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Electro-conducting glass-ceramics produced by ion-exchange and reduction treatments

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The crystallization characteristics of some bismuth-containing soda–lime–silica glasses have been studied. The addition of bismuth reduces the glass transition temperature as well as the crystallization temperatures of these glasses. Electrically conducting layers have been induced in such glass-ceramics by subjecting them to a $Na^+ \rightleftharpoons Ag^+$ ion-exchange reaction followed by a reduction treatment in hydrogen. Resistances of the surfaces vary from 0.08 Ω/square to 14.76 Ω/square depending on the glass composition as well as the reduction parameters. Induced surface conductance tends to rise with the increase of volume of the crystalline phase in the parent glass. The TCR values range between 400 and 2300 p.p.m. K^{-1}. The thicknesses of these layers are about 130 μm. The high surface conductivity arises from the percolation of the silver metallic phase in the glass–crystal boundary region. The glass–crystal interface is believed to act as heterogeneous nucleation sites.

1. Introduction

It was reported earlier that electrically conducting layers can be induced in some alkali-containing silicate glasses by subjecting them to a $Na^+ \rightleftharpoons Ag^+$ ion-exchange reaction followed by a reduction treatment in hydrogen [1]. Detailed electron micrographic investigations have shown that this conductance arises due to the presence of silver and bismuth particles having dimensions in the range of 50 to 2000 Å in the surface layers of the glasses. Bismuth granules are formed by the reduction of Bi_2O_3 present in the parent glass composition, whereas silver granules owe their origin to the silver ions injected into the surface layer of the glass by the ion-exchange mechanism. One of the important steps involved in the above technique is to grind the virgin glass surface in silicon carbide grit of particle sizes between 50 and 125 μm before subjecting it to the ion-exchange treatment [1]. The tentative explanation is that the imperfections introduced in the surface by the above mentioned grinding media increase the rate of nucleation of silver particles which can then grow sufficiently to ensure the percolation of the metallic phase through the glass matrix. For any potential application of conducting glass surfaces the latter should have a high degree of surface finish.

In order to obviate the surface roughness problem the above technique was tried on some glass-ceramic systems. The rationale behind this approach was that the glass–crystal interfaces could act as heterogeneous nucleation sites for silver particles thereby enhancing the rate of formation of their nuclei. In the latter case the need to grind the sample surface to a coarse finish would be eliminated completely. In this paper, we describe the results obtained on some ceramized glasses in the system Na_2O–CaO–Bi_2O_3–SiO_2 which developed high surface conductance after a $Na^+ \rightleftharpoons Ag^+$ ion-exchange treatment followed by reduction in hydrogen.

TABLE I Compositions of glasses investigated

Glass no.	Composition (mol%)			
	Na_2O	CaO	Bi_2O_3	SiO_2
1	25	17	–	58
2	25	15	1	59
3	25	17	3	55
4	25	13	7	55
5	25	10	10	55

2. Experimental

The compositions of the glasses investigated are given in Table I. The glasses were prepared from reagent grade chemicals. Na_2O and CaO were introduced as their respective carbonates and the rest of the components as their oxides. Glasses were melted in alumina crucibles in an electrically heated furnace over a temperature range 1200 to 1400° C. Glass plates were cast by pouring glass melts onto an aluminium mould. These were subsequently annealed.

Differential thermal analysis of all the glass compositions was carried out in a MOM Hungary, Derivatograph to determine their crystallization temperatures. The glasses were ground and the glass particles of sizes between -14 and $+20$ mesh were sieved out and mixed with Al_2O_3 powder in the ratio 70:30 by volume [2]. Special ceramic crucibles were used to mount the sample as well as the inert material (recrystallized alumina in our case). Platinum–platinum 10% rhodium thermocouples were used to measure the temperature difference (ΔT) between the samples. This was recorded by a galvanometer, its light spot drawing the differential thermo-analytical curve on a photographic chart. A heating rate of 7° C min^{-1} was used for all the specimens.

For ceramization of glasses in general, it is the usual practice to subject them to a two-stage heat treatment, that is to initially heat the specimen to a temperature corresponding to optimum nucleation followed by heating to a temperature for maximum crystallization [3]. The latter can be found from the exothermic peak in the DTA curve. However, the measurement of nucleation temperature from thermal analysis is quite uncertain. To a first approximation the nucleation temperature can be taken to lie between the glass transition point and a temperature 50° C higher than this [3]. In the present investigation a small diffuse endothermic peak was obtained for all compositions (see Section 3 below). This evidently represents the glass transition reaction. The average temperature corresponding to this diffuse peak was used for the first-stage heat treatment, of duration 1 h, that each specimen was subjected to for ceramization purposes [2]. The sample was then heated at the rate of 4° C min^{-1} until the crystallization temperature was reached. It was held at this temperature for a period of 3 h.

The crystalline phases were identified by taking powder patterns of the glass-ceramic samples in a General Radio XRD 6 diffractometer using CuKα line.

The per cent volume crystallization was determined from the optical micrographs of ceramized glass specimens using the point counting method [4].

The surfaces of the ceramized samples were successively ground in silicon carbide grit of mesh sizes 120, 240 and 600. They were then polished with 0.05 μm Al_2O_3 powder to get an optical finish. The polished samples were then subjected to a $Na^+ \rightleftharpoons Ag^+$ ion-exchange treatment in a molten bath of $AgNO_3$ contained in a pyrex crucible which fitted into a stainless steel cup. The interdiffusion treatments were carried out at around 300° C for a period of 6 h. After the diffusion run the ion-exchanged samples were dipped in distilled water for a period of 24 h in order to dissolve any silver nitrate adhering to their surface. These samples were then reduced in a chamber at temperatures ranging from 250 to 350° C by passing hydrogen gas over them at a rate of 100 cm^3 min^{-1}.

For surface resistance measurements all but one of the ion-exchanged and reduced surfaces of a specimen were ground off. Four strips of silver dag (supplied by N.P.L. Delhi) with about 1 mm gap between the successive strips of silver dag were painted on the treated surface. Copper wires were cemented on to the four electrodes by silver paste. The electrical circuit used consisted of the sample in series with a voltage source and a standard resistance. Two outer electrodes on the sample surface formed the current terminals and the two inner ones were used to measure the voltage across the conducting surface. The current through the sample surface was computed from the voltage developed across the standard resistance. The voltage–current curves in all the specimen surfaces were found to be linear over a decade of voltage, and hence the resistances were obtained from the slopes of their $V–I$

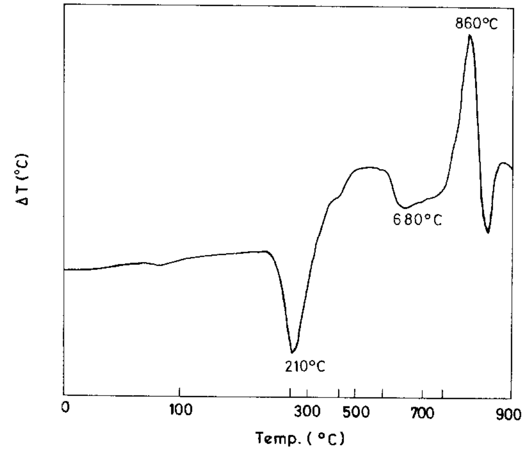

Figure 1 DTA curve for glass 1

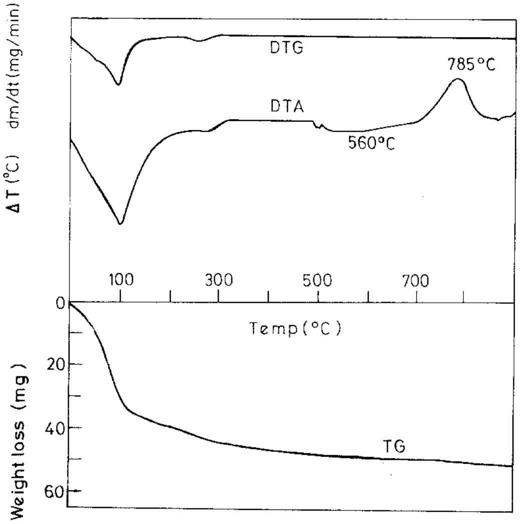

Figure 2 DTA, TG and DTG curves for glass 2.

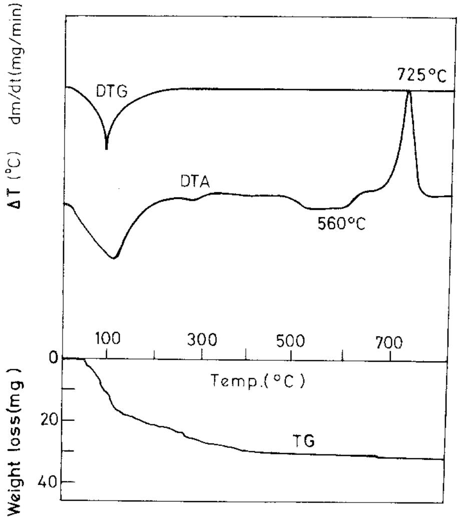

Figure 3 DTA, TG and DTG curves for glass 3.

characteristics. Surface resistances were calculated [1] from these values by using the relation

$$R = \rho S/W \qquad (1)$$

where, R is the specimen resistance in Ω,

ρ is the surface resistance in Ω/square

S is the separation between the central electrodes in mm,

and W is the width of the electrodes in mm.

The temperature coefficient of resistance (TCR) of the conducting surfaces were measured by the same method as described earlier [1].

The thicknesses of the conducting layers in some of the glass–ceramic specimens were estimated by measuring the surface resistances after polishing off successive layers. The polishing was done by Al_2O_3 powder of 0.05 μm size and the thickness of layers removed were measured by a micrometer with a least count of 1 μm.

3. Results and discussion

Figs. 1 to 5 give the DTA curves for glasses 1 to 5 respectively. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for compositions 2, 3 and 4 are also shown in the respective figures. The endothermic peak obtained in all these compositions around 100° C is ascribed to the loss of absorbed water. The endothermic peak obtained at 210° C for glass 1 is unexpected and no satisfactory explanation is available. The endothermic and exothermic peaks obtained at higher temperatures are attributed to the glass transition (T_g) and the growth temperatures respectively. These values are summarized in Table II. It is evident from this table that the effect of adding Bi_2O_3 to the base composition is to lower

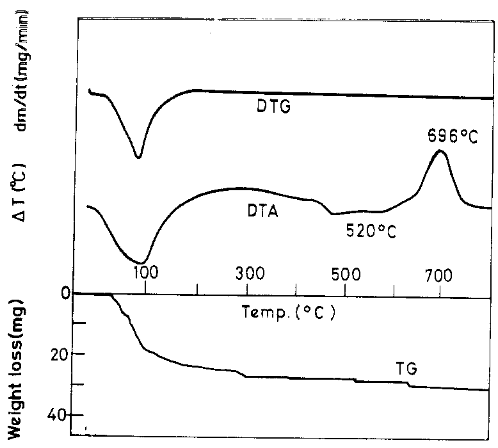

Figure 4 DTA, TG and DTG curves for glass 4.

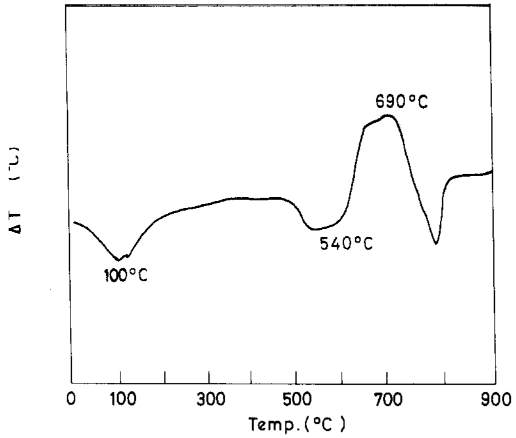

Figure 5 DTA curve for glass 5.

TABLE II Average endothermic peak and growth temperatures for different glasses as obtained from DTA study

Glass no.	Average endothermic peak temperature (° C)	Growth temperature (° C)
1	680	860
2	560	785
3	560	725
4	520	696
5	540	690

the glass transition temperature. The growth temperature also decreases with the addition of bismuth. This is to be expected since the viscosity corresponding to a maximum crystal growth rate should occur at lower temperatures for glasses having smaller T_g values.

In Table III the results of the X-ray diffraction studies on the ceramized samples obtained from the different glasses are summarized in the form of the various crystalline phases observed in each of them after the two-stage heat treatment mentioned earlier. For glasses 3 and 4, the phases listed in the table are the most likely ones. The uncertainties are due to the absence of some of the characteristic lines from the observed diffraction pattern. The range of per cent volume crystallization obtained in each case is also shown in the table. A typical optical micrograph obtained in the case of glass 5 is shown in Fig. 6. The crystal dimensions observed in all the glass-ceramic compositions are ~2 μm. The effect of a two-stage heat treatment as opposed to heating the specimen at the crystallization temperature only is demonstrated by the results on glass 5 and shown in Table III. It is evident that a higher volume fraction can be crystallized in the glass by the two-step heat treatment described in this study. This effect is believed to be related to the availability

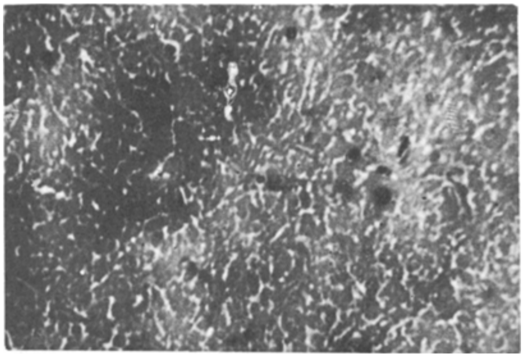

Figure 6 Optical micrograph of glass 5 after a heat treatment of 539° C for 1 h followed by 710° C for 3 h (× 258).

TABLE III Crystalline phases observed in different ceramized glasses

Glass no.	Heat treatment	Crystalline phases present	Range of % volume crystallization
1	680° C for 1 h and 866° C for 3 h	$Na_2O \cdot 2CaO \cdot 3SiO_2$	60–65
2	560° C for 1 h and 785° C for 3 h	$Na_2O \cdot 2CaO \cdot 3SiO_2$; $2Na_2O \cdot CaO \cdot 3SiO_2$ and $Na_2O \cdot CaO \cdot SiO_2$	60–65
3	560° C for 1 h and 785° C for 3 h	Tridymite; $CaO \cdot SiO_2$ and $Na_2O \cdot CaO \cdot SiO_2$	35–40
4	524° C for 1 h and 689° C for 3 h	$Na_2O \cdot SiO_2$; $CaO \cdot SiO_2$ and $Na_2O \cdot 2CaO \cdot 3SiO_2$	45–50
5	539° C for 1 h and 710° C for 3 h	$Na_2O \cdot SiO_2$ and $3CaO \cdot 2SiO_2$	50–55
5	700° C for 4 h	$Na_2O \cdot SiO_2$ and $3CaO \cdot 2SiO_2$	22–26

TABLE IV Surface resistance of glass 5 after different ceramization treatments

Ceramization treatment	Range of % volume crystallization	Surface resistance (room temperature) (Ω/square)	TCR (p.p.m. K^{-1})
500° C for 4 h	not measured	3.03	560
600° C for 4 h	25–30	0.53	1241
650° C for 4 h	30–35	0.71	1149
*539° C for 1 h and 710° C for 3 h	50–55	0.08	1494

*Reduction time for this sample was 1 h at 320° C.
Ion-exchange: 310° C for 6 h.
Reduction : 320° C for 2 h.

TABLE V Summary of surface resistance data for the ion-exchanged and reduced glass-ceramics

Glass no.	Treatment			Surface resistance (room temperature) (Ω/square)	TCR (p.p.m. K^{-1})
	Ceramization	Ion–exchange	Reduction		
1	680° C for 1 h and 866° C for 3 h	310° C for 6 h	320° C for 1 h	13.41	1893
			250° C for 0.5 h	14.76	879
2	560° C for 1 h and 785° C for 3 h	310° C for 6 h	320° C for 2 h	0.73	1453
			320° C for 1 h	0.87	2170
			250° C for 0.5 h	3.46	2268
3	560° C for 1 h and 785° C for 3 h	310° C for 6 h	320° C for 2 h	0.08	1860
			320° C for 1 h	0.09	2309
			250° C for 0.5 h	1.24	417
4	524° C for 1 h and 689° C for 3 h	310° C for 6 h	320° C for 1 h	0.22	1302
			250° C for 0.5 h	1.25	1822
5	539° C for 1 h and 710° C for 3 h	310° C for 6 h	320° C for 1 h	0.08	1494
			250° C for 0.5 h	0.42	994

TABLE VI Variation of surface resistance with thickness removed for different glass-ceramic samples

Glass-ceramic no.	Thickness removed (μm)	Surface resistance (room temperature) (Ω/square)
3	0.0	0.08
	10.0	0.13
	64.0	0.47
	94.0	1.99
	119.0	6.27
	135.0	2.8×10^4
	159.0	4.4×10^5
5	0.0	0.08
	9.0	0.17
	31.0	0.19
	61.0	1.10
	90.0	2.15
	119.0	11.05
	139.0	9.1×10^5

of a larger number of nuclei in the glass subjected to a pre-treatment at T_g as compared to the one which is heated directly to the crystallization temperature.

In Table IV the surface resistance data for the glass-ceramic obtained from composition 5 after different heat treatments are shown. The ion-exchange and reduction treatments were kept constant for all the samples. It is evident from this table that there is a trend for the conductivity induced in the surface layer to increase as the crystalline phase volume becomes larger. It is believed that in the latter cases the glass–crystal interface area increases thereby enhancing the number of heterogeneous nucleation sites for silver particles. Thus, it becomes easier for the metal phase to percolate through the insulating medium and generate higher surface conductivity values. A detailed electron micrographic study of the present glass–crystal–metal system will be able to verify this model.

The surface resistance values obtained in the different glass-ceramic compositions are given in Table V. It is evident that the glass-ceramic composition no. 1 which does not contain any bismuth develops higher surface resistance values than the others after the ion-exchange and reduction treatment. This difference in behaviour is believed to arise from the fact that some of the metallic bismuth particles also take part in the formation of a continuous conducting chain in the surface layers of the samples. It is also seen from these data that by decreasing the reduction time and temperature higher resistivity values can be induced in the specimen surfaces. This result is a direct consequence of the mechanism of formation of the silver particles which are precipitated by a nucleation and growth process [5].

Finally, we show in Table VI the variation of surface conductance as a function of the thickness removed for the specimens 3 and 5 respectively. These data show that the thickness of the conducting layers induced in bismuth-containing glass-ceramics is of the order of $130\,\mu$m.

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