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Superconducting $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ Ceramics by Rapid Melt Quenching and Glass Crystallization

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SUPERCONDUCTING $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ CERAMICS BY RAPID MELT QUENCHING AND GLASS CRYSTALLIZATION

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SUMMARY

A glass of nominal $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ composition, prepared by rapid quenching of the melt, showed a glass transition temperature of 383°C, crystallization temperature of 446°C, melting temperature of 855°C, and bulk density of 5.69g/cm^3 in air. The activation energy for crystallization of the glass has been estimated to be 292kJ/mol from non-isothermal DSC. On heating in oxygen, the glass showed a slow and continuous weight gain starting at ~530°C which reached a plateau at ~820°C. The weight gained during heating was retained on cooling to ambient conditions indicating an irreversible oxidation step. The influence of annealing conditions on the formation of various phases in the glass has been investigated. The $Bi_2Sr_2Ca_0Cu_1O_6$ phase crystallized out first followed by formation of other phases at higher temperatures. The high-T_c phase, isostructural with $Bi_2Sr_2Ca_2Cu_3O_{10}$, was not detected below 840°C, but its fraction increased with the annealing time at 840°C. A sample annealed at 840°C for 243h in air and furnace cooled showed the highest T_c(R = 0) of 107.2K and a narrow transition width, ΔT_c(10 - 90%), of ~2K.

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The high T_c phase does not seem to crystallize out directly from the glass but is rather produced at high temperature by reaction between the phases formed at lower temperatures. The kinetics of 110K phase formation was sluggish. It appears that the presence of lead helps in the formation and/or stabilization of the 110K phase.

INTRODUCTION

High-temperature superconductivity (HTS) in the bismuth oxide containing system was first discovered by Maeda et al.[1] The Bi-Sr-Ca-Cu-O system is known to have at least three different superconducting phases, $Bi_2Sr_2CuO_6$(2201), $Bi_2Sr_2CaCu_2O_8$(2212), and $Bi_2Sr_2Ca_2Cu_3O_{10}$(2223) with T_c's of ~10-20K, ~80K, and ~110K, respectively. It has been very difficult to synthesize the high-T_c 2223 single phase polycrystalline bulk material.

In sintered polycrystalline samples the high-T_c phase seems to occur in unconnected regions, separated by a lower T_c phase, which prevents the zero resistance of the high-T_c phase from being achieved. The partial substitution of Bi by Pb helps in the stabilization[2] of the high-T_c phase and also in solving the connectivity problem.[3] The melt quenching approach is a promising route for fabrication of almost fully dense, pore free superconductors which could lead to high critical current densities. This method is also of practical significance for the manufacture of ceramic superconductors into desired shapes (wires, tapes, fibers, etc.) by borrowing the well established techniques of glass technology.

The objectives of this work were to prepare the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ composition in the glassy state, study the kinetics of its crystallization, and optimize the annealing parameters for transforming the glass into a superconductor containing a large fraction of the high-T_c phase. Since the time this work was initiated, a number of reports[4-10] on the synthesis of Bi-containing HTS from the glass precursor approach have appeared.

EXPERIMENTAL METHODS

Appropriate amounts of Bi_2O_3 (ultrapure, Strem), PbO_2 (ACS certified reagent, Fisher), $SrCO_3$ (reagent grade, Alfa), CaO(99.95%, Strem), and CuO(ACS grade, Alfa) for the nominal composition $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ were slurry mixed in acetone and ground using a mortar and pestle. The mixture was calcined in a Pt crucible in air at ~795°C overnight, cooled and reground. The pulverized grey powder was melted in a covered Pt crucible in an electric furnace at ~1025°C for ~0.5h. The melt was rapidly quenched by pressing between two copper plates resulting in opaque black sheets of glass ~1mm thick. The powder x-ray diffraction pattern was characteristic of an amorphous material. Some low intensity peaks, which could be assigned to CaO, were also present.

The glass was characterized using a number of techniques. Differential thermal analysis(DTA) was carried out in air or oxygen at a heating rate of 10°C/min using a Perkin-Elmer DTA 1500 system. A Perkin-Elmer TGS-2 system was used for the thermogravimetric

analysis(TGA) under nitrogen or oxygen flow at heating and cooling rates of 5°C/min. The kinetics of crystallization of the glass was investigated from non-isothermal differential scanning calorimetry (DSC) using the Perkin-Elmer DSC-4 system at heating rates of 2 to 40°C/min.

Glass samples were annealed in air for various lengths of time at temperatures selected from the DTA results. Crystalline phases formed in the annealed specimens were identified from powder x-ray diffraction (XRD) patterns which were recorded at room temperature using a step scan procedure (0.03°/2θ step, count time 0.4s) on a Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing copper Kα radiation. Electrical resistance was measured from room temperature to ~60K in the standard four probe configuration at a current density of ~0.1A/cm^2. Silver paint was used to attach the leads. Morphologies of freshly fractured as well as polished surfaces were observed in a JEOL JSM-840A scanning electron microscope (SEM). X-ray dot mapping of various elements and the EDAX analysis were carried out using Kevex Delta Class Analyzer. Densities were measured from the Archimedes method using water. From atomic absorption spectroscopy, chemical composition of the as-quenched glass was determined to be within 1% of the nominal composition.

RESULTS AND DISCUSSION

The DTA curves in air and oxygen atmospheres at a heating rate of 10°C/min are shown in Fig. 1. The glass transition temperature,

T_g, is 383°C and the crystallization temperature, T_x, is ~446°C. The exotherm at 445°C is probably due to crystallization of $Bi_2Sr_2CuO_6$(2201) phase as seen from the XRD results (vide infra). The main melting endotherm occurs at a higher temperature (866°C) in oxygen than in air (855°C). A number of small endotherms above the main melting peak are probably due to the melting of minor crystalline phases present. The peaks at ~720 and 753°C are responsible for the formation of various crystalline phases either directly from glass or by reaction between the phases produced at lower temperatures.

DSC runs were recorded at different heating rates between 2 - 40°C/min. A typical DSC thermogram at a scan rate of 40°C/min in argon is presented in Fig. 2. The endotherm is the glass transition and the exotherm is due to crystallization of the glass. Values of T_g and the crystallization peak maximum temperature, T_p, at different scan rates are listed in Table I. The peak maximum corresponds to the temperature at which the rate of transformation of the viscous liquid into crystal becomes maximum. When the composition of the crystalline phase is different from that of the liquid, as in the present case (see XRD results below), the rate of transformation will be controlled by the rate of diffusion through the viscous liquid and the number of crystallization sites to which diffusion can occur. If the number of nucleation sites is increased, e.g. by using slower heating rates, the peak maximum

will occur at a temperature at which the melt viscosity is higher, i.e., at a lower temperature. This explains the increase in T_p with the scan rate (Table I).

The variable heating rate DSC method was employed to evaluate the kinetics of crystallization. Values of the kinetic parameters were calculated from the DSC data of Table I using the kinetic model of Bansal et al.[11,12] which is expressed by the relation:

$$\ln[T_p^2/\alpha] = \ln(E/R) - \ln\upsilon + E/(RT_p) \quad (1)$$

where T_p is the peak maximum temperature, α the heating rate, E the activation energy, R the gas constant, and υ the frequency factor. The kinetic parameters (E and υ) are related to the reaction rate constant (k) by an Arrhenius equation:

$$k = \upsilon \exp[-E/RT] \quad (2)$$

Equation (1) is an extension of the Johnson-Mehl-Avrami[13,14] isothermal kinetic model for use in non-isothermal methods. In the derivation of eq.(1) it was assumed that the rate of reaction is maximum at the peak which is a valid assumption for the power-compensated DSC. It has been shown in earlier studies[12,15,16] that the kinetic parameters determined from non-isothermal DSC using eq.(1) and from isothermal methods are in excellent agreement. A plot of $\ln[T_p^2/\alpha]$ versus $1/T_p$ for crystallization of the glass was linear (Fig. 3) verifying applicability of the

kinetic model of Bansal et al. From linear least-squares fitting, values of the kinetic parameters were calculated to be, E = 292 kJ/mol, and υ = 9.7 x 10^{18} s^{-1}, the correlation coefficient being 0.989. Higher E values, ranging from 375 to 437 kJ/mol, have been reported[17] recently for the crystallization of $Bi_xSrCaCu_2O_w$ (x = 1.5 or 2.7) glasses. In an earlier study[9] we reported an E value of 347 kJ/mol for crystallization of the $Bi_{1.5}SrCaCu_2O_y$ glass.

TGA curves at the heating and cooling rates of 5°C/min in nitrogen and oxygen gas flow are shown in Fig. 4. In nitrogen, weight loss starts at ~750°C, the total loss in weight being 0.53% when heated to 850°C. There is further weight loss when the sample is held at this temperature which may be ascribed to the loss of oxygen due to decomposition during melting. These bismsuth compounds are known[9] to melt at lower temperatures in inert atmosphere than in oxygen. On cooling to room temperature, almost no further change in weight is observed. In contrast, when heated in oxygen, there is a slow and continuous weight gain commencing at ~530°C which reaches a plateau at ~820°C. The total increase in weight was 2.1%. There was no further change in weight on cooling to room temperature in oxygen. The weight gain in oxygen is probably due to oxidation of the material. Numata et al[18] reported reversible weight change on heating and cooling $BiSrCaCu_2O_{5.5}$ specimen in contrast to the irreversible weight changes observed in the present and earlier[9] studies.

Hwang et al.[19] have recently investigated the influence of annealing in air or nitrogen atmospheres on the formation of low-T_c

and high-T_c phases in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3.6}O_x$. The fraction of the high-T_c phase increased with sintering time in air, there was virtually no effect even after annealing for 264h in N_2. The absence of oxygen favored the formation of the low-T_c phase and inhibited the formation of the high-T_c phase. These results get support from our TGA data where at high temperature, a gain in sample weight was observed in O_2 and the sample lost weight in N_2. The weight gain in O_2 is probably due to oxidation of Bi and/or Cu to a higher oxidation state which may be necessary for the formation of the 2212 phase.

The glass was annealed in air at temperatures between 500 and 850°C, chosen from positions of DTA peaks, for different times as listed in Table II. After thermal treatment all samples were furnace cooled except one which was rapidly quenched to ambient temperature in air. Room temperature bulk densities of the glass and the crystallized specimens are presented in Table II and Fig. 5. Density increased with the annealing temperature, reached a maximum for the 750°C annealed sample, and decreased with further rise in annealing temperature. The decrease in bulk density at higher annealing temperatures is probably associated with the formation of the high-T_c superconducting phase(s). A decrease in sample bulk density with increasing sintering temperature in the range 830 to 855°C was also observed in the $Bi_{0.8}Pb_{0.2}Sr_{0.8}Ca_1Cu_2O_x$ system by Kikuchi et al.[20] which was assigned to the expanding volume with increase in sintering temperature. A decrease in density on sintering in the Bi-Pb-Sr-Ca-Cu-O system has also been

reported[21] by Hatano et al. A large expansion during sintering in the Bi-Sr-Ca-Cu-O system has been ascribed[22] to the formation of Kirkendall voids. On sintering samples of nominal composition $BiSrCaCu_2O_Y$ at 860°C, a ~10% expansion in sample diameter, associated with the formation of the 2212 phase, has been observed[3]. A density of 6.42g/cm^3 has been reported[23] for a glass sample of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+x}$ composition which had been annealed for 15.5h at 830°C in oxygen and for 156h at 840°C in air followed by rapid quenching to room temperature in air.

Temperature dependence of the resistivity normalized to its value at 130K for various specimens annealed under different conditions is shown in Fig. 6 and the results are summarized in Table II. The as-quenched glass was an insulator and the sample annealed at 500°C was semiconducting. The specimen annealed at 720°C showed a superconducting transition, $T_c(R = 0)$, at 75K. The sample annealed at 750°C for 24h showed a sharp drop in resistance but had a long tail and the resistance did not become zero even at 63K. The 802°C sample had a sharp resistivity drop starting at ~80K with $T_c(R = 0)$ of 69K. The zero resistance temperature increased with the time of annealing at 840°C (Fig. 7). The specimen heat treated at 840°C for 24h showed a small drop in resistance at ~110K and a sharp transition at ~78K with $T_c(R = 0)$ at 68K. The one baked for 94h showed a sharp transition at 110K with $T_c(R = 0)$ of 98K. The specimen annealed for 243h at 840°C and furnace cooled exhibited a very sharp transition with T_c(onset) of ~111K, $T_c(R = 0)$ at 107.2K and ΔT_c(10 - 90%) of ~2K. These results indicate slow

kinetics of the 110K phase formation reaction. A further increase in firing temperature degraded the superconducting characteristics. The sample annealed at 850C^{o} for 94h showed a large resistance drop at 110K but had a very long tail with $T_c(R = 0) < 77K$. This sample also showed signs of partial melting and poor mechanical integrity. Poor intergrain superconducting coupling may be an explanation for this behavior. Liquid phases containing both Pb and Ca would be expected in the samples annealed at temperatures higher than the melting point of Ca_2PbO_4 which is reported[24] to be 822^{o}C. However, in the present study partial melting was observed only in the specimen annealed at 850^{o}C.

The influence of cooling rate on the temperature dependence of resistance is shown in Fig. 8. Two samples were annealed for 94h at 840^{o}C in air; one was furnace cooled and the other was rapidly quenched to ambient temperature in air. The former sample showed a sharp transition at 110K with $T_c(R = 0)$ of 98K whereas the latter exhibited a large resistance drop at 110K with another sharp transition at ~90K and $T_c(R = 0)$ of 68K. In contrast, for specimens prepared from the glass precursor of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ composition, Sato et al.[23] observed higher $T_c(R = 0)$ in air-quenched samples than those which were furnace cooled after prolonged annealing at 840^{o}C in air. The reason for these conflicting results is not clear at this time.

Figure 9 shows the SEM micrographs of fracture surfaces of specimens annealed at various temperatures. The samples annealed

for 24h at 720, 802, or 840°C show acicular morphologies. The samples annealed at 840°C for 94h or 243h and slow cooled show larger crystals and better intergrain connectivity. In contrast, the fast quenched specimen shows a platelet microstructure. The microstructures correlate well with the T_c results for various samples.

The SEM micrograph and the x-ray dot maps of each element taken on the polished surface of the sample BI-9 sintered at 840°C for 243h and slow cooled in air are presented in Fig. 10. The regions which are rich in Ca are deficient in Bi, Pb, and Sr. From EDAX analysis, the Ca-rich regions were found to consist mainly of Ca and Cu along with a small concentration of Sr. The EDAX analysis of the Sr-rich regions showed the absence of all other metals. Some Pb-rich regions are also present. Powder XRD spectra of the samples annealed under different conditions were recorded and the crystalline phases identified. Typical XRD patterns and the phases present are shown in Figures 11 to 13. The XRD spectra of the as-quenched glass was typical of an amorphous material except for a low intensity peak at d = 0.243nm for CaO. Probably part of the CaO did not dissolve in the melt or precipitated out during quenching.

All the specimens were multiphase. The fraction of the high-T_c phase was highest in the sample fired for 243h at 840°C and furnace cooled. The fraction of this phase was much lower in both the fast quenched and the 850°C annealed specimens. The high-T_c phase is not formed below 840°C. Surprisingly no 2201 phase was detected in the specimen fast cooled from 840°C. Fractions of the 2201 and 2212

phases increased and that of the high-T_c phase decreased in the 850°C baked sample which had shown signs of partial melting. This probably indicates that at high temperature the high-T_c phase is unstable and decomposes into the low-T_c 2201 and 2212 phases.

On the basis of the above results it may be inferred that the following crystallization sequence occurs on heating the glass. 2201 phase first precipitates out followed by formation of the 2212 phase at higher temperature. The 110K-T_c phase is formed at still higher temperature just below the melting point probably by reaction between the low-T_c 2201 and 2212 phases and the residual calcium and copper oxides. The high-T_c phase formation rate is sluggish and takes a long time (days) due to relatively long range diffusive ordering involved. Even after prolonged heating at 840°C for more than 10 days, the product contained an appreciable amount of the 80K phase in addition to the 110K phase as seen from the powder XRD results. TGA curve in oxygen (Fig. 4) shows that formation of the 2212 phase is accompanied by a rapid absorption of O_2 and no further uptake of O_2 occurs when the high-T_c 2223 phase is produced at ~840°C.

The influence of Pb addition on the superconductivity of the nominal compositions $(BiPb_x)_2Sr_2Ca_2Cu_3O_y$, $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$, and $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_{3.6}O_y$ has been investigated by Oota et al.[25] Addition of Pb lowered the melting temperature and had a catalytic effect on the formation of the high-T_c phase. The optimum value of x for the highest T_c and the maximum fraction of the high-T_c phase was ~0.3. At higher Pb concentration Ca_2PbO_4 formed which assisted

in the formation of the low-T_c phase. The optimum value of the Pb content is determined by the competition between the two reactions which result in the formation of the high-T_c phase and Ca_2PbO_4, respectively.

In the Bi-Sr-Ca-Cu-O system, the optimum annealing temperature to form the high-T_c phase is ~870°C. In the presence of PbO this temperature is lowered to ~840°C. Prolonged firing at 840°C is very effective in enhancing the fraction of the 110K phase. Incorporation[26] of PbO lowers the melting point and viscosity of the glass probably by acting as a fluxing agent. However, it has been suggested[26] that a mechanism other than a lowered melting temperature or fluxing action is probably responsible for the beneficial effect of PbO addition. According to Shi et al.[27] the 2212 phase is always formed first because of the higher free energy of the 2223 phase due to a longer c-axis of its unit cell. Kinetics of 2223 phase formation is controlled by calcium and copper diffusion. The presence of lead accelerates growth of the 2223 phase by enhancing diffusion of calcium and copper during insertion of an extra layer of Ca-O and Cu-O into the unit cell of 2212.

Lead is known to partially substitute[28] into the bismuth oxide planes of the crystal structure of the 110K phase. The effect[29] of this substitution is to stabilize the structure and facilitate its formation as a nearly pure phase. From high resolution analytical electron microscopy it has been found[30] that Pb atoms are located in the Bi-O layers of the structure with an atomic ratio of Pb to Bi of 1:9. The Pb atoms are easily incorporated into the structure

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

In the present study, the prolonged annealing at 840°C has circumvented the connectivity problem of the 110K phase, but the sample is still multiphase and contains an appreciable fraction of the 2212 phase. The advantage of all the starting components being intimately mixed in the melt is lost as the 2223 phase does not precipitate out directly from the glass. Its formation is preceded by the crystallization of other phases from the glass. Further efforts are needed in order to achieve single phase 110K-T_c bulk material.

SUMMARY AND CONCLUSIONS

The glass of composition $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ prepared by rapid quenching of the melt had T_g of 383°C, T_x of 446°C, T_m of ~855°C, and bulk density of 5.69g/cm^3 in air. From non-isothermal DSC, crystallization activation energy of the glass was determined to be 292kJ/mol. On heating in oxygen, the glass showed an irreversible, slow, and continuous weight gain due to oxidation commencing at ~530°C. The bulk density peaked for a sample sintered in air at 750°C. On thermal annealing in air at various temperatures, a number of phases crystallized out from the glass. All glass ceramic samples were multiphase. Prolonged annealing (>10

days) in air at 840°C followed by slow cooling resulted in the highest $T_c(R = 0)$ of 107.2K and sharp transition, $\Delta T_c(10 - 90\%)$ 0f ~2K. The sluggish kinetics of the high-T_c phase formation presently offer a severe limitation on the utility of the melt quenching approach to Bi- superconductor fabrication, particularly for continuous fiber or wire.

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TABLE I. Effect of Scan Rate on DSC Peak Positions for $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ Glass

Heating rate, α (°C/min)	Glass transition temperature, T_g (°C)	Crystallization peak maximum temperature, T_p (°C)
2	-	435
5	-	444
10	383	457
20	383	464
30	391	474
40	392	473[a]

[a]Excluded from linear least-squares fitting.

TABLE II. Transition Temperatures, Densities, and the Phases Formed in $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ Glass Samples Annealed in Air Under Different Conditions

Sample	Heat Treatment			Density ρ(g cm^{-3})	T_c(R = 0) (K)	Phases Identified From Powder XRD
	Temp. (°C)	Time (h)	Cooling Rate			
BI-0	---	---	-----	5.695	-----	Amorphous, CaO(trace)
BI-1	500	24	Slow	6.145	-----	2201[a]
BI-2	720	24	Slow	6.202	75	2212[b], 2201, Ca_2PbO_4, CuO
BI-3	750	24	Slow	6.425	<63	2212, 2201, Ca_2PbO_4, CuO
BI-4	802	25	Slow	5.665	69	2212, 2201, Ca_2PbO_4, CuO
BI-5	840	24	Slow	5.580	68	2212, 2223[c], 2201, Ca_2PbO_4
BI-6	840	94	Slow	5.543	98	2223, 2212, 2201, Ca_2PbO_4
BI-7	840	94	Fast	5.371	68	2223, 2212, Ca_2PbO_4
BI-9	840	243	Slow	-----	107.2	2223, 2212, Ca_2PbO_4
BI-8	850	94	Slow	5.160	<77	2212, 2223, Ca_2PbO_4

[a]$Bi_2Sr_2Ca_0Cu_1O_6$
[b]$Bi_2Sr_2Ca_1Cu_2O_8$
[c]High-T_c phase isomorphic with $Bi_2Sr_2Ca_2Cu_3O_{10}$

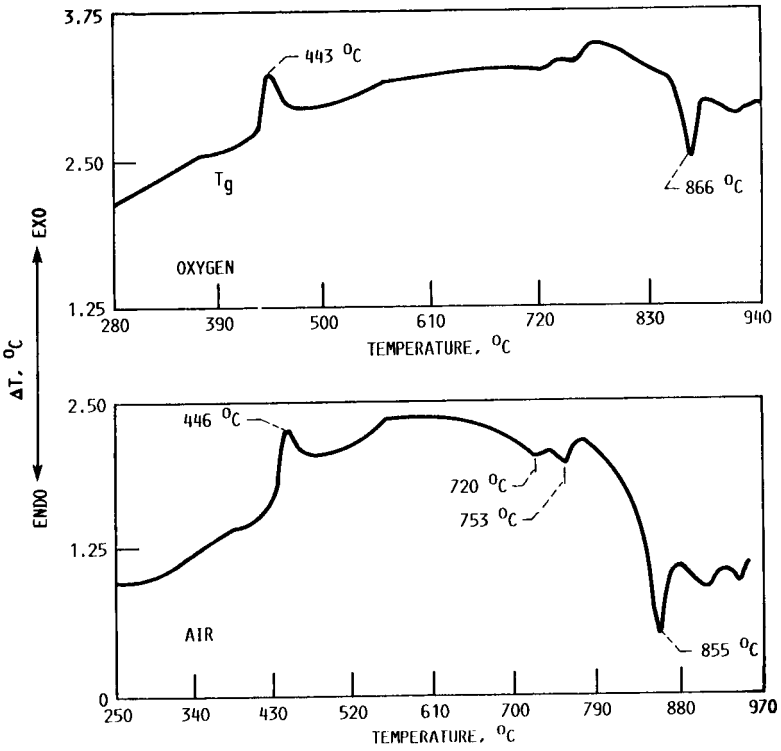

FIGURE 1. - DTA THERMOGRAMS OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS AT 10°C/MIN IN OXYGEN AND AIR.

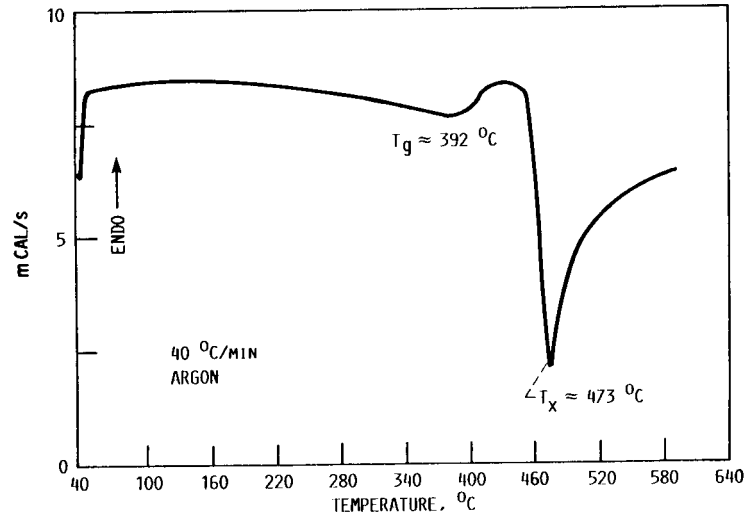

FIGURE 2. - A TYPICAL DSC SCAN OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS RECORDED AT 40°C/MIN IN ARGON.

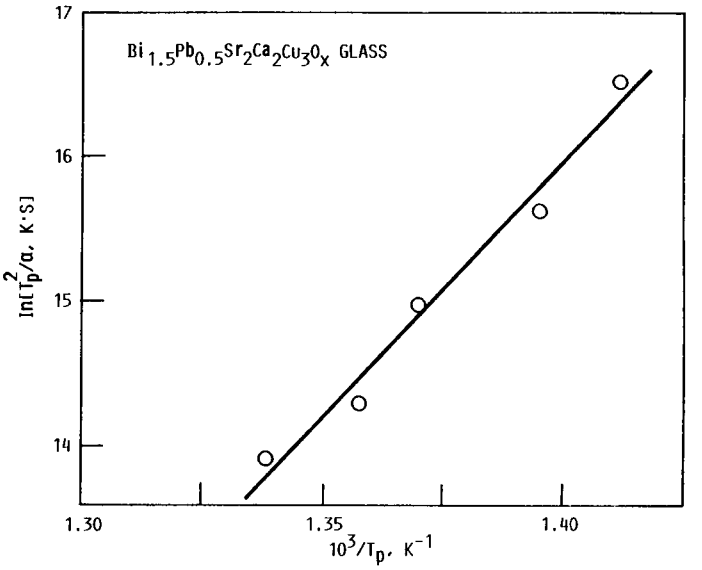

FIGURE 3. - A PLOT OF $\ln [T_p^2/\alpha]$ vs. RECIPROCAL OF PEAK MAXIMUM TEMPERATURE FOR THE CRYSTALLIZATION OF $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS. THE LINE IS A LINEAR LEAST SQUARES FIT TO THE DATA.

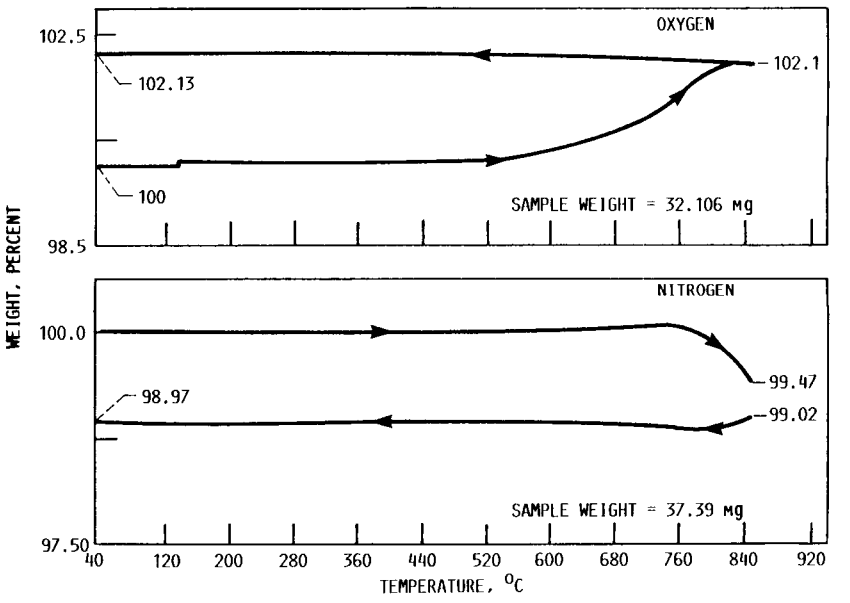

FIGURE 4. - TGA CURVES FOR THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS RECORDED AT THE HEATING AND COOLING RATES OF 5°C/MIN IN OXYGEN AND NITROGEN.

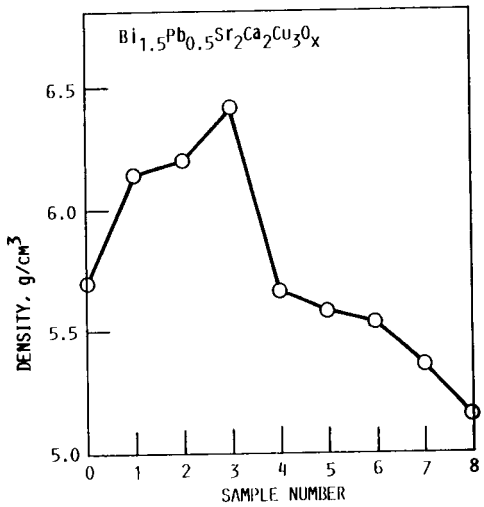

FIGURE 5. - BULK DENSITIES OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS SAMPLES AFTER VARIOUS THERMAL TREATMENTS AS SHOWN IN TABLE II.

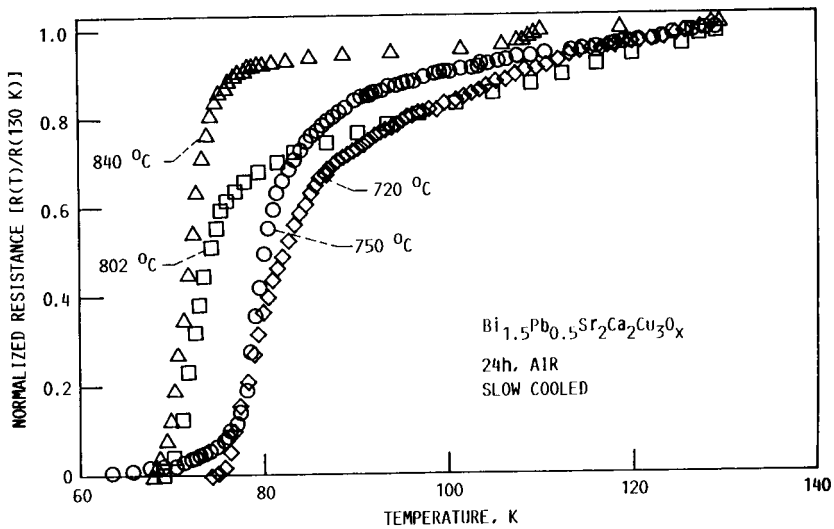

FIGURE 6. - TEMPERATURE DEPENDENCE OF ELECTRICAL RESISTANCE OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS SPECIMENS AFTER ANNEALING AT DIFFERENT TEMPERATURES FOR 24h IN AIR AND FURNACE COOLED.

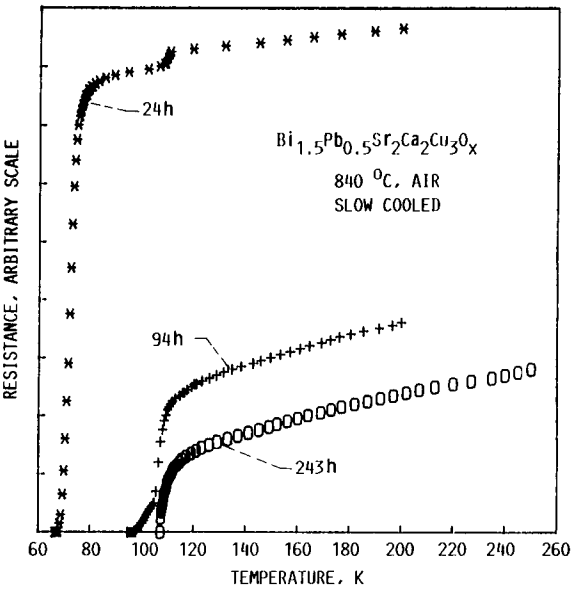

FIGURE 7. - PLOTS OF ELECTRICAL RESISTANCE AGAINST TEMPERATURE OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS SAMPLES ANNEALED AT 840 °C IN AIR FOR DIFFERENT TIMES AND SLOW COOLED.

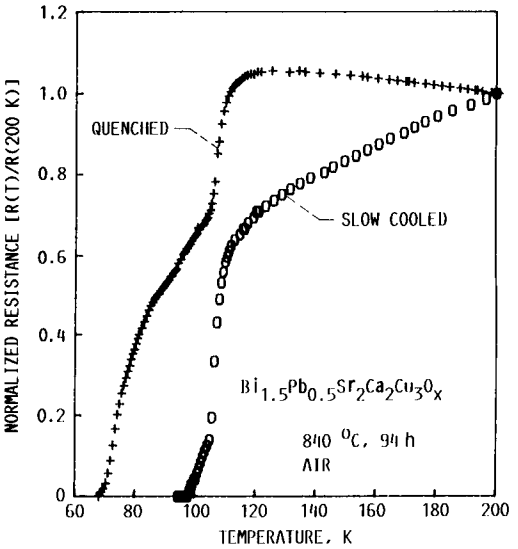

FIGURE 8. - INFLUENCE OF COOLING RATE ON THE TEMPERATURE DEPENDENCE OF ELECTRICAL RESISTANCE OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS ANNEALED AT 840°C FOR 94h IN AIR.

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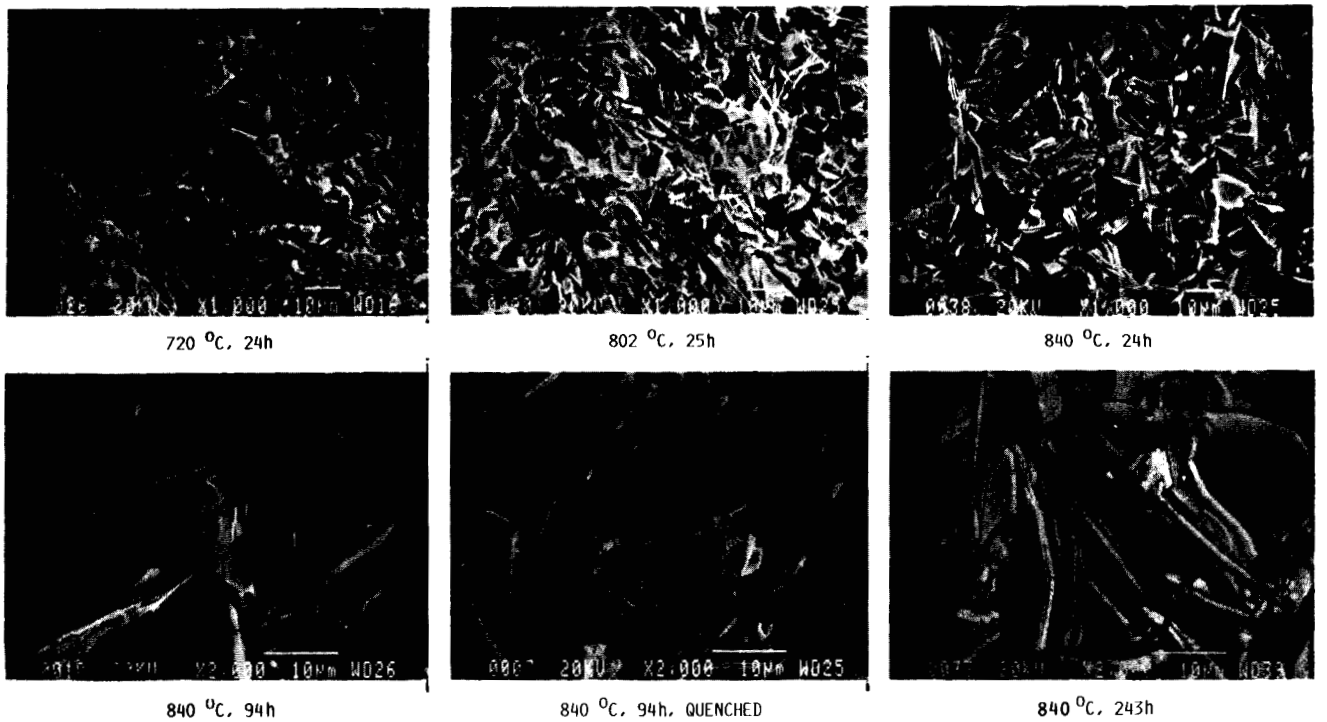
BLACK AND WHITE PHOTOGRAPH



720 °C, 24h | 802 °C, 25h | 840 °C, 24h

840 °C, 94h | 840 °C, 94h, QUENCHED | 840 °C, 243h

FIGURE 9. - SEM MICROGRAPHS OF FRACTURE SURFACES OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS SPECIMENS ANNEALED AT VARIUOS TEMPERATURES IN AIR FOR DIFFERENT TIMES AND SLOW COOLED.

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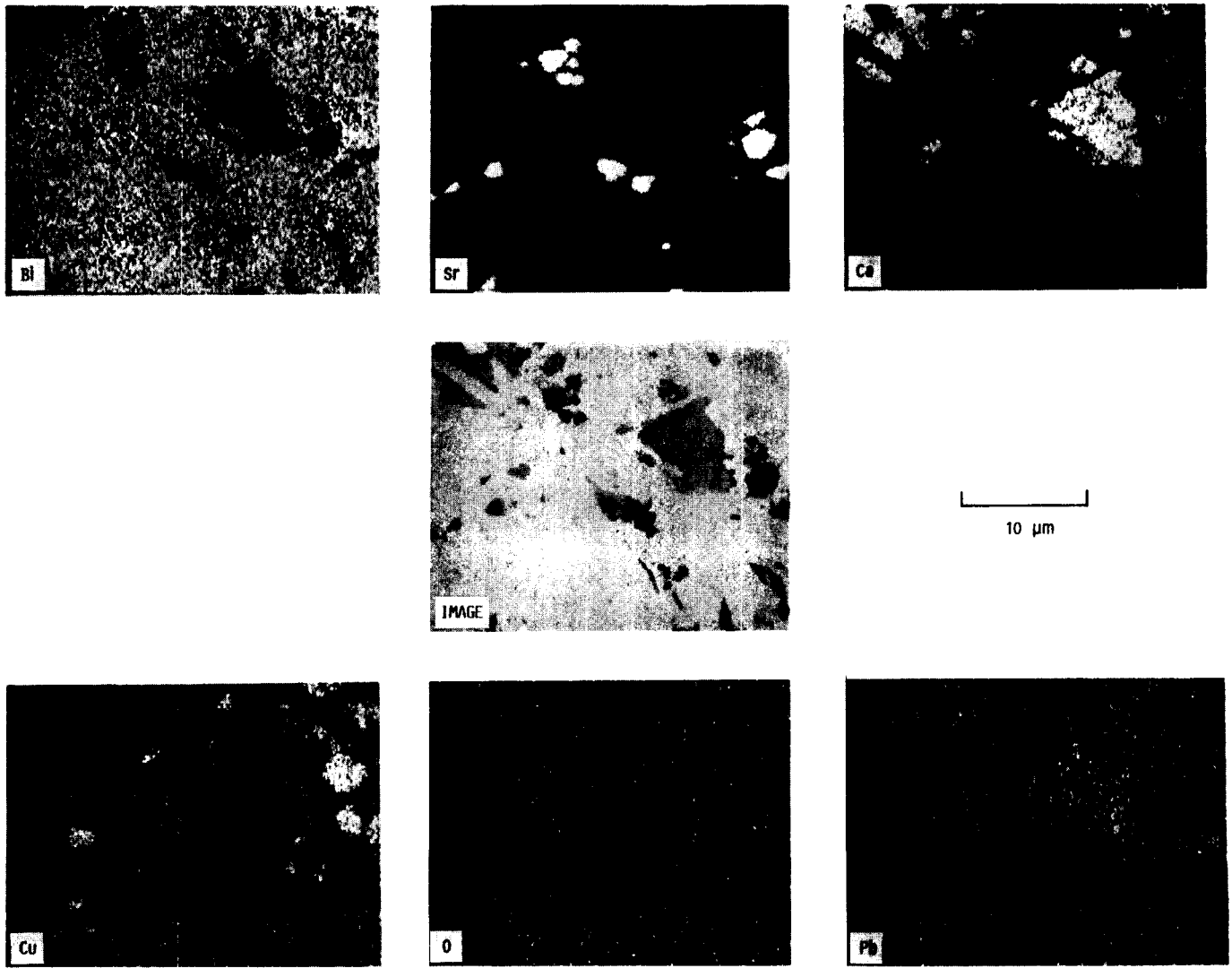

FIGURE 10. - SEM MICROGRAPH AND X-RAY DOT MAPS OF DIFFERENT ELEMENTS TAKEN ON THE POLISHED SURFACE OF THE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS ANNEALED AT 840°C IN AIR FOR 24 AND FURNACE COOLED.

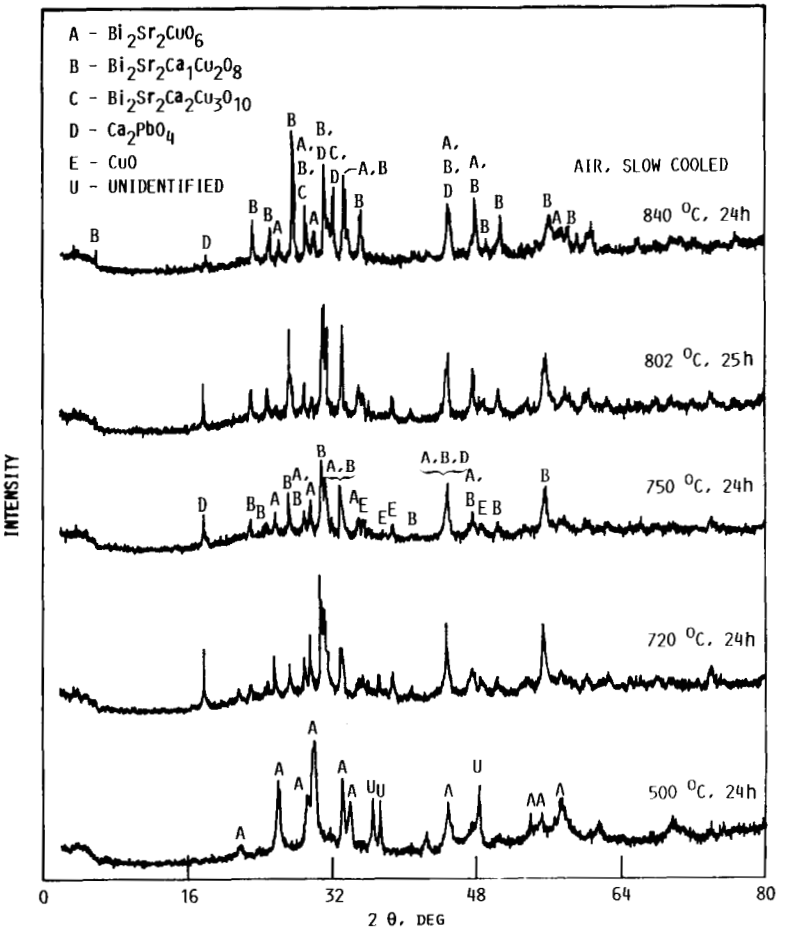

FIGURE 11. - X-RAY POWDER DIFFRACTION PATTERNS OF $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS SAMPLES ANNEALED AT VARIOUS TEMPERATURES FOR 24h IN AIR AND SLOW COOLED.

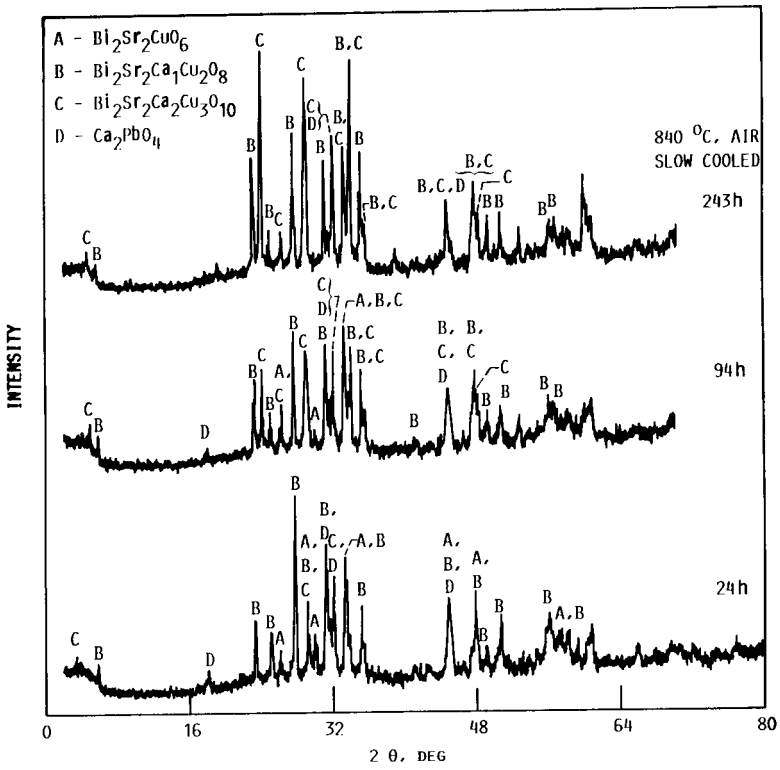

FIGURE 12. - X-RAY POWDER DIFFRACTION PATTERNS OF $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS SPECIMENS HEAT TREATED AT 840°C FOR VARIOUS TIMES IN AIR AND FURNACE COOLED.

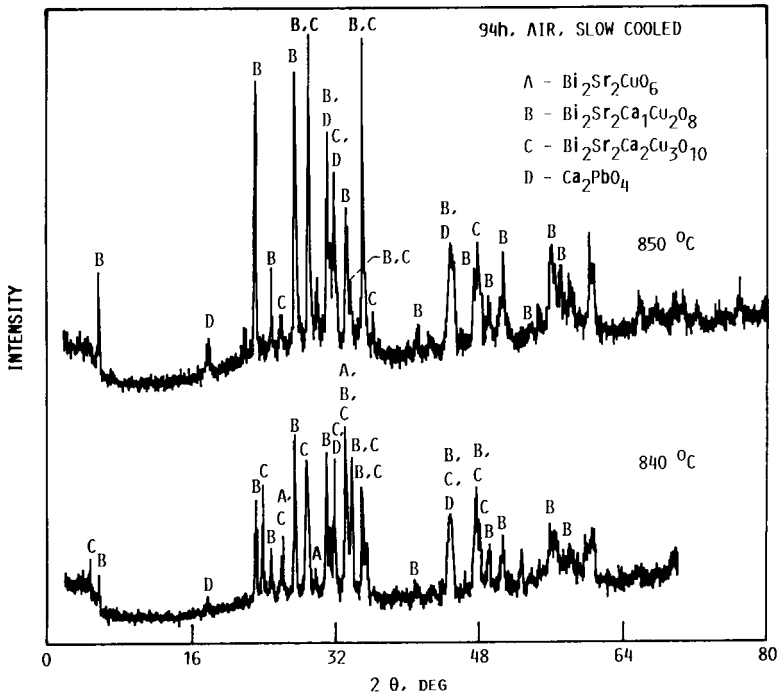

FIGURE 13. - X-RAY POWDER DIFFRACTION PATTERNS OF $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ GLASS SAMPLES ANNEALED FOR 94h IN AIR AT 840°C OR 850°C AND SLOW COOLED.

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16. Abstract

A glass of nominal $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ composition, prepared by rapid quenching of the melt, showed a glass transition temperature of 383°C, crystallization temperature of 446°C, melting temperature of 855°C, and bulk density of 5.69g/cm^3 in air. The activation energy for crystallization of the glass has been estimated to be 292kJ/mol from non-isothermal DSC. On heating in oxygen, the glass showed a slow and continuous weight gain starting at ~530°C which reached a plateau at ~820°C. The weight gained during heating was retained on cooling to ambient conditions indicating an irreversible oxidation step. The influence of annealing conditions on the formation of various phases in the glass has been investigated. The $Bi_2Sr_2Ca_0Cu_1O_6$ phase crystallized out first followed by formation of other phases at higher temperatures. The high-T_c phase, isostructural with $Bi_2Sr_2Ca_2Cu_3O_{10}$, was not detected below 840°C, but its fraction increased with the annealing time at 840°C. A sample annealed at 840°C for 243h in air and furnace cooled showed the highest $T_c(R = 0)$ of 107.2K and a narrow transition width, $\Delta T_c(10 - 90\%)$, of ~2K. The high T_c phase does not seem to crystallize out directly from the glass but is rather produced at high temperature by reaction between the phases formed at lower temperatures. The kinetics of 110K phase formation was sluggish. It appears that the presence of lead helps in the formation and/or stabilization of the 110K phase.

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