Some aspects of glass–ceramic superconductors

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Abstract. In this review article we have discussed, in brief, the general procedure for making glass-ceramic superconductors and some of their physical properties. All these glasses which become superconductors after properly annealing at higher temperatures are, in general, transition metal oxides (TMO) with copper ions. So the usual theoretical models of polaronic hopping conduction mechanisms are valid for explaining the semiconducting behaviour of these oxide glasses. Some of the transport properties of the glass-ceramic (GC) phases, viscosity of the glassy state, wire making feasibility etc have also been discussed in short.

Keywords. Glass-ceramics; superconductors.

1. Introduction

The semiconducting transition metal oxide (TMO) glasses, in general, have been vastly studied during the last couple of decades (Mott and Davis 1979). This is because of their probable technological applications (Hirashima *et al* 1987; Sakuri and Yamaki 1985; Nakamura and Ichinose 1987). Above all, these glasses with various compositions are relatively easy to prepare compared to other non-oxide glasses. Moreover, the cost of sample preparation is also low and for these reasons a small research group having moderate research facilities can start working on different aspects of TMO glasses. But the investigations of the structural as well as the physical properties of such glassy systems provide wealth of new informations about the basic mechanism of semiconducting behaviour in these and similar other glasses. Magnetic, optical, dielectric, and thermal properties are also equally important for all these glasses elucidating many interesting features (Mott and Davis 1979).

However, it had not been guessed earlier (before 1987) that some of the TMO glasses might even show high temperature superconducting behaviour in their crystalline (called glass-ceramic or GC) phases obtained by annealing the glass samples at higher temperatures (below the respective melting points).

After the discovery of high T_c superconductors in the Y–(Ba, Sr)–Cu–O (Bednorz and Muller 1986), Bi–Sr–Ca–Cu–O (Michel *et al* 1987; Maeda *et al* 1988) etc systems (where Cu is the transition metal atom), special importance has also been attributed to make these high T_c materials from the corresponding glassy phases. It was first shown by Komatsu *et al* (1987) that the glass made by melting Y–Ba–Cu–O oxide becomes superconductor in the corresponding GC phase. This is definitely an important discovery. This is because, the superconductors obtained by this GC route would be highly homogeneous, their grain sizes could be controlled, wires/tapes could be drawn from the glasses which could then be converted in the corresponding high T_c phases and necessary technology could be developed for the proper utilization of these wires/tapes. Mixing of the components occur at molecular level in the melts. Almost fully dense, uniform, pore-free materials can be fabricated from the glassy phase leading to high critical density of the prepared superconductors. Heat treatments of

the quenched glasses can lead to the metastable crystalline phases having unusual properties which cannot be synthesized by the usual normal means. However, there are also certain limitations of the melt quenching approach. The components should not be volatile at about one to two hundred degrees above the melting temperature. The melt must not phase separate and not react with the container used for the melt. Recently, containerless melting technique is being used to make pure glassy phases.

Another part of research with these precursor glasses is to understand their physical properties and to know why these glasses become superconductors in their glass-ceramic phases while many similar TMO glasses do not show superconductivity in their respective GC phases. Therefore, proper understanding of the behaviour of these glasses is also necessary. However, this second part of research is in the rudimentary stage and we will not discuss this part in the present article.

2. Preparation of the glassy phase

The starting materials (carbonates and metal oxides), in general, are well mixed in appropriate proportions and then melted in Pt or crystalline Al_2O_3 crucibles between 1000 and 1300°C for a few hours. Before melting, pre-heating around 500°C is essential.

Figure 1. X-ray diffraction pattern of a typical Pb-doped $\text{Bi}_{4-n}\text{Pb}_n\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ ($n = 0.1, 0.5$ and 1.0) glass.

The melt is rapidly quenched by a twin roller or by pressing between two metal plates resulting in black opaque glass with metallic lustre. Now a days, containerless glass making process has also been well developed to avoid contamination effect. X-ray diffraction patterns of some typical glasses, viz. $\text{Bi}_{4-x}\text{Pb}_x\text{Sr}_3\text{Ca}_3\text{Cu}_y\text{O}_x$ ($x = 0.1, 0.5, 1.0$), are shown in figure 1 indicating an amorphous character with broad peaks. Sometimes low intensity diffraction due to some unreacted CaO etc might appear in the diffraction pattern. Furthermore, phase separation is also observed in such glasses (Chaudhuri and Som 1992; Mollah *et al* 1994). The appearance of crystalline superconducting phases with increase of annealing time is shown in figure 2. The following procedure is generally followed to make good quality glassy precursors for high T_c superconductors: (i) Mixing of the raw oxide (if carbonates are used they should be calcined around 900°C for 8–10 h to decompose carbonates) materials for an hour or more with pure acetone or alcohol, (ii) the mixture is pre-heated at 500°C for about 5 h, (iii) the preheated oxide is melted between 1000 and 1300°C for 1 to 2 h, (iv) the melt is quenched rapidly between two copper blocks to obtain the glassy precursors for high T_c superconductors and (v) the glasses thus obtained are properly heat-treated under appropriate conditions to get high T_c superconducting oxides.

We are discussing below some of the most common glasses and the corresponding superconducting glass-ceramics.

3. Bi–Sr–Ca–Cu–O system

Bi-based glasses have been widely used for the preparation of high T_c superconducting materials. Several glasses with different concentrations of Bi or the transition metal

Figure 2. Change of X-ray diffraction patterns depending on annealing time for a typical $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ glass.

ions have been prepared (Tohge *et al* 1989) and their superconducting properties studied. The glass forming region of a typical Bi–Sr–Ca–Cu–O system is shown in the phase diagram in figures 3a, b. Many other glass compositions of this group follow similar phase diagram. A wide glass forming region as shown by the broken line in figure 3 exists in this system. It is highly interesting to note that no glass former oxide is present in this system and the glass transition temperature (T_g) depends mainly on the Bi_2O_3 concentration in the glass as shown in figure 4 for a typical $\text{Bi}_x\text{SrCaCu}_2\text{O}_x$. The DSC scan of a Bi–Sr–Ca–Cu–O glass showing T_g and crystallization temperature T_x , is drawn in figure 5 (Komatsu *et al* 1988). Influence of calcium content on T_x and T_g for some Bi-based glass is shown in figure 6. Zheng *et al* (1989) reported that the values of T_g and T_x decrease with increase in CuO or Bi_2O_3 concentration and increase with increasing the alkaline earth (CaO and SrO)

Figure 3. A. Phase diagram of a typical $\text{BiO}_{1.5}(\text{SrO} \cdot \text{CaO})_{0.5}\text{CuO}$, $\text{SrO}/\text{CaO} = 1$ composition. (a) $\text{BiSrCaCu}_2\text{O}$ and (b) $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (Tohge *et al* 1989). B. Isotherms of T_g in $\text{Bi}_{1.5}(\text{SrO}, \text{CaO})_{0.5}\text{CuO}$, $\text{SrO}/\text{CaO} = 1$. (a) $\text{BiSrCaCu}_2\text{O}$, and (b) $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_{30}$ (Tohge *et al* 1989). (●, Glass, ○, glass + CaO; ●, crystal and ■, decomposition).

Figure 4. Effect of Bi content on T_g and T_x for the $\text{Bi}_x\text{SrCaCu}_2\text{O}_y$ glassy precursor (Bansal and Guire 1989).

Figure 5. DSC scan of $\text{Bi}_{1.5}\text{SrCaCu}_2\text{O}_y$ glass in inert atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ (Komatsu *et al* 1989).

Figure 6. Influence of calcium content on T_x and T_g for the $\text{Bi}_{1.2}\text{SrCa}_z\text{Cu}_2\text{O}_y$ glasses (Komatsu *et al* 1989).

content. The difference $T_x - T_g$ called thermal stability factor is large for glasses with large Bi_2O_3 content. Therefore, Bi_2O_3 plays an important role in glass formation and also in thermal stability which is required for making glass fibre or glass tape.

4. Bi-Pb-Sr-Ca-Cu-O system

This is another very important glassy precursor for high T_c superconductors with superconducting transition temperature T_c more than 115 K with $T_{c0} = 100$ to 110 K. The values of T_g and T_x (figure 7 for a typical Pb doped glass) increase slowly with increase of Bi_2O_3 content and reach a maximum for $x = 3.0$ (figure 8) and decrease with further increase of bismuth content.

5. Bi-Sr-Ca-Li-Cu-O system

This is another glassy system almost similar in its behaviour with that of the Bi-Pb-Sr-Ca-Cu-O type system discussed above. The main functions of Li doping are to decrease the glass melting temperature as well as glass annealing temperature required for making them superconductors. The superconducting transition temperature is also increased in such systems by about 5–10 K.

6. Y-Ba-Cu-O system

It is very difficult to make glass with these oxides (Y_2O_3 , BaCO_3 and CuO) requiring high melting temperature (1300–1400°C) and high quenching rate. However, with little B_2O_3 (1–5 wt%) good quality glass of such system can be prepared. In such a case, however, the superconducting transition temperature is reduced below 80 K or so. However, there is some report that rapid quenching of small droplets of $\text{YBa}_2\text{Cu}_3\text{O}_x$ melt on steel plates resulted (Koo *et al* 1889) in an amorphous material which showed $T_g = 330^\circ\text{C}$ and $T_x = 780^\circ\text{C}$.

Figure 7. DSC scan of $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ glass recorded at a heating rate of $40^\circ/\text{min}$ in argon (Bansal 1990).

Figure 8. Dependence of T_g and T_x of $\text{Bi}_x\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ glasses on their bismuth content (Komatsu *et al* 1990).

7. Tl–Ba–Ca–Cu–O system

Report on the preparation of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ glasses (Nassau *et al* 1989) is available in the literature. But loss of Tl_2O_3 during melting makes it difficult to get superconducting glass-ceramic phases.

8. Ba–K(Li, Na)–Bi–O type non copper oxide system

This is a new glass system showing very interesting semiconductor–metal–semiconductor like transition even in the glassy phase (Bera *et al* 1994; Mollah *et al* 1994).

9. Ba–Pb–Bi–O-type non-copper oxide system

This is also a new and very interesting glassy precursor for high T_c superconductors. These glasses can be prepared with different concentrations of Pb showing non-linear physical properties (Sadhukhan *et al* 1994). Recently, many other glasses like V–Bi–St–Ti–O, V–Bi–Ba–Ti–O, V–Bi–Cr–Sr–Ca–O etc have also been discovered showing some superconducting behaviour (around 20 K or below) in their glassy phases. However, elaborate investigations of such glasses have not yet been made. It is apparent that in the near future more and more glassy precursors for high T_c

superconductors with many interesting physical and structural properties would be discovered. But the main problems related to the understanding of the mechanism of such superconducting transitions in these oxide glasses and the peculiar behaviour exhibited by some of these glassy precursors for high T_c superconductors like metal-insulator behaviour (Bera *et al* 1994), increase of ac conductivity and its superlinear behaviour in the low temperature region (Mollah *et al* 1994) etc are still not clear.

10. Glass viscosity

Temperature dependence of glass viscosity is very important for a successful drawing of the glass fibres. Generally, beam-bending technique has been used for the determination of viscosity in the glass transition range of the glasses like $\text{Bi}_x\text{SrCaCu}_2\text{O}_y$ ($x = 1.5$ to 2.7) (Tatsumisago *et al* 1990). The temperature dependence of viscosity follows an Arrhenius behaviour with an activation energy, E_0 of 800 to 9980 kJ/mol. Glasses with lower Bi content showed lower E_0 . Such a large value of E_0 indicates that from the Bi-Sr-Ca-Cu-O system glass fibres can be drawn only at around the glass softening point rather than from the pure melt because of high fluidity like water. Since the range $T_x - T_g$ is very narrow for these glasses, crystallization would be the main problem for drawing fibres at around the glass softening point. However, an increase in the Bi content in the glass lowers the value of E_0 and hence facilitate drawing glass fibres. Unfortunately, addition of Bi to a large extent lowers the value of T_c . So an appropriate choice of the composition of glasses is necessary for the successful drawing of the glass fibres and then making them superconducting by properly annealing at a higher temperature. Temperature dependence of viscosity in a very narrow temperature range is shown in figure 9 where the shaded region shows the allowable fibre drawing range. The temperature dependence of viscosity of $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_y$ glass is shown in figure 10. The temperature dependence of the melt viscosity has been measured for the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ glass. The melt viscosity

Figure 9. Temperature dependence of viscosity of the melt quenched $\text{Bi}_{1.5}\text{SrCaCu}_2\text{O}_y$ glass. The allowable drawing range is shown as in the shade region (Onishi *et al* 1989).

Figure 10. Temperature dependence of viscosity for the melt and glass of $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_y$ composition (Zheng *et al* 1991a, b).

varies from 45 to 100 Poise in the temperature range of 885 to 985°C (LeBeau *et al* 1989).

11. Crystallization process from glassy phase

Crystallization process or crystallization kinetics is important for a successful drawing of the glass fibres. Non-isothermal (Tatsumisago *et al* 1989a, b; Tohge *et al* 1989; Bansal 1990) or isothermal (Zheng and Mackenzie 1991) differential scanning has been used to study the kinetics of crystallization in the Bi-based oxide glasses leading to superconductivity in their ceramic phases. The isothermal crystallization of a glass can be expressed by the Avrami equation (Avrami 1939) viz.

$$x = 1 - \exp[-(kT)^n],$$

where x is the volume fraction crystallized after time t , n the Avrami parameter which depends on the crystal growth morphology, and k the crystallization rate constant which can be expressed as the activation energy, R the gas constant and T the isothermal absolute temperature. The values of E_a for crystallization of glasses of various compositions are found to vary from 290 to 489 kJ/mol. The value of the Avrami exponent for crystallization of the $\text{Bi}_4\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$ glass was found (Zheng and Mackenzie 1991) to be close to 3 suggesting a three dimensional crystal growth at a constant number of nucleation state.

12. Crystal phases obtained under heat treatment of glasses

Time, temperature and atmosphere have great influence on the crystal formation from the glass phase under heat treatment studied by several researchers. Some results on the Bi-based glasses are discussed below. When a glass sample is heat-treated, it takes quite a long time to become crystalline, and this crystallization is not a continuous process leading to the final single superconducting phase. Several factors are involved

to control the different phase formations. Composition, phase separation in the glass phase, annealing time, temperature, heating rate, cooling rate etc are important parameters to get a single superconducting crystalline phase from a typical glass phase under investigation.

Several authors (Tohge *et al* 1989; Tatsumisago *et al* 1990) have studied time (T)–temperature (T)–transformation (T) diagram of the Bi–Sr–Ca–Cu–O system. A typical T – T – T diagram for the $\text{BiSrCaCu}_2\text{O}_x$ glass is shown in figure 11. Each symbol is a mixture of crystalline phase. Figure 12 shows the T – T – T diagrams for the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ glass composition. The transformation behaviour of the melt cast material of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ composition into the 2212 superconducting phase is different in air and nitrogen atmospheres. Due to a large fraction of copper ions present as Cu(I) in these glasses, the crystallization mechanism is affected by the

Figure 11. T – T – T diagram for $\text{BiSrCaCu}_2\text{O}_x$ glass (●, glass; ○, 10 K phase; ■, 80 K phase). (Tohge *et al* 1989).

Figure 12. T – T – T diagram for $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ glass. ▲: glass + Cu_2O + (CaO):80 K phase + CaO + Cu_2O :80 K phase + CaO + CuO:80 K phase + CaO + Cu_2O + CuO:80 K phase + CaO, ○:80 K phase (Komatsu *et al* 1989).

oxygen partial pressure. The amount of Cu(I) ions in these glasses depends on the cooling rate and thus their crystallization behaviour is affected by condition of glass making. The glass preparation conditions have an effect (Zheng *et al* 1991a, b) on the ratio Cu(I)/Cu (total) in the glass which in turn affects the glass structure and its crystallization mechanism. The glasses melted at lower temperature have lower values of this ratio and yield larger crystallites. The value of this ratio also changes with increase/decrease of melting time. So it is always advisable to melt all glass compositions of a particular base glass at fixed temperature, if possible, and quench them for making superconducting samples.

The initial crystallization phase precipitating out of a glass depends on the composition and also on the ratio $\eta = \text{Cu(I)}/\text{Cu (total)}$. The initial crystallization phase from the $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_y$ glass is 2201 phase. The glasses with low η value produces large 2201 crystals and *vice versa*. It might be possible to control crystallization by controlling the atmosphere and the ratio η since crystal growth needs oxygen and the size of the crystal depends on ratio η . Continuous glass fibre drawing is possible (Zheng *et al* 1991a, b) by using higher values of η . In this connection we would like to mention that all these glasses with Cu ions behave like transition metal oxide glasses and are semiconducting in nature as mentioned earlier (Som *et al* 1992). The semiconductivity arises due to the presence of mixed valence states of Cu. Elaborate investigations of the semiconducting properties of the Bi-based Li and Pb doped glasses have been carried out in our laboratory (Mollah *et al* 1993, 1994).

A single phase 110 K superconductor has been prepared (Shi *et al* 1988, 1989) by crystallization of $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_y$ glasses by annealing at 870°C in air. The starting composition as well as annealing temperature are important for obtaining a 110 K phase. The 80 K and the Ca_2CuO_3 phases first coprecipitate from the glass. The 110 K phase nucleates and grows at the interface between these two phases which is controlled by interface diffusion of calcium and copper.

Like undoped Bi–Sr–Ca–Cu–O system Pb doped system has also been elaborately studied (Mollah *et al* 1993, 1994). Thorough investigations of $T-T-T$ diagrams for the $\text{Ba}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ and $\text{Ba}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ glasses were conducted by Tatsumisago *et al* (1990). The Ca_2PbO_4 phase is formed in the Bi–Pb–Sr–Ca–Cu–O glass on short term annealing at 855°C. However, on long term annealing the Ca_2PbO_4 phase disappears and 110 K phase is formed. It therefore appears that Ca_2PbO_4 plays an important role on the formation of the high T_c phase in the Pb doped glassy precursors for high T_c superconductors.

13. Dependence of T_c and J_c on the processing conditions

It has already been mentioned that if the glasses of our present interest are annealed at a higher temperature (above T_g) they become crystalline and ultimately superconducting depending on various factors like glass melting temperature, quenching rate, atmosphere, and also on the cooling rate. Therefore, it is not very easy to satisfy all the conditions at a time for achieving high T_c and high J_c values for a particular glass concentration. Furthermore, superconducting properties as well as J_c values also depend on the glass compositions. That is, if all the processing conditions are similarly maintained for two different compositions of the Bi–Sr–Ca–Cu–O glasses, for example, the T_c and J_c values might not be the same. It is further mentioned that

the glass melting temperature, superconducting transition temperature etc also depend on the additives like Pb, K, Li, iodine etc. Some typical results on the dependence of T_c and J_c on some of the above mentioned factors are discussed below in brief.

Figure 13 shows the variation of T_{c0} (zero resistance temperature) of $\text{Bi}_x\text{SrCaCu}_2\text{O}_y$ glasses annealed at 840°C for 45 h in air and then furnace cooled. There are some optimum values of x for which T_{c0} is maximum. However, the glasses $\text{Bi}_{1-2}\text{SrCa}_z\text{Cu}_2\text{O}_y$ annealed under the same condition show variation of T_{c0} with z (calcium content) as shown in figure 14. Here T_{c0} does not depend very much on the Ca content in the glass. The variation of electrical resistivity of a typical $\text{Bi}_{1-2}\text{SrCaCu}_2\text{O}_y$ glass sample is shown in figure 15 where the sample is annealed at various temperatures. T_c increases with increase of annealing temperature, but for very high temperature annealing T_c decreases appreciably.

The effect of annealing time on T_c and J_c for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (or 2212) glass sample annealed at 820°C in air is shown in figures 16 and 17. Weak links at the grain boundaries are responsible for low values of J_c in the glass-ceramic superconductors.

Figure 13. Superconducting transition temperatures, $T_c(R=0)$, of $\text{Bi}_x\text{SrCaCu}_2\text{O}_y$ glasses annealed at 820°C for 40 h in air and furnace cooled (Komatsu *et al* 1989).

Figure 14. Superconducting transition temperatures, $T_c(R=0)$, of $\text{Bi}_{1-2}\text{SrCa}_z\text{Cu}_2\text{O}_y$ glasses annealed at 820°C for 40 h in air furnace cooled (Komatsu *et al* 1989).

Figure 15. Variation of resistivity of a typical $\text{Bi}_{1.2}\text{SrCaCu}_2\text{O}_y$ glass with annealing temperature (T_{c0} , zero resistance).

Figure 16. Effect of annealing temperature on critical current density (J_c) and T_{c0} .

Figure 17. Values of critical temperature T_c and critical current density J_c (77 K, zero magnetic field) of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ glass samples annealed at 820°C in air for various times and furnace cooled (Komatsu *et al* 1990).

Recently, efforts are being made to reduce the density of weak links at the grain boundaries. Air, oxygen or vacuum annealed samples have different T_c values (Gan and Li 1991). Annealing in O_2 greatly enhances T_c of $Bi_4Sr_3Ca_3Cu_4O_x$ type glasses to a value of 110 K. The vacuum annealed sample has small T_c (75 K or so) with very low T_{c0} .

The rate at which a sample is cooled after annealing at higher temperature largely affects the superconducting transition temperature. The $Bi_{1.5}SrCaCu_2O_y$ glass, for example, annealed at 840°C for 90 h in air followed by fast cooling showed (Bansal and Guire 1989; Guire *et al* 1990) semiconducting behaviour in the normal state. On the other hand, similar sample annealed similarly and cooled slowly showed metallic in the normal state. The glass sample annealed at 840°C for 200 h is superconducting at 77 K. However, it is interesting to note that the $BiSrCaCu_2O$ glass sample annealed at 850°C for 24 h in oxygen and cooled rapidly (Komatsu *et al* 1988) showed a sharp superconducting transition and higher T_c , whereas the furnace cooled sample showed a broad transition with a tail and low T_c value. The effect of cooling conditions on the superconducting properties of $Bi_{1.2}SrCaCu_2O_y$ and $Bi_2Sr_2CaCu_2O_y$ glass-ceramics have also been investigated. Two glass samples of $Bi_{1.2}SrCaCu_2O_y$ compositions were annealed at 880°C for 20 h in air and one sample was rapidly quenched in air and the other was furnace cooled. The temperature dependence of electrical resistivities of these samples is shown in figure 18. The quenched sample has a high normal state resistivity with a sharp drop at 90 K followed by a long tail which persists to very low temperature. On the other hand, the furnace cooled sample showed a much smaller value of normal state resistivity. It also exhibited a drop in resistivity at 105 K indicating the formation of high T_c phase followed by a sharp drop at 85 K with T_c at 68 K (zero resistance value). The effect of cooling condition on the value of T_c of the glass-ceramics obtained by annealing a glass of $Bi_2Sr_2CaCu_2O_y$ composition at 820°C for 48 h in air differs from that of similar glass like $Bi_{1.2}Sr_2CaCu_2O_y$. The normal state resistivity of the furnace cooled sample was smaller than that of the air cooled sample. But the former showed a T_c ($R = 0$ value) of 85 K compared with 88 K for the latter. The reason for this difference in behaviour is not clear. The influence of various cooling rates on T_c of $BiSrCaCu_2O_y$, $Bi_2Sr_2Ca_2Cu_3O_y$, $Bi_3Sr_3Ca_3Cu_4O_y$ and $Bi_3Sr_3Ca_4Cu_5O_y$ glasses annealed for 24

Figure 18. Temperature dependence of electrical resistivity of $Bi_{1.2}SrCaCu_2O_y$ glass samples annealed for 20 h in air.

or 48 h at 870–888°C in air, O₂, or vacuum has also been studied (Som *et al* 1992; Chatterjee *et al* 1994). The T_c (onset) increased with decrease in cooling rate.

The Pb and Li doped Bi–Sr–Ca–Cu–O systems have also been elaborately investigated in recent years because of the fact that addition of Pb or Li reduces the glass transition temperature as well as increases the superconducting transition temperature as mentioned earlier. Temperature dependence of resistivity of Pb doped $\text{Bi}_{4-n}\text{Pb}_n\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ (with $n = 0.1, 0.5$ and 1.0) is shown in figure 19. These glass ceramics are obtained by annealing the glasses at 840°C for 24 h in air. All the samples show T_c between 110 and 115 K which is about 10 to 15° higher than the corresponding undoped systems. Similar curves with Li doped $\text{Bi}_4\text{Sr}_3\text{Ca}_{3-z}\text{Li}_z\text{Cu}_4\text{O}_x$ systems have also been studied (Mollah *et al* 1993). Interesting informations are obtained from the thermoelectric power (TEP) measurements of both the glass and the glass ceramics. For the glasses thermopower is negative (electronic carrier) but for the superconducting glass-ceramics the thermopower is found to be positive (hole carriers). In figure 20 we have shown the temperature dependence of thermoelectric power of the Pb-doped $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass-ceramics. Choice of correct starting composition to prepare the 110 K superconducting phase in the bismuth system is also very important. $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ composition results in the formation of the 75 K phase whereas 110 K phase is mainly produced in the $\text{Bi}_{1.84}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$. Recently, we have been successful in preparing 110 to 115 K phase in the Pb doped

Figure 19. Temperature dependence of electrical resistivity of $\text{Bi}_{4-n}\text{Pb}_n\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass ceramics ($n = 0.1, 0.5$ and 1.0). (a) $n = 0.1$, (b) $n = 0.5$ and (c) $n = 1.0$.

Figure 20. Temperature dependence of thermopowers of $\text{Bi}_{4-n}\text{Pb}_n\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass-ceramics ($n = 0.0, 0.1$).

$\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass-ceramics (Bose 1994; Chatterjee *et al* 1994; Mollah *et al* 1994). It has also been shown by Baker *et al* (1989) that superconducting 2212 phase is obtained from the $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glassy precursor. The influence of Pb content on the superconductivity of the nominal compositions $\text{BiPb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, $\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3$, $\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_{3.6}\text{O}_y$ etc systems have also been elaborately investigated. The optimum value of x for higher T_c was found to be 0.3 to 0.35. At higher PbO concentration Ca_2PbO_4 formed which caused the formation of low T_c phase. PbO can be added until the Ca_2PbO_4 is formed in the glass-ceramic phase. Pure 2223 phase has been formed with Pb addition (Hatano *et al* 1988; Koyama *et al* 1988; Luo *et al* 1990). However, the effect of Pb substitution is not well understood. Pb is considered to be partially substituted (Takano *et al* 1988) into the bismuth oxide planes of the crystal structure of the 110 K phase. The effect of this substitution is to stabilize the lattice and to facilitate the formation of the pure 2223 phase. Addition of PbO or LiO lowers the melting point as well as increases the viscosity of the glass probably by acting as a fluxing agent. The Pb atoms are easily incorporated

into the structure probably because Bi in the 3^+ oxidation state and Pb in the 2^+ state have the same outer electronic shell configuration of $6s^2 6p^0$ (Bansal 1992). On the other hand, substitution of the bigger Pb^{2+} cation (ionic radius = 1.20 Å) for Bi^{3+} (ionic radius = 0.96 Å) probably results in the distortion of the crystal lattice.

Values of critical temperature T_c and critical current density J_c (at 77 K and zero magnetic field) of a typical $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ ($x = 1.5, 1.8$ and 1.2) glass-ceramics annealed at 840°C in air is shown in figure 21. Excess amount of CaO or CuO always reduces J_c values in the glass-ceramics. The Pb-doped high T_c phase has been observed with high resolution transmission electron microscopy and it was found that Pb atoms were located in the Bi–O layers with an atomic ratio of Pb/Bi being 0.1. It is also observed that for low Pb/Bi ratio, Pb atoms incorporated into the structure of both the low T_c and high T_c phases, whereas for high Pb content ($x > 0.25$) the Pb rich phase appeared. From all such considerations it appears that a value of $x \sim 0.2$ would be the optimum substitution of Pb for Bi for the formation of the high T_c phase in the $Bi_{1-x}Pb_xSrCaCu_{1.5}O_y$ system. This might be closely related to the maximum Pb content incorporating in the high T_c phase. This is in agreement with the results of many other researchers. The optimum starting glass composition appears to be $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$. When annealed at 840 – 945°C in air for a long time, a large volume fraction of the 110 K phase is formed in this glass which shows a T_{c0} at 107 K along with high J_c value. There are definitely other possible glass compositions for preparing superconductors with high T_c and high J_c values.

14. Superconducting wires, tapes, films from glass phase

We have already discussed in our previous review (Chaudhuri and Som 1992) the development of superconducting wires or tapes from the glassy phases. Glass precursor approach for the preparation of high T_c superconducting fibres is very interesting (Zheng *et al* 1989, 1991a, b; Onishi *et al* 1989, 1990, 1991; Komatsu *et al* 1990; Miller *et al* 1990; Chaudhuri *et al* 1989; Bose 1994). So far this technique has been

Figure 21. Variations of J_c and T_c of a typical $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ glass with CuO content (Komatsu *et al* 1991).

used for making fine rods, tapes and thick films of the Bi–Sr–Ca–Cu–O or Pb–Sr–Ca–Cu–O glassy phases. Continuous glass fibres with diameter $\sim 110\ \mu\text{m}$ have been successfully drawn (Zheng *et al* 1991) with [4334] glass. The superconducting T_c value after heat treatment of about 12 h is about 85 K. Figure 22 shows some hand drawn fibres from the glass melt. The J_c values for such superconducting wires are relatively small (100 to 200 A/cm²). Glass fibres of several diameters have also been drawn from the Pb doped Bi–Sr–Ca–Cu–O glassy phase (Komatsu *et al* 1990) with T_c as high as 109 K and $J_c = 1480\ \text{A/cm}^2$ (Komatsu *et al* 1990). Attempts have also been made for fabrication of long fibres from melts of 2212 phase and 1112 phase using a gas jet fibreization technique. Glass fibres of short lengths have also been prepared (Zheng *et al* 1989) by spinning a melt of 4334 glass. Another technique of making glass wire by depositing glass melt on Pt wires has also been made (Bhargava *et al* 1991). Interesting development has been made in recent years to make fine filaments or powder by spraying the liquid melts. Another technique involves the glass coating on metal or ceramic surfaces and subsequent annealing to make high T_c superconductors.

15. Summary and conclusion

We have reviewed some of the properties of the glass-ceramic superconductors as prepared and studied by different researchers. Most of the studies on the GC phase have been concentrated on the Bi–Sr–Ca–Cu–O based systems either undoped or doped with Pb, Li etc. Y–Ba–Cu–O and Tl–Ba–Ca–Cu–O systems have not been well studied in their respective GC phases as they are difficult to prepare in the respective glassy phase. However, homogeneous glass is formed when Y–Ba–Cu–O is mixed with appropriate amount of B_2O_3 and PbO. Crystalline Y–Ba–Cu–O can be nucleated in this glass by proper annealing treatment. Such studies are being made in recent years. Because of the presence of transition metal ions (Cu^{1+} and Cu^{2+}) all the glassy phases showing semiconducting behaviour are almost similar in their behaviour with those of usual TMO glasses. Superconductivity in the glassy phase has not been observed in any of the glasses down to 8 K or so. However, very recently

Figure 22. Glass-ceramic superconducting wires from $\text{Bi}_{3.5}\text{Pb}_{0.5}\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glassy precursors.

we have observed some increase in the conductivity of the Pb-doped $\text{Bi}_{4-n}\text{Pb}_n\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glasses in the low temperature (below 150 K) region but they do not show superconductivity down to 10 K. Moreover, the ac conductivity ($\sigma_{ac}(\omega)$) of the TMO glasses show the general behaviour like $\sigma_{ac}(\omega) \propto \omega^s$ (where the exponent is ≤ 1). But most of the glasses becoming high T_c superconductors show slightly greater value of s than unity in the low temperature region. Furthermore, these glasses also show quite large glass transition temperature, and Debye type dielectric relaxation behaviour. In the Bi-based glasses one also observes the presence of BiO_3 and BiO_6 structural units. Bi_2O_3 acts as the glass former and plays an important role increasing the thermal stability factor ($T_x - T_g$) with increase of Bi_2O_3 in the glass which is essential for drawing glass fibres from the melts. Very interesting behaviour was shown by the Ba–K (Li or Na)–Bi–O based glasses. Most of these glasses showed non-linear variations of dc and ac conductivities and even semiconductor–metal–semiconductor like transition was exhibited between 300 and 340 K (depending on concentrations). These glasses also showed superconductivity in their ceramic phases (when annealed in oxygen atmosphere). The strong electron-phonon interaction can be attributed to explain the above mentioned non-linear behaviour. However, proper understanding of the behaviour of these and similar other glasses becoming high T_c superconductors in their GC phases has not been possible. The nature of carriers in these glasses are negative as observed from the thermoelectric power measurements but with the increase of crystallinity (by annealing) the nature of carrier changes from negative to positive in the superconducting GC phase. More elaborate microstructural and spectroscopic studies of such glasses might be interesting to elucidate the causes as to why these glasses unlike many TMO glasses become superconductors in their GC phases.

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