions shown by points in Fig. 1 were melted. Clear glasses were obtained from most of the compositions by pressing the melt to 0.4–0.5 mm thick sheet quickly. No clear glass was obtained, however, from the composition without P2O5 in the present experiment. It should be noted that more rapid cooling of the melt of smaller amount leads to glass formation. Generally, glass forming ability became poor as the P2O5 content decreased. The line in Fig. 1 marks the glass formation limit under the present conditions of glass preparation.

All the glasses used in the experiment could be crystallized into the products which show red, orange, purplish brown or black color on the surface, depending on the composition of the original glass. Some of the samples deformed, probably because crystallization occurred only after glasses softened.

X-ray identification showed that the crystalline phase at the surface is tungsten bronze for red, orange or purplish-brown samples, while β-W and WO3, are found at the black surface.
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Fig. 1. Na$_2$O-WO$_3$-P$_2$O$_5$ compositions used in the experiment.
Line L: tentative glass formation limit.
C: no clear glass was obtained.

Fig. 2. Glass formation and crystallization in the Na$_2$O-WO$_3$-P$_2$O$_5$ system

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Figure 2 summarizes crystallization behavior of glasses in the composition diagram. It can be seen that glasses suitable for the formation of tungsten bronze glass-ceramics are in the region of Na$_2$O 32.5–40, WO$_3$ 57.5–66 and P$_2$O$_5$ 1.5–5 mole%.

Microscopic examination of cross sections of the crystallized samples revealed that only a surface layer of 5 μ to 20 μ in thickness is colored and the interior is colorless, as photomicrographs in Fig. 3 show. X-ray diffraction taken on the surface of the sample after grinding the original surface away indicated that, generally, β-W and/or WO$_3$ is precipitated at the original surface and Na$_3$W$_4$O$_{13}$ in the interior for glasses of lower Na$_2$O content, while tungsten bronze Na$_5$WO$_4$ is precipitated at the surface and Na$_3$W$_2$O$_7$ in the interior for glasses of higher Na$_2$O content. Figure 4 shows the structure of the crystallized samples schematically.

Fig. 3. Cross sections of the glass-ceramics having a tungsten bronze surface layer. See Table 1 for the compositions of the samples.

Fig. 4. Schematic representation of cross sections of crystallized glasses.

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Fig. 5. X-ray diffraction of a crystallized glass having a bronze layer at the surface. Glass NWP 16 Na2O 33.5, WO3 65, P2O5 1.5

Fig. 6. Variation of lattice constant with bronze composition (Brown and Banks)

<table>
<thead>
<tr>
<th>Glass</th>
<th>Na2O</th>
<th>WO3</th>
<th>P2O5</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWP 34</td>
<td>35</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>&quot; 35</td>
<td>35</td>
<td>60</td>
<td>1.5</td>
</tr>
<tr>
<td>&quot; 50</td>
<td>37.5</td>
<td>57.5</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 5 shows the x-ray diffraction patterns for a glass at the surface of which tungsten bronze layer was formed. It is seen that the crystal at the surface is cubic tungsten bronze.\(^7\)

In order to determine the \(x\) value in the formula \(\text{Na}_x\text{WO}_3\), the lattice constant of precipitated tungsten bronze crystal, \(a\), was precisely determined for three samples having different colors, orange, red and purplish brown. The application of the \(a\)-\(x\) relation obtained by Brown and Banks\(^7\) gave \(x\) values ranging from 0.67 to 0.77, as shown in Fig. 6.

Absorption spectra of the orange and red samples are shown in Fig. 7, together with those given by Brown and Banks.\(^7\) The \(x\) values determined from the peak wavelengths on the absorption curves ranged from 0.66 to 0.74. Formation of a slight amount of black crystals in the bronze crystal layer may influence the shape of the absorption curve and, therefore, the \(x\) value determined from x-ray diffraction would be more reliable.

The experimental results for some of the crystallized glasses are summarized in Table 1. Surface resistivity data are included in the table. The resistivity is expressed by the value for 1 cm in electrode length and 1 cm in distance between the two electrodes. It is seen from Table 1 that the surface of the crystallized samples
Formation of Tungsten Bronze by Crystallization of Glasses

Table 1. Na$_2$O-WO$_3$-P$_2$O$_5$ Glasses Crystallized by Heating in Hydrogen Atmosphere

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>NWP</th>
<th>30</th>
<th>19</th>
<th>36</th>
<th>35</th>
<th>42</th>
<th>43</th>
<th>46</th>
<th>34</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td></td>
<td>27.5</td>
<td>25</td>
<td>36.5</td>
<td>37.5</td>
<td>35</td>
<td>36.25</td>
<td>33.75</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>WO$_3$</td>
<td></td>
<td>70</td>
<td>70</td>
<td>62</td>
<td>60</td>
<td>61.25</td>
<td>60</td>
<td>61.25</td>
<td>60</td>
<td>57.5</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td></td>
<td>2.5</td>
<td>5</td>
<td>1.5</td>
<td>2.5</td>
<td>3.75</td>
<td>3.75</td>
<td>5</td>
<td>5</td>
<td>7.5</td>
</tr>
<tr>
<td>Color of the surface</td>
<td></td>
<td>black</td>
<td>orange</td>
<td>red</td>
<td>Purple</td>
<td>brown</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal phase at the surface</td>
<td></td>
<td>β-W + WO$_2$</td>
<td>cubic bronze</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition of the bronze</td>
<td></td>
<td>Na$_{0.77}$ WO$_4$</td>
<td>Na$_{0.76}$ WO$_3$</td>
<td>Na$_{0.67}$ WO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice constant</td>
<td></td>
<td>3.8476</td>
<td>3.8472</td>
<td>3.8392</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remark</td>
<td></td>
<td>deform</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Approximate surface resistivity (ohm)</td>
<td></td>
<td>1</td>
<td>1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>3</td>
<td>1</td>
<td>70</td>
</tr>
</tbody>
</table>

are fairly conducting independently of the crystal phase. The surface resistivity values cited in Table 1 should be considered to give only the order of magnitude, because the thickness of the surface conducting layer is different for different samples.

**K$_2$O-WO$_3$-P$_2$O$_5$ system**

Eight compositions shown in Fig. 8 were melted and clear glasses were obtained.

Fig. 8. K$_2$O-WO$_3$-P$_2$O$_5$ compositions used in the experiment.

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Among these, three glasses (KWP 35, 16 and 30) could be crystallized upon heating without deformation. Table 2 summarizes the results on the three glasses heated in H₂ atmosphere. It can be seen that β-W is a major crystal phase precipitated at the surface of the crystallized glasses. No tungsten bronze was formed in this system. When the glasses were heated in air, K₂WO₄, K₂W₁₀O₁₇ and a metastable potassium tungstate (a compound X designated by Gelsing et al[^5]) precipitated.

**Table 2. Crystallized Glasses in the System K₂O-WO₃-P₂O₅ (Heated at 500–530°C in H₂)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>KWP 35</th>
<th>KWP 16</th>
<th>KWP 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂O</td>
<td>30</td>
<td>30</td>
<td>32.5</td>
</tr>
<tr>
<td>WO₃</td>
<td>67.5</td>
<td>65</td>
<td>5</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>2.5</td>
<td>5</td>
<td>62.5</td>
</tr>
<tr>
<td>Color</td>
<td>Blue black</td>
<td>Dark grey</td>
<td>Black</td>
</tr>
<tr>
<td>Approximate surface resistivity (ohm)</td>
<td>10⁷</td>
<td>35</td>
<td>150</td>
</tr>
<tr>
<td>Major crystalline phase at the surface</td>
<td>β-W</td>
<td>β-W</td>
<td></td>
</tr>
</tbody>
</table>

Besides K₂O-WO₃-P₂O₅ compositions, mixed alkali glasses Na₂O-K₂O-WO₃-P₂O₅ were melted and heated for crystallization. Substitution of K₂O for Na₂O was found to lower the softening temperature of glasses compared with Na₂O-WO₃-P₂O₅ glasses which contain the same amount of total alkali oxide and lead to softening before crystallization. No mixed alkali tungsten bronze was obtained by the crystallization of mixed alkali glasses.

**Li₂O-WO₃-P₂O₅ system**

The compositions melted are shown in Fig. 9. For this system the condition for melting and forming glasses different from that for the other systems was employed; a 50 g batch was melted and formed into a glass plate more than 2 mm thick. The glass formation limit for this condition is shown in the figure. It can be seen that more than 15% P₂O₅ is necessary to obtain glass. With composition 9, which did not form glass under the present condition, the method of forming thinner film 0.3–0.4 mm thick as used in the other systems also failed to give clear glass; the melt crystallized upon cooling even by this method of quenching.

Table 3 shows the behavior of Li₂O-WO₃-P₂O₅ glasses upon heat treatment in various atmospheres. Glasses as prepared in air have blue or dark blue color. When these glasses are heated at 200–400°C in H₂ atmosphere, the color becomes darker, indicating that glasses are reduced. If the glasses are heated in air or O₂ at 450–500°C, the blue or black color is lost and transparent, colorless glasses result. It is considered that lower valent tungsten ions in glass which were the origin of the color have been oxidized to W⁶⁺ ions that are colorless. Heating glasses at 500–530°C leads to crystallization of glasses without deformation. Crystallized products show green color...
when glasses are crystallized in air, O₂ or N₂ and show violet or blue color when glasses are crystallized in H₂. The similar, reduced crystallized glasses are obtained both upon heating the crystallized-in-air glass in H₂ atmosphere and upon crystallization of the glass in H₂ atmosphere.

With Li₂O-WO₃-P₂O₅ glasses no particular surface layer was formed; color and x-ray diffraction pattern were the same in the interior as at the surface of the sample, as distinct from the crystallized products of the Na₂O-WO₃-P₂O₅ system.

X-ray diffraction patterns were obtained as shown in Fig. 10, but crystal phases could not be identified. In the x-ray diffraction pattern of a reduced sample, there are several peaks (designated B in Fig. 10 b) which agree pretty well in 2θ values (d values) with those of lithium tungsten bronze LiₓWO₃. However, the presence of
the bronze cannot be definitely confirmed for the two reasons: 1. the non-reduced sample, in which the bronze does not form obviously, shows almost the same pattern (Fig. 10 a) as that of the reduced sample and 2. various tungsten oxides can show the similar patterns.

Resistivity measurement showed: 1. blue-colored glasses as prepared or colorless ones as oxidized by heat treatment in air at 450–500°C have volume resistivities higher than $10^7 \, \Omega \, \text{cm}$, 2. green-colored glass-ceramics obtained by heating glasses in air or $\text{N}_2$ have resistivities of $10^6$–$10^7 \, \Omega \, \text{cm}$ in the order of magnitude and 3. blue or violet glass-ceramics obtained by heating glasses in $\text{H}_2$ have resistivities of 10 to $10^3 \, \Omega \, \text{cm}$, that is, they are fairly conducting.

**Na$_2$O-WO$_3$-B$_2$O$_3$ system**

This system is characterized by another glass forming oxide B$_2$O$_3$ replacing P$_2$O$_5$ in the systems mentioned above. Glass formation and crystallization behaviors of compositions in this system are shown in Fig. 11. Similarly to the Na$_2$O-WO$_3$–P$_2$O$_5$ system, there is a compositional area where glass formation is possible and, upon heating in $\text{H}_2$, the glass is crystallized to tungsten bronze exhibiting a characteristic color (yellow, orange or red). Heating temperatures suitable for these glasses were 400 to 480°C. The tungsten bronze formed only at the surface of the glass sample. Non-conductive sodium tungstates formed in the interior. It should be
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Fig. 11. Glass formation and crystallization of Na₂O-WO₃-B₂O₃ glasses.

noted that glasses of lower WO₃ content were phase-separated when prepared, although tungsten bronze formed also in such glasses upon heating in H₂.

The crystallized glasses with a tungsten bronze surface layer exhibited surface resistivities similar to those of the Na₂O-WO₃-P₂O₅ system.

IV. DISCUSSION

Process of Crystallization

The process of crystallization of the glasses in H₂ atmosphere is not clear. In view of the fact that the present glasses crystallize in air at relatively low temperatures (350–500°C) and form, for example, Na₂W₃O₇ and/or Na₃W₅O₁₅, however, it is possible that the glasses crystallize in H₂ also to such crystals at lower temperatures than 500–550°C and then such crystals are reduced to tungsten bronze, β-W, WO₂ or other electrically conducting crystals at 500–550°C. It is known that the reduction of alkali tungstate compounds of the general formula $R_nW_nO_{3n+1}$, where $R$ = Li, Na or K and $n \geq 2$, leads to formation of tungsten bronze, β-W, etc. The formation of tungsten bronze layer only at the surface of the sample can be attributed to the reduction reaction being governed by diffusion of hydrogen from the surface or

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diffusion of oxygen to the surface. The rate of diffusion of these species through a bronze layer should be pretty slow.

**Composition Relation between Glass and Tungsten Bronze**

According to x-ray studies on the reduction of alkali tungstate powders by Spier, sodium ditungstate Na$_2$W$_2$O$_7$ and sodium tetratungstate Na$_4$W$_4$O$_{13}$ are reduced mainly to cubic sodium bronze Na$_x$WO$_3$ at 500°C and 600°C. The present results confirming the formation of cubic tungsten bronze at the surface of crystallized samples of Na$_2$O-WO$_3$-$P_2$O$_5$ glasses essentially agree with Spier's results if the glasses crystallized to glass-ceramics containing normal alkali tungstates are assumed to be reduced by hydrogen. Spier showed that smaller amounts of tetragonal bronze and Na$_2$WO$_4$ were also formed, but the present work did not confirm formation of these compounds. The difference may be attributed to the presence of glassy phases containing P$_2$O$_5$ in our samples.

No information is available as to the composition of cubic tungsten bronze (x in Na$_x$WO$_3$, or Na/W ratio) formed from Na$_2$W$_2$O$_7$ and Na$_4$W$_4$O$_{13}$. In the present study the value x varied in a very small range (x=0.67–0.77), irrespectively of the composition of crystals before reduction (that is, the crystals precipitated in the interior of the samples, Na$_2$W$_2$O$_7$ or Na$_4$W$_4$O$_{13}$). This value of x corresponds to the Na/W ratio between those for Na$_2$W$_2$O$_7$ (1/1) and Na$_4$W$_4$O$_{13}$ (1/2) and much smaller than those corresponding to the Na/W ratio (1.2/1) in the original glass compositions. More details on this problem is beyond the scope of the present preliminary study, although it is interesting to clarify the mechanism of reduction or mechanism of crystallization of glasses in H$_2$ atmosphere.

In the present work no tungsten bronze was obtained in K$_2$O-containing systems. Spier obtained tetragonal and hexagonal bronzes from K$_2$W$_n$O$_{3n+1}$ (n=2, 3, 4) compounds by reduction. This may be attributed to the difference in heating conditions and starting materials. Since certain tetragonal and hexagonal bronzes show superconductivity with a superconductive transition temperature around 1 K, it would be interesting to do more detailed study on the crystallization of K$_2$O–WO$_3$-$P_2$O$_5$ glasses to precipitate such bronzes.

**V. CONCLUSION**

The present exploratory work showed that the crystallization of glasses having appropriate compositions can produce electrically conducting glass-ceramics and, from certain compositions, glass-ceramics with a tungsten bronze layer at the surface. The present results are still preliminary and many other interesting glass-ceramics are expected to be prepared by the similar method, since there are a great number of bronze compounds besides alkali tungsten bronzes.

**ACKNOWLEDGMENTS**

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