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Preparation and characterization of rapidly quenched glasses in the systems R_2O–WO_3 (R = Li, Na, K)

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In the systems R_2O–WO_3 (R = Li, Na, K), the glass-forming region was extended by use of the rapid quenching technique combining a thermal-image furnace with a twin roller. The infra-red spectra revealed that the Li_2WO_4 glass contains no condensed macro-anions but only discrete ions of Li^+ and WO_4^{2-}. The glass transition temperature (T_g) and the crystallization temperature (T_c) were determined. T_g is affected very slightly by the type of alkali cations, whereas it is decreased with increase in the alkali oxide content. More than one T_c was observed in Li_2O–WO_3 glasses, which is due to the formation of metastable phases. The conductivity of glasses containing the same amount of alkali oxide (of different types) increased with decrease in the radius of the alkali cation. Electrochromism was observed in the glasses with R = Li, Na; the electric field required for colouration is lower than that in WO_3 films. The electro-colouration is due to H_xWO_3 formed in the glass matrix by the double injection of protons and electrons.

1. Introduction

The development of several rapid quenching techniques from the melt [1,2] has made it easy to prepare glass in the systems in which glass formation by the usual procedure is difficult [3,4]. We presented a new rapid quenching technique combining a thermal-image furnace and a twin roller [5]. The glass preparation using this technique has been tried for several systems [6,7]. In this study, we have applied it to glass formation in the systems R_2O–WO_3 (R = Li, Na, K) and found that the glass-forming region was extended, compared with the splat-cooling technique; the glasses prepared showed electrochromism when an electric field lower than that in WO_3 films was applied [6].

In this paper, the structure, glass transition temperature and conductivity, as well as glass formation and electrochromism, are reported in more detail for the rapidly quenched glasses in the systems R_2O–WO_3 (R = Li, Na, K).

2. Experimental procedure

The glass preparation technique has been reported previously [6]. The glass transition temperature (T_g) and the crystallization temperature (T_c) were determined by differential thermal analysis (DTA) using a Rigaku Denki thermal analyser. The DTA was measured from room temperature to 793 K with a heating rate of 10 K min^{-1}.

The infra-red spectra were recorded on a Hitachi 260-50 infra-red spectrophotometer in the range 4000 to 250 cm^{-1} at room temperature; the measurements were made on glass powders dispersed in KBr pellets (about 1.5 wt %).

The ionic conductivity was obtained using impedance measurements at 1 kHz [7] in dry O_2 in the temperature range 423 to 773 K. The samples used for the measurements were pellets 13 mm in diameter and 0.5 mm thick (pulverized and pressed from as-quenched glass flakes), and evaporated gold was used as electrodes on both surfaces.

For electrochromic experiments, flat parts of

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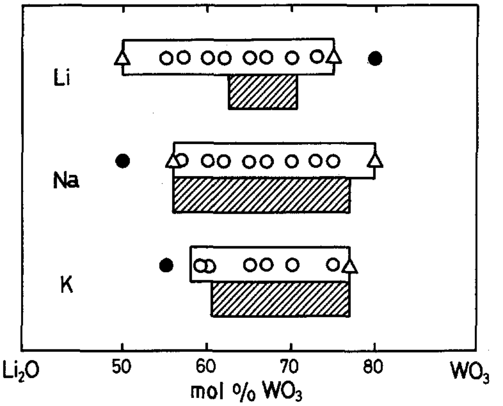

Figure 1 Glass-forming region in the systems R_2O–WO_3 (R = Li, Na, K). The open region is determined in the present study and the cross-hatched area is cited from Gossink [9], in which glasses were prepared by a splat-cooling technique. o: glassy, △: partially crystalline, •: crystalline.

the glass flakes obtained were used, on which two parallel gold electrodes, about 0.5 mm apart, were evaporated. The optical absorption was measured using a procedure described elsewhere [8]. The d.c. conductance was measured in order to investigate the influence of protons on colouration and to characterize the coloured glass flake.

3. Results and discussion

3.1. Glass-forming regions and infra-red spectra

Fig. 1 shows the glass-forming regions for the systems R_2O–WO_3 (R = Li, Na, K). The open region is determined in this work; the open and closed circles denote glassy and crystalline samples, respectively, and the triangles denote the samples in which a small amount of crystalline inclusion was observed. On the other hand, the cross-hatched region in the figure is taken from Gossink, who determined the region using a splat-cooling technique [9]. Our quenching technique extends the glass-forming region in each system compared with that by the splat-cooling technique. In the present study, the glass-forming tendency decreases with increase in the ionic radius ($Li^+ > Na^+ > K^+$), which is in contrast to the results obtained by Gossink. The lithium ion is the cation which promotes glass formation to the highest degree in the present systems and the glass can be obtained even in the composition corresponding to the lithium orthotungstate, Li_2WO_4, although the glass contained a very small amount of crystalline phase.

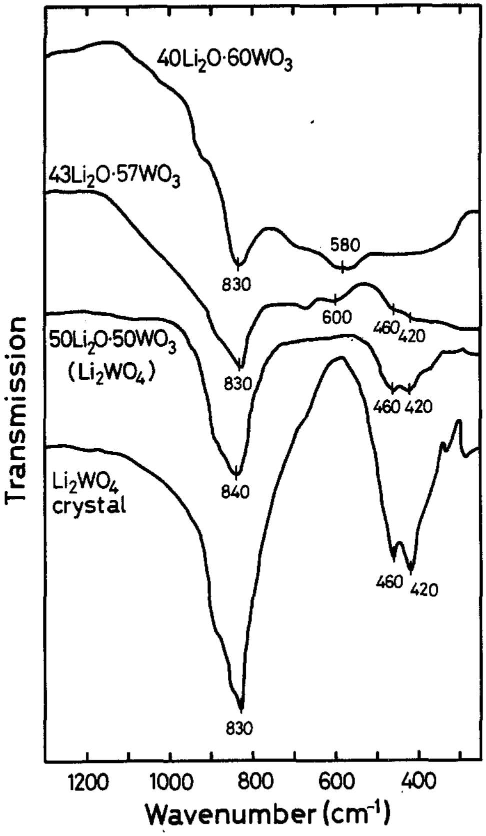

Figure 2 Infra-red spectra of Li_2O–WO_3 glasses and Li_2WO_4 crystal.

Fig. 2 shows the infra-red spectra of Li_2O–WO_3 glasses containing high Li_2O content and of Li_2WO_4 crystal. The infra-red spectra of the glass samples display three absorption bands around 830, 600 and 450 cm^{-1}. With increase in Li_2O content, the bands around 830 and 450 cm^{-1} are strengthened and the band around 600 cm^{-1} is weakened. The glass $50Li_2O{\cdot}50WO_3$ (corresponding to the composition of lithium orthotungstate, Li_2WO_4) has no band around 600 cm^{-1}. The Li_2WO_4 crystal exhibits only two absorption bands at about 830 and 450 cm^{-1}, which were respectively assigned to the ν_3 and ν_4 modes of $WO_4{}^{2-}$ tetrahedral ions [10]. On the other hand, the band around 600 cm^{-1} is ascribed to the ν_{as} mode of the W–O–W bond which results from the presence of condensed ions of WO_4 tetrahedra [10]. Thus the glasses $40Li_2O{\cdot}60WO_3$ and $43Li_2O{\cdot}57WO_3$ contain condensed anions of WO_4 tetrahedra, and the glass $50Li_2O{\cdot}50WO_3$ contains no condensed anions, as expected from the chemical composition of these glasses. In other words, the glass $50Li_2O{\cdot}50WO_3$ consists

TABLE I Glass transition temperature (T_g), crystallization temperature (T_c) and ratio T_g/T_l of some glasses in the systems R_2O–WO_3 (R = Li, Na, K)

R	Composition (mol %) R_2O	WO_3	T_g(K)	T_c(K)	T_g/T_l*
Li	30	70	643	664, 714	0.61
	35	65	628	650, 715	0.61
	40	60	606	619, 729, 763	0.61
Na	30	70	641	684	0.64
	35	65	613	626	0.60
	40	60	600	631	0.61
K	30	70	643	680	0.66
	35	65	605	638	0.68
	40	60	573	655	0.58

* T_l = liquidus temperature.

of discrete WO_4^{2-} ions and Li^+ ions only. The infra-red spectra of other Li_2O–WO_3 glasses and the glasses containing Na_2O or K_2O have also been investigated, and they were consistent with the results reported by Gossink [9]; the spectra of these glasses hardly depend on the WO_3 content and types of the alkali ions.

3.2. Thermal analysis

Table I lists T_g, T_c and T_g/T_l for some glasses in the systems R_2O–WO_3 (R = Li, Na, K), where T_l is the liquidus temperature cited from Levin *et al.* [11]. Among those systems, the DTA data of all the glasses prepared in the system Li_2O–WO_3 are shown in Fig. 3 together with the phase diagram [11].

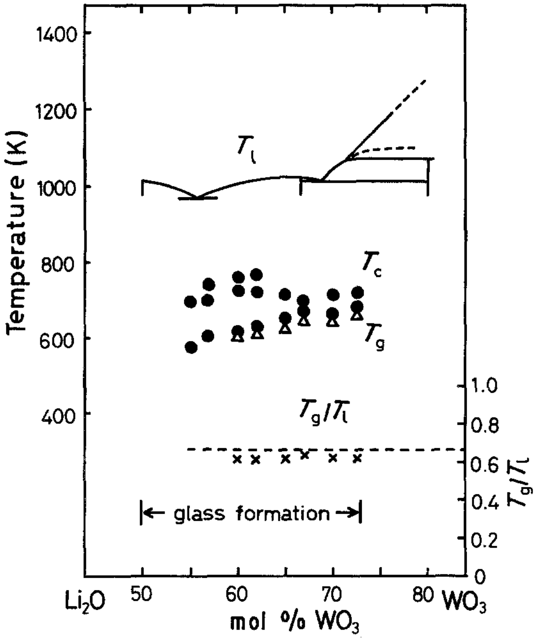

Figure 3 Phase diagram showing T_g(△) and T_c(●) for the system Li_2O–WO_3. The values of T_g/T_l (×) are also shown and the broken line corresponds to T_g/T_l = 2/3.

The observation of T_g was difficult for the glasses containing more than 40 mol % Li_2O. T_g is slightly affected by the type of akali ions whereas it is decreased with increase in the content of alkali oxide. Two or three values of T_c were observed in Li_2O–WO_3 glasses, while every glass containing Na_2O or K_2O shows only one T_c. The observation of more than one T_c is due to the formation of a metastable crystalline phase, as reported by Nassau *et al.* [12]. The T_c (or the lowest T_c in the case of the Li_2O–WO_3 system) is also affected very slightly by the type of alkali ions. For the Li_2O–WO_3 glasses the lowest T_c is decreased with increase in Li_2O content, similar to the case of T_g. On the other hand, the second T_c is lowered at the composition $33.3Li_2O{\cdot}66.7WO_3$ corresponding to lithium ditungstate, $Li_2W_2O_7$.

In the glasses for which T_g's were observed, the ratio T_g/T_l is almost constant and follows the so-called "two-thirds rule", $T_g/T_l = 2/3$ [13]. This is in contrast to the result for the glasses containing a high content of Li_2O in the system Li_2O–SiO_2 also prepared by the twin roller quenching technique: in Li_2O–SiO_2 glasses, T_g decreased rapidly with increase in Li_2O content, and consequently the T_g/T_l ratio deviated greatly from the the rule [5].

3.3. Conductivity

Fig. 4 shows the temperature dependence of conductivity for the glasses $30R_2O{\cdot}70WO_3$ (R = Li, Na, K). The vertical arrows in the figure indi-

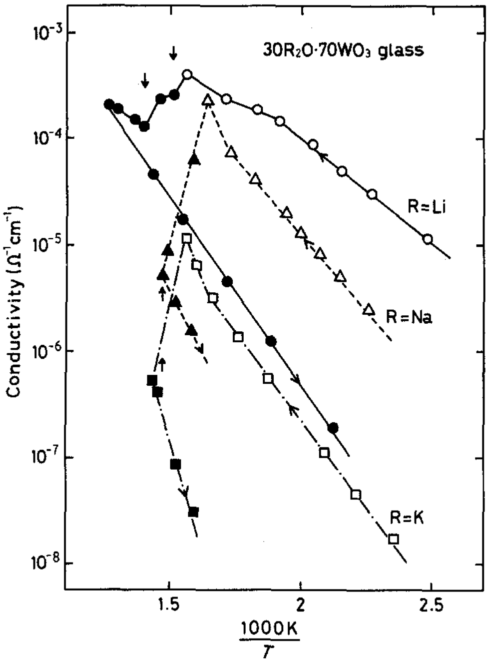

Figure 4 The temperature dependence of conductivity for the $30R_2O{\cdot}70WO_3$ (R = Li, Na, K) glasses.

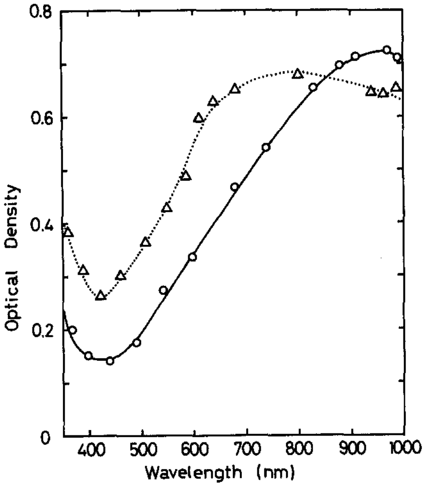

Figure 5 Absorption spectra of coloured $30Li_2O{\cdot}70WO_3$ glass before (○) and after (△) reversing the polarity.

cate values of T_c determined from DTA for each sample, and the open marks are for glasses and the solid ones for crystallized samples. The conductivities of the glass decrease at temperatures near T_c for each sample, indicating that the glass is more conductive than the crystallized sample. The conductivity for the glass samples decreased with increase in the radius of the R^+ ion. The activation energy for conduction was increased from 0.39 to 0.65 eV in the order $R = Li < Na < K$. The glass $30Li_2O{\cdot}70WO_3$ exhibits a conductivity of $10^{-4}\,\Omega^{-1}\,cm^{-1}$ at 500 K, which is relatively large among lithium-ion conducting glasses [14].

3.4. Electrochromism

The electrochromic properties of the glasses xR_2O–$(100 - x)WO_3$ (R = Li, Na; $x = 30$, 35) were examined. The electro-colouration occurred in air for every glass flake when a d.c. voltage of 100 V was applied, but no colouration was observed in dry N_2 atmosphere. The electric field for colouration in this work ($2 \times 10^3\,V\,cm^{-1}$) is lower than that ($= 10^4\,V\,cm^{-1}$) for a WO_3 amorphous film [15] by one order of magnitude. Colour-deepening was observed when the polarity was reversed.

Fig. 5 shows the absorption spectra of the coloured $30Li_2O{\cdot}70WO_3$ glass before (solid curve) and after (dotted curve) reversing the polarity. In both spectra a broad absorption band is observed at the near infra-red region, similar to the case of coloured WO_3 films. In addition, the absorption maximum is shifted towards shorter wavelengths by reversing the polarity; the shift is associated with the colour-deepening in reverse of the polarity. It has been concluded that the electro-colouration of R_2O–WO_3 glasses is due to the double injection of electrons from the cathode and protons from H_2O in air, resulting in formation of H_xWO_3 in the glass matrix. The spectral change has been explained by the increase in x values of H_xWO_3 when reversing the polarity; the x value is increased with incorporation of more protons into the glass matrix by the space charge formed near the anode [6].

Table II lists the d.c. conductance of the glass $30Li_2O{\cdot}70WO_3$. The conductance of the uncoloured glass is slightly larger in air than in dry N_2 atmosphere. This may be due to the additional conduction by protons incorporated into glass from H_2O in the air. The conductance of the coloured glass is larger than that of the uncoloured glass. This result supports the colouring mechanism that the double injection of protons and electrons leads to the formation of highly conductive H_xWO_3 in the glass matrix.

TABLE II d.c. conductance of the $30Li_2O{\cdot}70WO_3$ glass

	Conductance (Ω^{-1})	
	in air	in dry N_2
Uncoloured	8.3×10^{-9}	2.7×10^{-10}
Coloured	1.4×10^{-8}	7.7×10^{-9}

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