

Formation of Tungsten Bronze and Other Electrically Conducting Crystals by Crystallization of Glasses Containing Alkali and Tungsten Oxide

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An experimental study has been made to explore a new method for preparing electrically conducting glass-ceramics. Glasses of selected compositions in the systems $\text{Na}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$, $\text{K}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$, $\text{Li}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ and $\text{Na}_2\text{O}-\text{WO}_3-\text{B}_2\text{O}_3$ 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 $0.1-1 \Omega$ 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),¹⁾ lower tungsten oxides²⁾ and alkali tungsten bronzes,^{3,4)} which are electrical conductors. A series of alkali tungsten bronzes are non-stoichiometric compounds having a general formula, R_xWO_3 , where R is Li, Na or K and x is less than unity. They are metallic conductors^{3,4)} and some of them are reported to be superconductors.⁵⁾ 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 $\text{Na}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$, $\text{K}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$, $\text{Li}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ and $\text{Na}_2\text{O}-\text{WO}_3-\text{B}_2\text{O}_3$ 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 $\text{Li}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ compositions, batches of about 20 grams consisting of appropriate mixtures of materials were melted in 20 cc silica glass crucibles at $1,000-1,100^\circ\text{C}$ for 10-20 minutes. Melting and forming of $\text{Li}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ 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 $\text{Li}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ 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 $\text{CuK}\alpha$ 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

$\text{Na}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ 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 P_2O_5 in the present experiment. It should be noted that more rapid cooling of the melt of smaller amount leads to glass formation.⁶⁾ Generally, glass forming ability became poor as the P_2O_5 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 WO_3 , are found at the black surface.

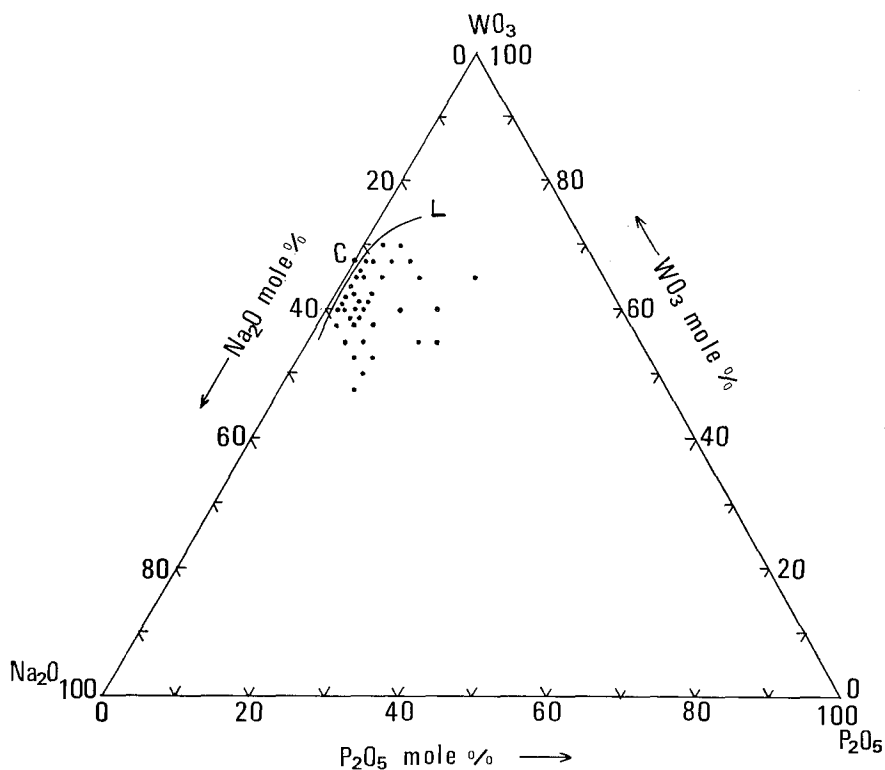


Fig. 1. Na_2O - WO_3 - P_2O_5 compositions used in the experiment.
Line L: tentative glass formation limit.
C : no clear glass was obtained.

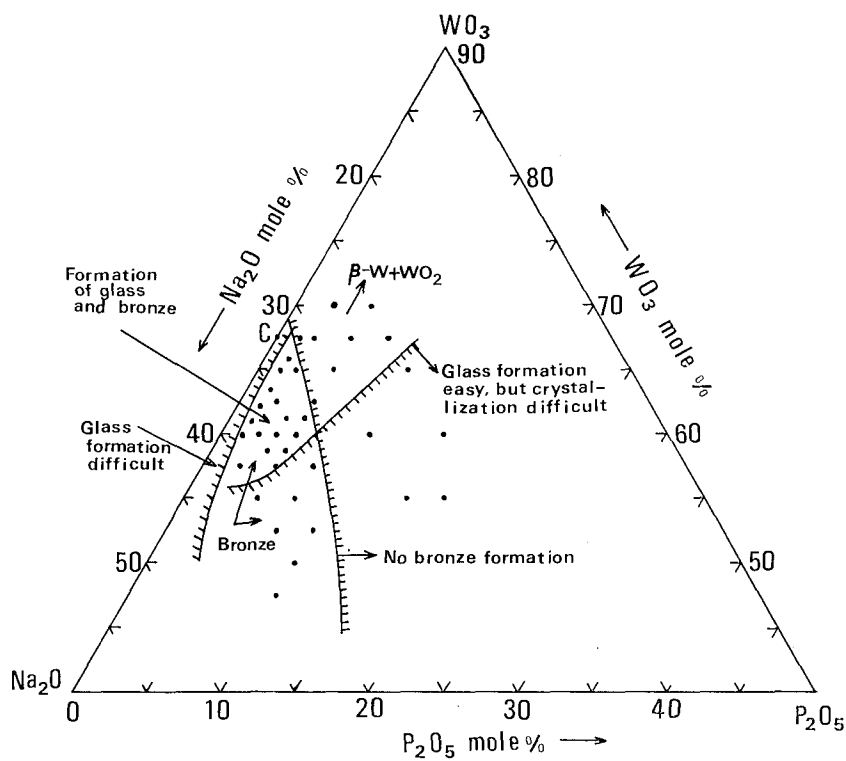


Fig. 2. Glass formation and crystallization in the Na_2O - WO_3 - P_2O_5 system

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_2O 32.5–40, WO_3 57.5–66 and P_2O_5 1.5–5 mole %.

Microscopic examination of cross sections of the crystallized samples revealed that only a surface layer of 5μ to 20μ 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_2 is precipitated at the original surface and $\text{Na}_2\text{W}_4\text{O}_{13}$ in the interior for glasses of lower Na_2O content, while tungsten bronze Na_xWO_3 is precipitated at the surface and $\text{Na}_2\text{W}_2\text{O}_7$ in the interior for glasses of higher Na_2O content. Figure 4 shows the structure of the crystallized samples schematically.

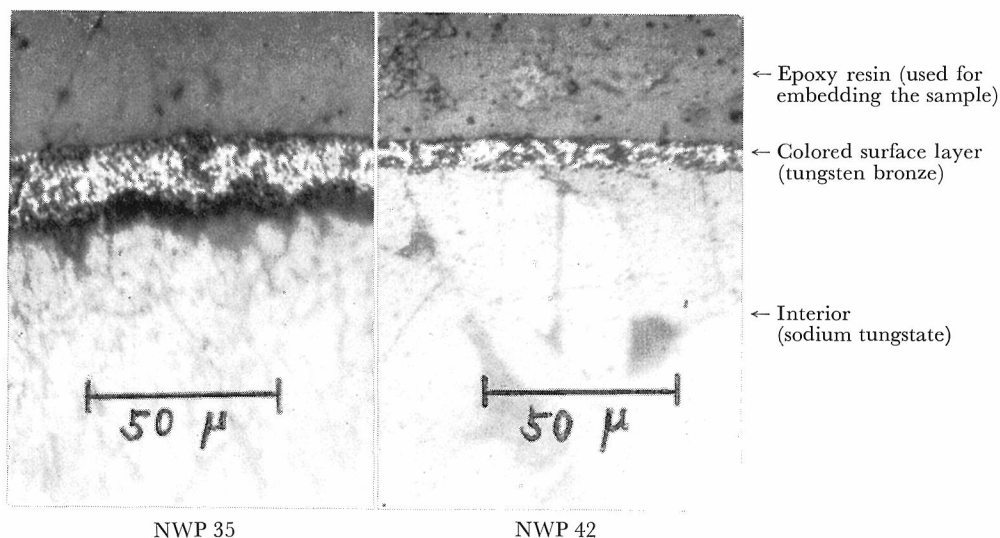


Fig. 3. Cross sections of the glass-ceramics having a tungsten bronze surface layer. See Table 1 for the compositions of the samples.

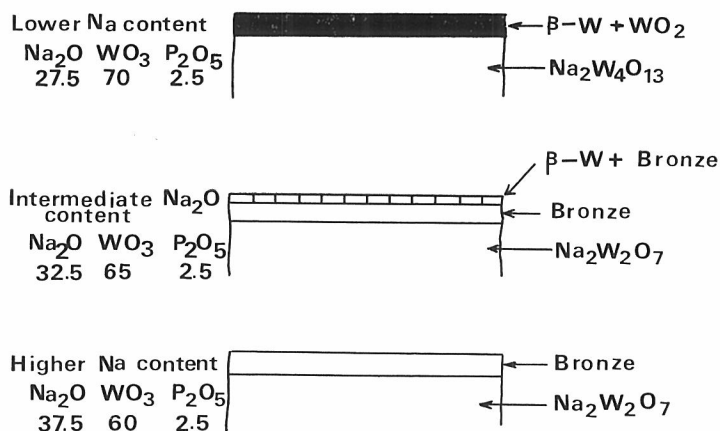


Fig. 4. Schematic representation of cross sections of crystallized glasses.

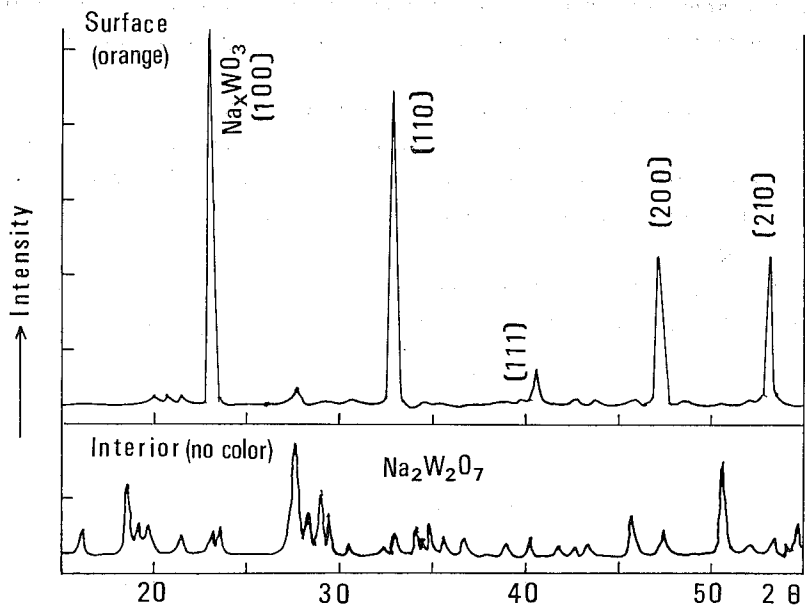


Fig. 5. X-ray diffraction of a crystallized glass having a bronze layer at the surface. Glass NWP 16 Na_2O 33.5, WO_3 65, P_2O_5 1.5

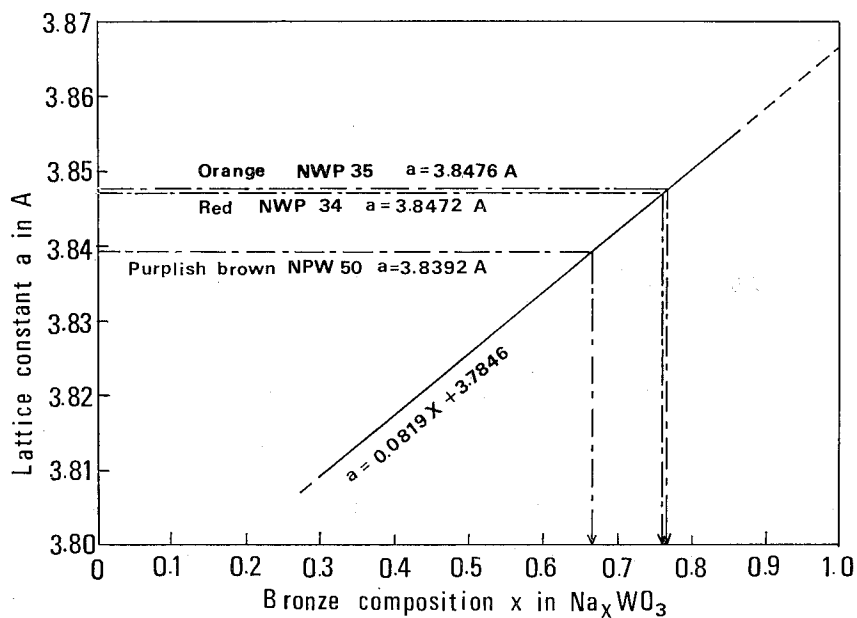


Fig. 6. Variation of lattice constant with bronze composition (Brown and Banks)

Glass	Na_2O	WO_3	P_2O_5
NWP 34	35	60	5
" 35	37.5	60	1.5
" 50	37.5	57.5	5

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 Na_xWO_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 Banks⁷⁾ 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

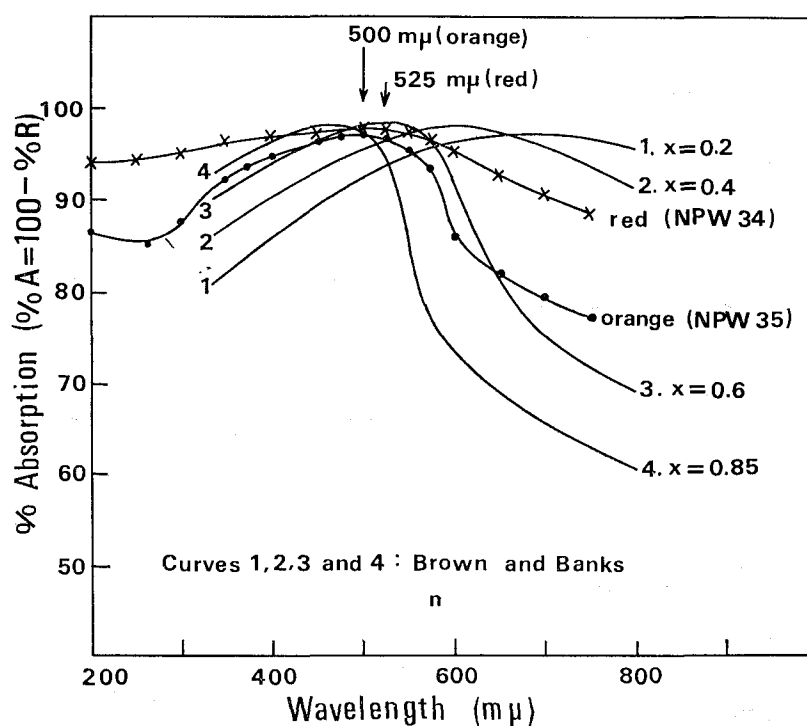


Fig. 7. Absorption spectra of sodium tungsten bronzes.

Glass	Na_2O	WO_3	P_2O_5
NWP 34	35	60	5
" 35	37.5	60	1.5

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. $\text{Na}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ Glasses Crystallized by Heating in Hydrogen Atmosphere

	NWP	30	19	36	35	42	43	46	34	50
Glass composition										
Na ₂ O		27.5	25	36.5	37.5	35	36.25	33.75	35	35
WO ₃		70	70	62	60	61.25	60	61.25	60	57.5
P ₂ O ₅		2.5	5	1.5	2.5	3.75	3.75	5	5	7.5
Color of the surface		black		orange				red		Purple brown
Crystal phase at the surface		$\beta\text{-W}+\text{WO}_2$		cubic bronze						
Composition of the bronze				Na _{0.77} WO ₃				Na _{0.76} WO ₃		Na _{0.67} WO ₃
Lattice constant				3.8476				3.8472		3.8392
Remark										deform
Approximate surface resistivity (ohm)		1	1	0.2	0.3	0.2	0.1	3	1	70

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.

$\text{K}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ system

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

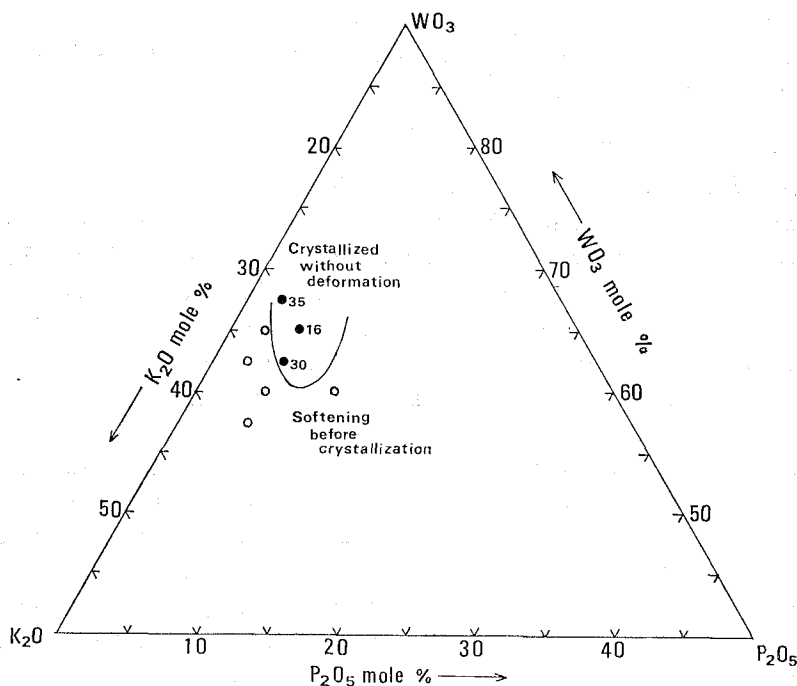


Fig. 8. $\text{K}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ compositions used in the experiment.

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 H_2 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, K_2WO_4 , $K_2W_3O_{10}$ and a metastable potassium tungstate (a compound X designated by Gelsing *et al*⁽⁹⁾) precipitated.

Table 2. Crystallized Glasses in the System $K_2O-WO_3-P_2O_5$ (Heated at 500–530°C in H_2)

	KWP 35	KWP 16	KWP 30
Composition			
K_2O	30	30	32.5
WO_3	67.5	65	5
P_2O_5	2.5	5	62.5
Color	Blue black	Dark grey	Black
Approximate surface resistivity (ohm)	10^7	35	150
Major crystalline phase at the surface	β -W	β -W	

Besides $K_2O-WO_3-P_2O_5$ compositions, mixed alkali glasses $Na_2O-K_2O-WO_3-P_2O_5$ were melted and heated for crystallization. Substitution of K_2O for Na_2O was found to lower the softening temperature of glasses compared with $Na_2O-WO_3-P_2O_5$ 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.

$Li_2O-WO_3-P_2O_5$ 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% P_2O_5 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 $Li_2O-WO_3-P_2O_5$ 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 H_2 atmosphere, the color becomes darker, indicating that glasses are reduced. If the glasses are heated in air or O_2 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 W^{6+} ions that are colorless. Heating glasses at 500–530°C leads to crystallization of glasses without deformation. Crystallized products show green color

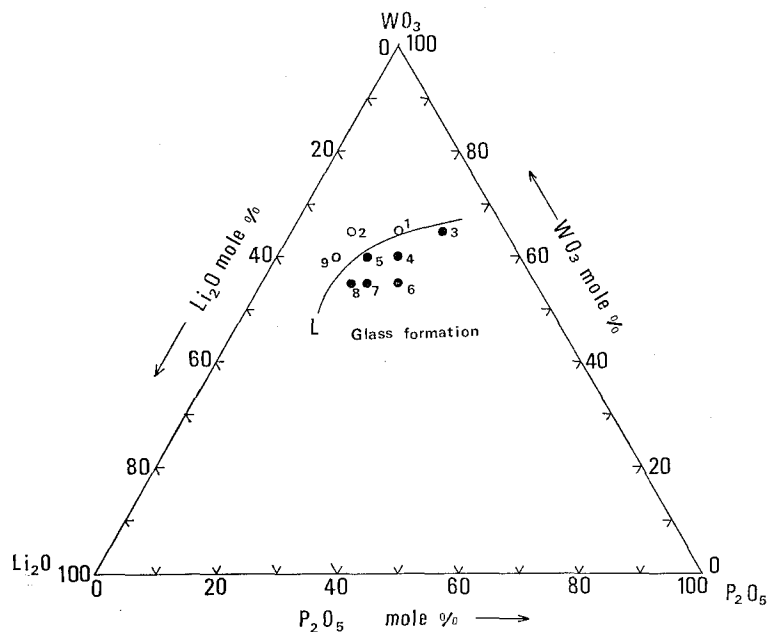


Fig. 9. Li_2O - WO_3 - P_2O_5 compositions melted in the experiment.
Line L: tentative glass formation limit.

Table 3. Heat Treatment of Li_2O - WO_3 - P_2O_5 Glasses

Atmosphere	Original glass	Heated at		
		200-400°C	450-500°C	500-530°C
Air or O_2	Dark blue		Oxidation: colorless, clear glass	Crystallization: green
N_2				Crystallization: green
H_2		Reduction: black glass		Crystallization: violet or blue

when glasses are crystallized in air, O_2 or N_2 and show violet or blue color when glasses are crystallized in H_2 . The similar, reduced crystallized glasses are obtained both upon heating the crystallized-in-air glass in H_2 atmosphere and upon crystallization of the glass in H_2 atmosphere.

With Li_2O - WO_3 - P_2O_5 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 Na_2O - WO_3 - P_2O_5 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 Li_xWO_3 . However, the presence of

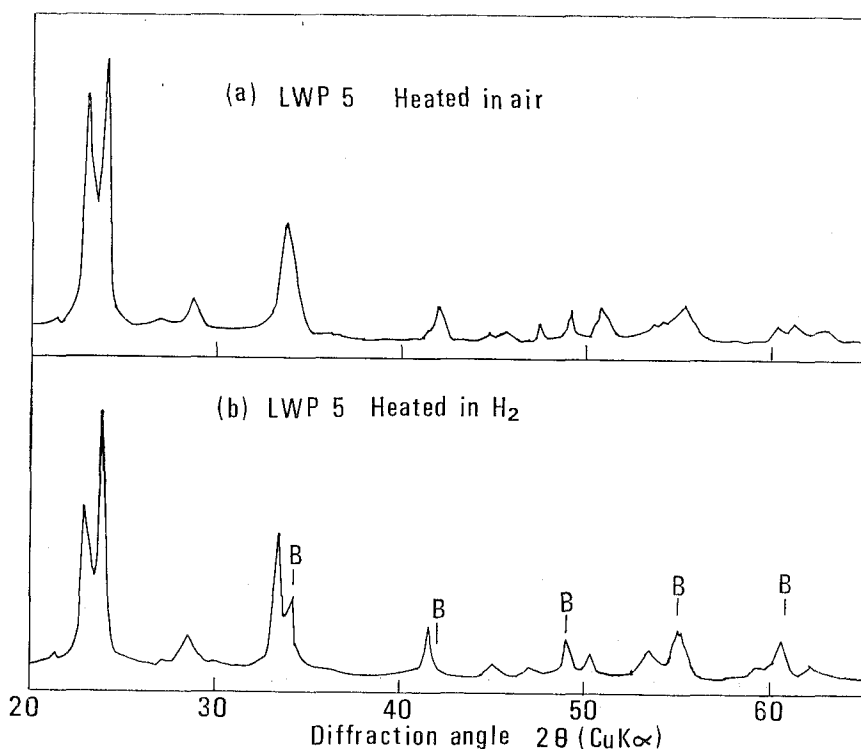


Fig. 10. X-ray diffraction patterns of a $\text{Li}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ glass (LWP 5) after crystallization.

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 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 H_2 have resistivities of 10 to $10^3 \Omega \text{ cm}$, that is, they are fairly conducting.

$\text{Na}_2\text{O}-\text{WO}_3-\text{B}_2\text{O}_3$ system

This system is characterized by another glass forming oxide B_2O_3 replacing P_2O_5 in the systems mentioned above. Glass formation and crystallization behaviors of compositions in this system are shown in Fig. 11. Similarly to the $\text{Na}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ system, there is a compositional area where glass formation is possible and, upon heating in 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

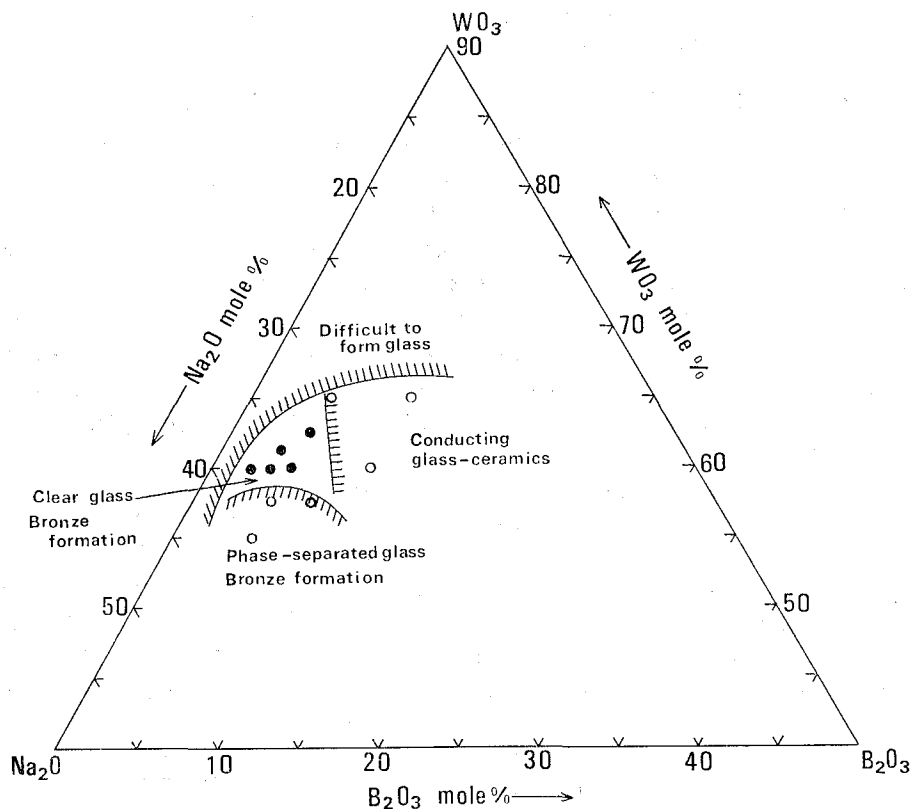


Fig. 11. Glass formation and crystallization of $\text{Na}_2\text{O}-\text{WO}_3-\text{B}_2\text{O}_3$ glasses.

noted that glasses of lower WO_3 content were phase-separated when prepared, although tungsten bronze formed also in such glasses upon heating in H_2 .

The crystallized glasses with a tungsten bronze surface layer exhibited surface resistivities similar to those of the $\text{Na}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ system.

IV. DISCUSSION

Process of Crystallization

The process of crystallization of the glasses in H_2 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, $\text{Na}_2\text{W}_2\text{O}_7$ and/or $\text{Na}_2\text{W}_4\text{O}_{13}$, however, it is possible that the glasses crystallize in H_2 also to such crystals at lower temperatures than 500–550°C and then such crystals are reduced to tungsten bronze, $\beta\text{-W}$, WO_2 or other electrically conducting crystals at 500–550°C. It is known that the reduction of alkali tungstate compounds of the general formula $\text{R}_2\text{W}_n\text{O}_{3n+1}$, where $\text{R}=\text{Li}$, Na or K and $n \geq 2$, leads to formation of tungsten bronze, $\beta\text{-W}$, etc.^{9,10} 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

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,⁹⁾ sodium ditungstate $\text{Na}_2\text{W}_2\text{O}_7$ and sodium tetratungstate $\text{Na}_2\text{W}_4\text{O}_{13}$ are reduced mainly to cubic sodium bronze Na_xWO_3 at 500°C and 600°C. The present results confirming the formation of cubic tungsten bronze at the surface of crystallized samples of $\text{Na}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ 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_2WO_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_2O_5 in our samples.

No information is available as to the composition of cubic tungsten bronze (x in Na_xWO_3 , or Na/W ratio) formed from $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{Na}_2\text{W}_4\text{O}_{13}$. 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, $\text{Na}_2\text{W}_2\text{O}_7$ or $\text{Na}_2\text{W}_4\text{O}_{13}$). This value of x corresponds to the Na/W ratio between those for $\text{Na}_2\text{W}_2\text{O}_7$ (1/1) and $\text{Na}_2\text{W}_4\text{O}_{13}$ (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_2O -containing systems. Spier⁹⁾ obtained tetragonal and hexagonal bronzes from $\text{K}_2\text{W}_n\text{O}_{3n+1}$ ($n=2, 3, 4$) compounds by reduction. This may be attributed to the difference in heating conditions and starting materials. Since certain tetragonal and hexagonal bronzes show superconductivity^{5,11)} with a superconductive transition temperature around 1°K, it would be interesting to do more detailed study on the crystallization of $\text{K}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ 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.

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