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STUDY OF THE GLASS FORMATION OF HIGH TEMPERATURE SUPERCONDUCTORS

CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT (PROJECT #89-04)

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13. ABSTRACT *(Maximum 200 words)*

A number of compositions of ceramic oxide high T_c superconductors were elevated for their glass formation ability by means of rapid thermal analysis during quenching, optical, and electron microscopy of the quenched samples, and with subsequent DSC measurements. Correlations between experimental measurements and the methodical composition changes identified the formulations of superconductors that can easily form glass. The superconducting material was first formed as a glass; then, with subsequent devitrification, it was formed into a bulk crystalline superconductor by a series of processing methods.

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TECHNICAL MEMORANDUM

INTRODUCTION

The revolutionary and historic advances in high temperature superconductivity starting with La-Sr-CuO [1] and followed by the discovery of the 123 Y-Ba-CuO, [2] Bi-Sr-Ca-CuO, [3] and Th-Ba-CuO [4] oxide ceramics have become widely known. It has been shown that the Bi-Sr-Ca-CuO is a reasonably good glass forming system. [5-8] It was immediately recognized that if superconducting materials could be melted, formed into glass, and crystallized, there was a possibility for having a wide range of processing methods to shape the superconductor into monolithic shapes, filaments, and wires. [9-10]

The purpose of this study was to examine the critical cooling rates and glass formation ability for oxide high temperature superconducting materials. From the onset, it was known that modifications to the batch compositions would be required in order to enhance glass formation to the extent required to form bulk materials. The goal was to produce glass precursor material from which high superconducting critical transition temperature (T_c) crystalline glass ceramics could be produced.

Besides the obvious advantages of producing useful products from glass preforms, it is believed that the crystalline grain boundaries formed by in situ crystallization from the glass are fundamentally different from the crystal grain boundaries produced by the solid state diffusion processes. Interesting research into the current-limiting interface could be performed from detailed studies of superconducting glass ceramics.

EXPERIMENTAL PROCEDURE

The plan of the investigation was to evaluate the glass forming ability with emphasis on the compositional dependence of glass formation in the BSCCO system. The goal was to quantify the glass formation ability of the materials to find the best glass forming compositions. Glass formation data were obtained from quenching experiments, thermal analysis, and microstructural analysis studies of the materials.

The six compositions from the system Bi-Sr-Ca-Cu-O examined in this study are shown in Table 1 and are plotted on a triaxial diagram in Fig. 1 with Bi_2O_3 and CuO on two corners and the total of CaO plus SrO at the third corner. A literature search indicated 2112 and 4334 were prospective good glass forming candidates (Komatsu et al., 1988; Tatsumisago et al., 1989; Bhargave et al., 1989). The other compositions, including 2212, 2223, 2234, and 2245, were selected based on results of the literature search and preliminary results from this work. It should be noted that the batch proportions 2112, 4334, and 2212 represent the stochiometric proportions of the three known superconducting phases in this system.

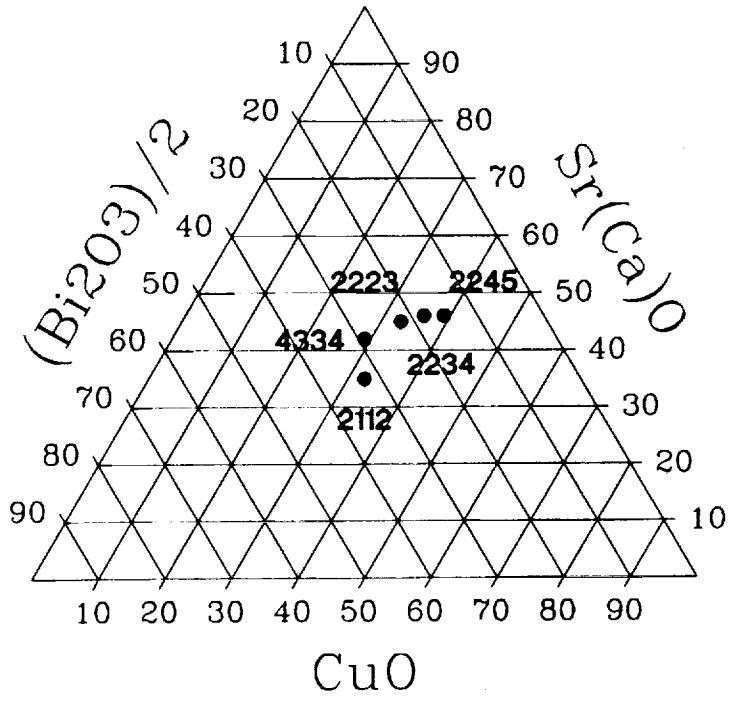


Figure 1. Triaxial composition diagram of the BSCCO glass ceramic compositions investigated in this study. The two alkaline Earth oxides, SrO and CaO, have been added together to facilitate the graphical representation.

Table 1. Nominal Compositions (Mole Fraction)

Sample	(Bi203)/2	SrO	CaO	CuO
2112	0.33	0.165	0.165	0.33
4334	0.286	0.21	0.21	0.286
2212	0.286	0.286	0.14	0.286
2223	0.222	0.222	0.222	0.333
2234	0.182	0.182	0.273	0.364
2245	0.154	0.154	0.308	0.385

Glass batches were produced using calcined reagent grade oxides and carbonate powders calcined at temperatures greater than 500 °C and stored in desiccators. The appropriate oxide or carbonate for each constituent was precisely weighed, the batch was mixed, charged into platinum crucibles, and melted in a SiC furnace in air at around 1250 °C to 1300 °C for less than 30 minutes. The molten material was very fluid for all the batches tested. To ensure that the melt was homogeneous, the crucible containing the melt was briefly removed from the furnace and swirled to mix the liquid and then returned to the furnace.

Splat quenches were performed by pouring the melt onto a graphite plate and pressing with another graphite plate, both initially at room temperature. Spacers of various thicknesses were used to produce foils of different thicknesses resulting in a range of cooling rates, with the thinner samples having the higher cooling rates. The foil-shaped samples were examined and a subjective qualitative evaluation of the extent of glass formation was made from observations of the fracture surfaces of the quenched samples using optical and scanning electron microscopy.

For some quench runs the actual cooling rate was measured by inserting a fine (0.005 in. diameter) wire type S platinum thermocouple into the melt immediately upon pouring and prior to pressing of the graphite plates. A computer-controlled, rapid thermal analysis system permitted the high resolution and high data rate quenches and the subsequent determination of the cooling rates of the splatted melts. The temperature data in the form of a millivolt signal from the thermocouple was collected at 10 ms intervals for a total of 10 seconds via Keithly System 500 Data Acquisition and a MSDOS PC-AT type computer. Unexpected problems were encountered with the thermocouple measurements. Wildly fluctuating millivolt values representing temperatures from below zero to several hundred degrees above the starting melt temperature were recorded in the glass melt. This is attributed to electrical conduction in the melt and thermoelectric effects between the thermocouple wires and the melt. It was found that an insulating layer of lacquer applied to the thermocouple usually prevented this electrical interaction between the melt and the thermocouple elements. The lacquer immediately burnt on contact with the hot glass and although not every measurement was successful, useful data were obtained in many cases. Cooling rates ranging from 50 °C/sec to 4000 °C/sec were measured.

The rapid thermal analysis apparatus (RTAA) and the high temperature strip heater furnace designed at MSFC were used to study glass formation in reluctant glass forming systems. The RTAA consists of an ellipsoidal furnace that has been automated for computer control and data acquisition; see Fig. 2. Repeated heating and quenching can be accomplished under unattended software control with thermal data being saved to hard disk in Lotus 123 compatible files.

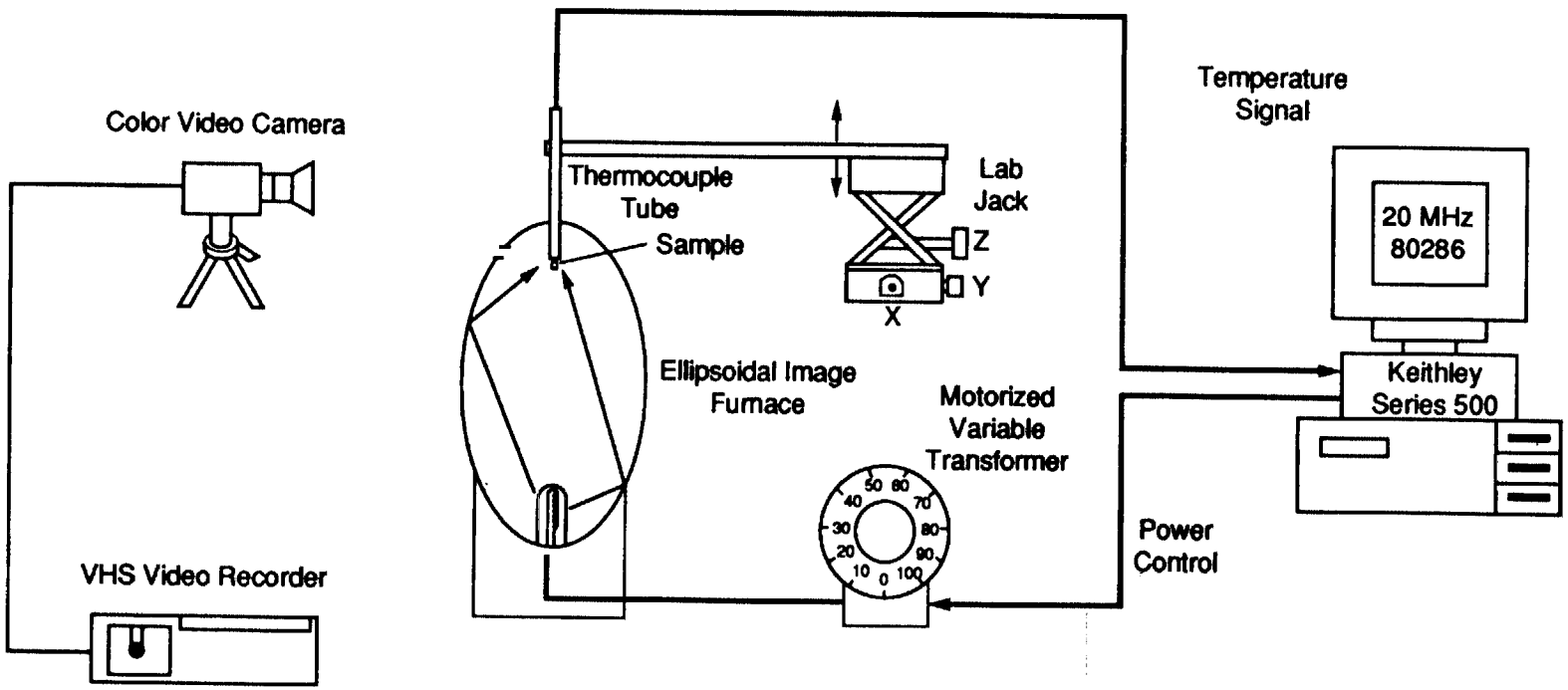


Figure 2. The MSFC Automated Rapid Thermal Analyzer utilized for nucleation and crystallization studies on the glasses.

A strip heater was utilized for sample preparation for use in the RTAA. Pieces of premelted glass were placed onto Pt strip heater foil. The voltage was ramped up until melting was observed. A prefabricated fine gauge type S platinum thermocouple connected to a thermocouple meter was inserted into the molten material to produce a superconducting coating on the thermocouple bead.

Differential scanning calorimetry and differential thermal analysis are very useful methods for the investigation of nucleation kinetics. It was recognized that our group needed a state-of-the-art system for these studies and to correlate thermal data obtained with known methods with those obtained with the RTTA. At the beginning of the study a differential scanning calorimeter was ordered. Due to the long procurement time it did not arrive until nearly 1 year after the scheduled completion of the study. In the interim we were able to utilize an Omnitherm STA 1500 DTA/TG at the Co-I's UAH laboratory.

The research was focused on the processing of compositions that could form the highest temperature superconducting phases. Initial experiments indicated that compositions around the stoichiometric high T_c phase could be quenched to glass quite easily. The glass could then be transformed into the high T_c phase with the appropriate thermal annealing process. Glass batches of a number of BSCCO compositions were prepared. The good glasses were crystallized and annealed in an oxygen-containing atmosphere in the temperature range of 775 °C to 825 °C for extended times (1 to 48 hours) to develop the high temperature superconducting phases. Superconducting properties of nominally 50 mg size samples were determined with a Quantum Design Magnetic Measurement System SQUID magnetometer using standard procedures.

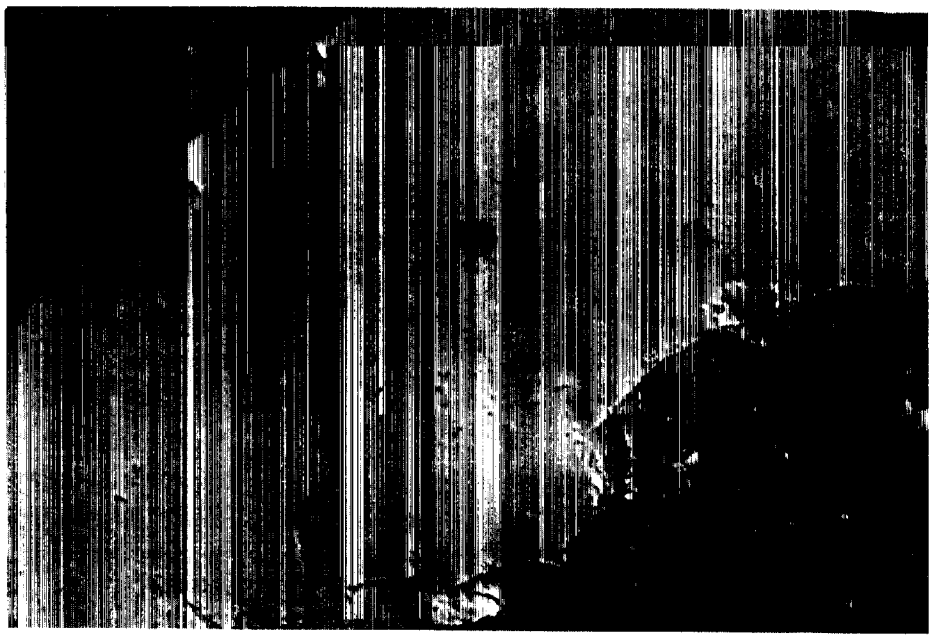
RESULTS AND DISCUSSION

Some of the results from this study have been reported. [11-14] Figure 3 shows a collection of optical micrographs of glass samples from four selected compositions in the as-quenched state prepared by splat quenching between graphite plates. The uniform areas of material without structural detail are amorphous regions. Some small crystallites are frequently found within the amorphous continuous phase, but represent only a small fraction of the total bulk material. Glass formation was confirmed with x-ray diffraction, microscopy, and thermal analysis. The best glasses were formed from the 2112 and 4334 compositions.

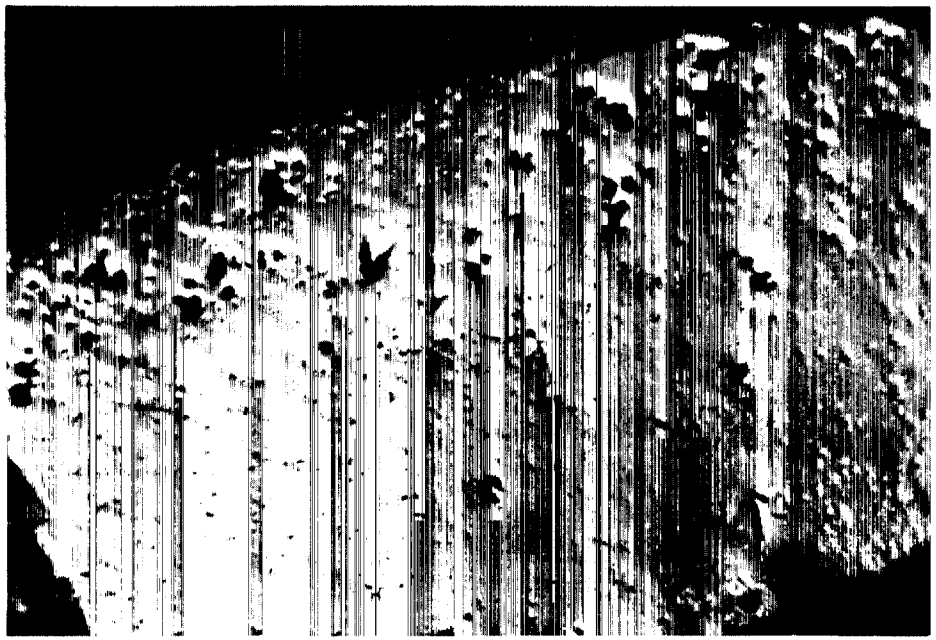
The 2112 batch is the easiest glass former of the set and appears to have the lowest melting temperature. Glass formation was also found over a wide range of quench rates with both 2112 and 4334. Glass formation is favored by compositions closer to the Bi_2O_3 corner of the diagram (Fig. 1) as indicated from published results with 2.7,1,1,2 and our results with 2112. The two compositions (4334 and 2212) have the same ratios of Bi_2O_3:CuO:SrO (CaO) and therefore appear on the same point in Fig. 1; however, the glass formation ability is not similar. The 4334 composition has more CaO (less SrO) and is a better glass former. It is also a better high T_c glass ceramic. This indicates that extra CaO enhances both glass formation and high T_c properties in the glass ceramic.

Glass formation ability decreased as the percentage of Bi_2O_3 decreased and the series of batches 2223, 2234, and 2245 were relatively poor glass formers. Even splatting to very thin foils did not produce glasses from these compositions. The latter two melted with difficulty and were also the poorest glass formers.

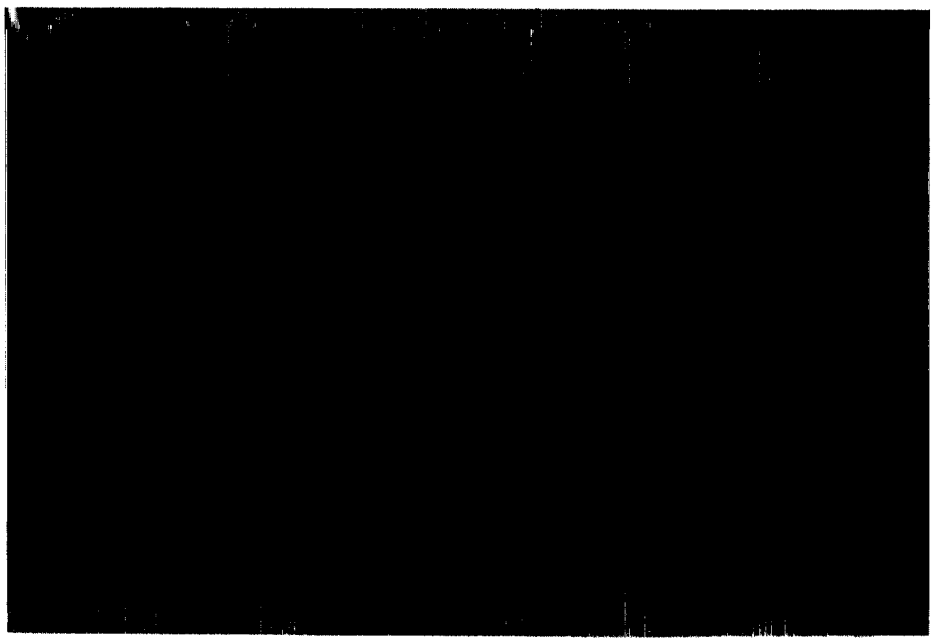
2112



4334



2223



2212

Figure 3. Light micrographs of polished surfaces of four as-quenched glasses.

Estimates were made of the critical cooling rates for glass formation based on a set of quenches covering a wide range of quench rates. Critical cooling rates for formation were measured as low as 200 °C/sec for the good glass formers and as high as 2000 °C/sec for the poor glass formers. Typical cooling curves produced by rapid cooling between graphite plates are shown in Figs. 4, 5, and 6. Quench rates from 50 to 4000 °C/sec could be obtained. Analysis of the data was performed using a spreadsheet to permit plotting the cooling curves and their derivatives to determine cooling rates. Most of the quenches were in the range from 60 to 800 °C/sec. Table 2 shows qualitative data on the extent of glass formation, sample thicknesses, and quench rates for some of experiments.

In several hundred quenching experiments with the automated rapid thermal analyzer it was shown that many of the compositions from the BSCCO system are glass formers without the addition of glass forming additives. The RTA was also used to quench samples to determine critical cooling rates. Figures 7a and 8a show quenching and reheating curves, respectively, for 2112, whereas Figs. 7b and 8b show the calculated derivative of the cooling (heating) curve, which is the instantaneous quenching or heating rate.

Rapid thermal analyzer quenching data from sample 2112 using the automated rapid thermal analyzer are shown in Fig. 7. Figure 7a shows the temperature data, whereas Fig. 7b shows the derivative of the temperature data calibrated in °C/sec being equivalent to an uncalibrated plot of heat capacity. One can see an inflection in the cooling curve at about 780 °C. This is an anomalous heat capacity effect at glass transition. Before the glass transition the cooling rate is 275 °C/sec and after the glass transition the cooling rate is 325 °C/sec. This indicates that the heat capacity of the undercooled liquid is more than the heat capacity of the glass, which is reasonable for most oxides.

Figure 8 shows reheating data from the rapid thermal analyzer for a glass sample of 2112 (8a) and the calculated delta temperature data (8b). The plot of cooling rate vs. time (temperature) is very similar to conventional differential thermal analyzer (DTA) data. A peak indicating an increased heating rate corresponds to an exotherm (i.e., glass crystallization being attributed to a peak at about 520 °C). Endotherms are indicated by a decrease in the heating rate (i.e., glass transition at 460 °C). Melting begins with an endotherm at about 760 °C.

Crystallization from glass is most dependent on the viscosity of the undercooled liquid. A viscometer was ordered and set up for measurements. Utilizing viscosity data for composition close to 2112, theoretical nucleation and crystal growth calculations were performed with Math-CAD. Calculations of the crystallization rate were performed. These classical calculations predicted glass formation in agreement with the splat quenching and RTAA experiments. [13-15] Based on these experiments we found the crystallization behavior of these glasses is similar to the LBAN class of fluoride glass. A wealth of information exists for the formation of glass fibers and bulk performs of the low viscosity fluorides. The same processing methods might be utilized to produce useful shapes from the high temperature superconductors.

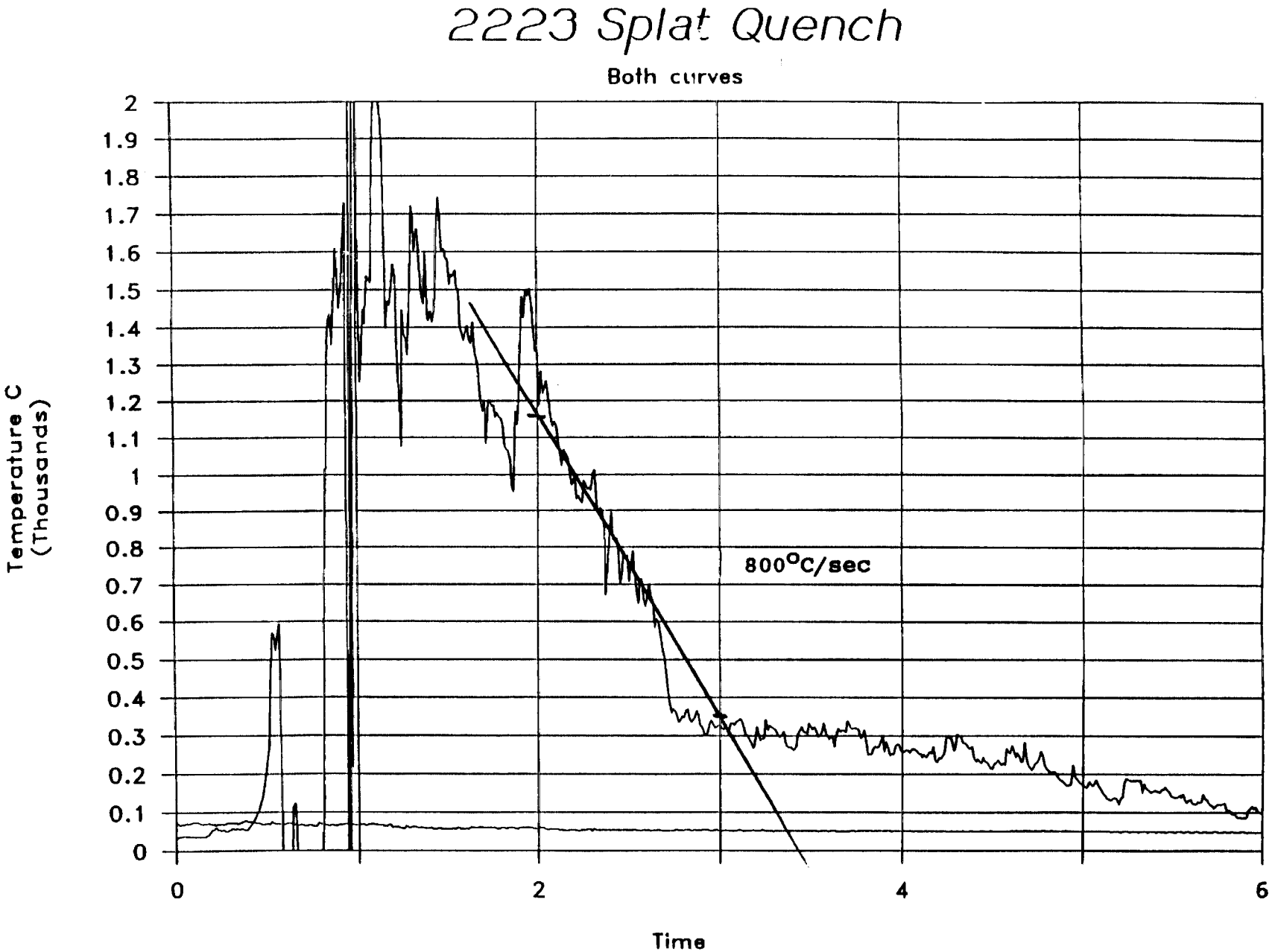


Figure 4. Quenching thermal plot for a splat quenched 2223 composition (temperature °C vs. time in sec). In spite of the noisy signal caused by residual EMF effects between the molten material and the thermocouple, the quench rate is approximately 800 °C/sec.

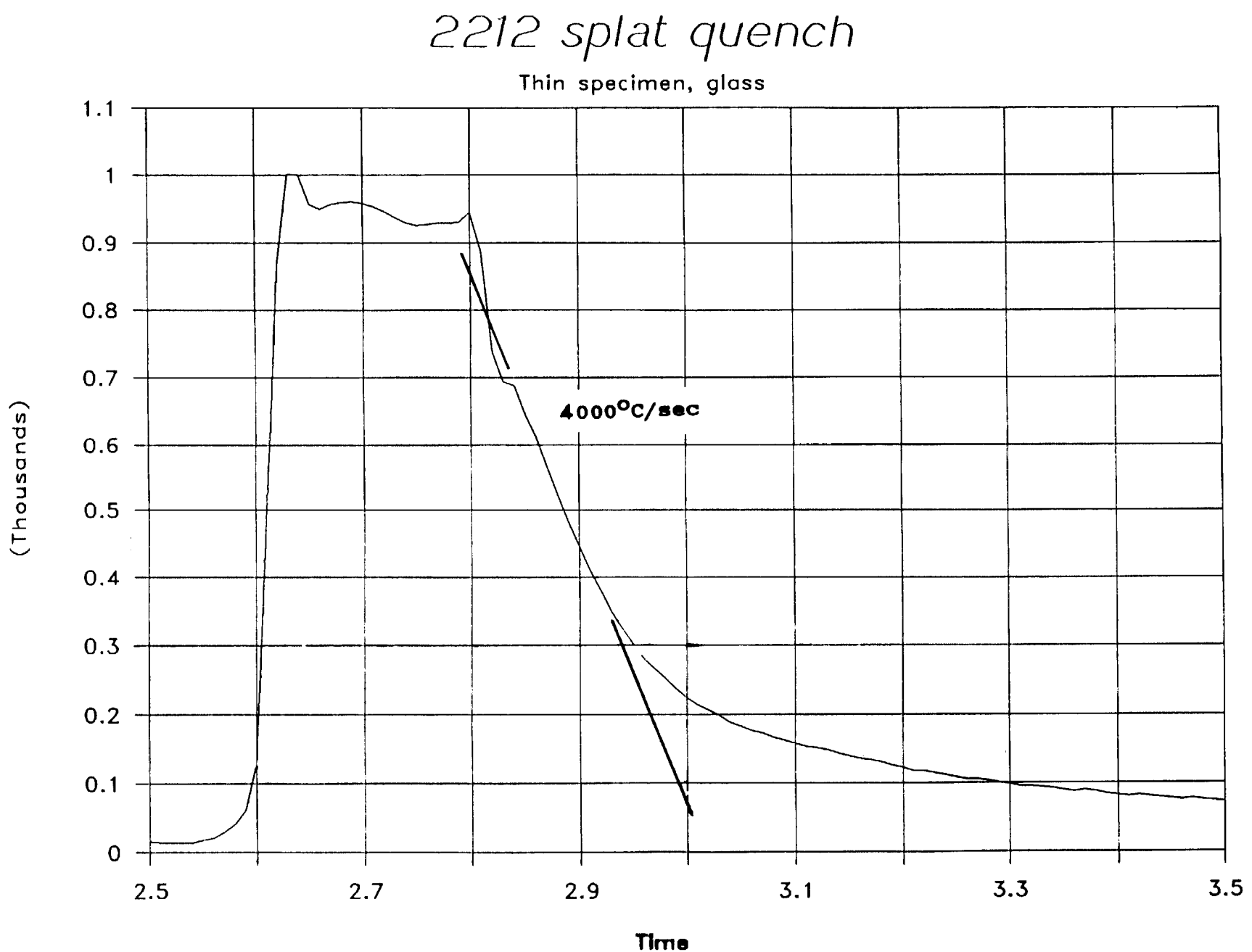


Figure 5. Rapid splat quench of 2212 with very little thermal noise. The quench rate is 4000 °C/sec. One can see a slight inflection in the cooling curve at about 690 °C. This is caused by the passage through the glass transition temperature at this temperature at the very fast cooling rate.

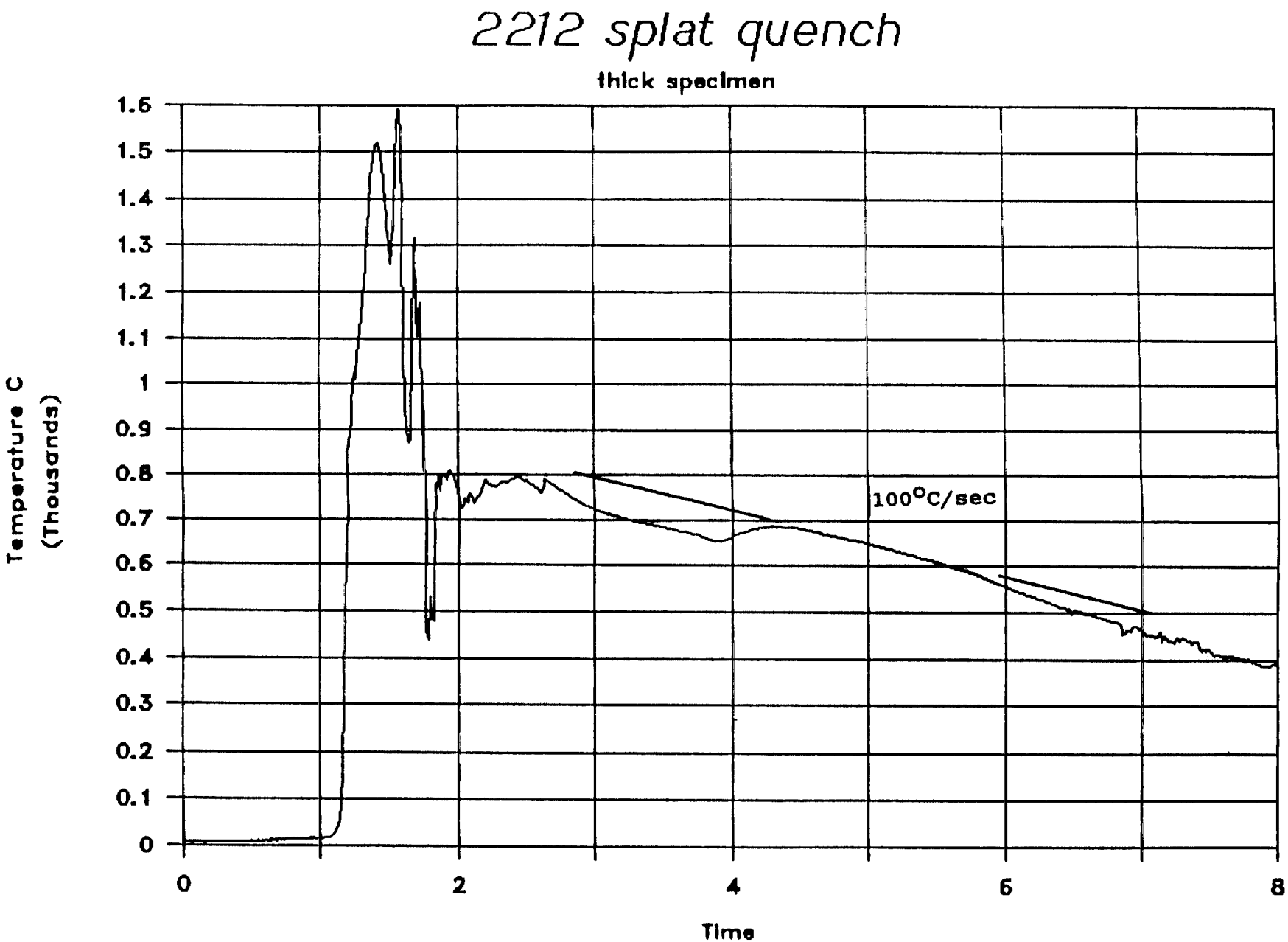
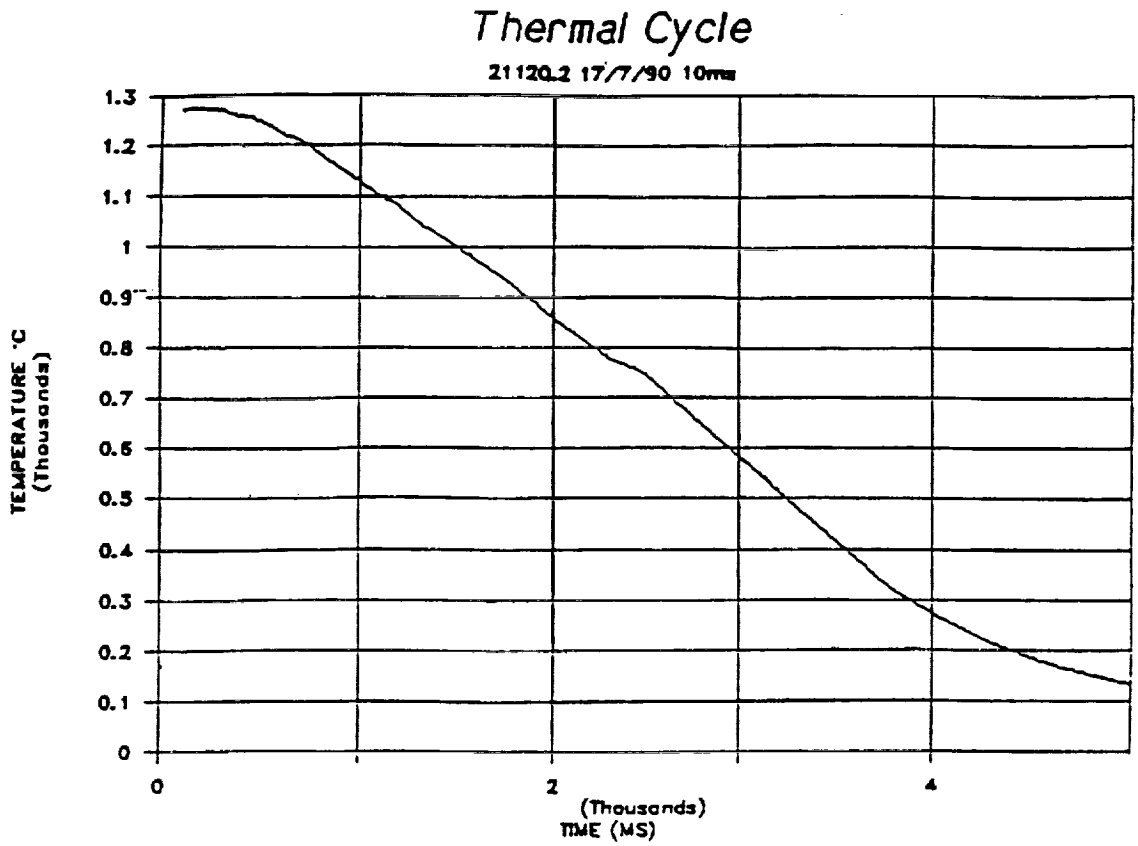


Figure 6. Thermal plot for a slowly quenched sample of 2212 with a quench rate of approximately 100 °C/sec. One can see an inflection of the cooling curve at about 650 °C/sec caused by the release of latent heat of fusion during the crystallization of this sample.

TABLE 2. Glass Formability in the BSCCO System

Composition	Thickness (mm)	Glass Formation (vp, p, g, vg)*
2112	0.55	g
2112	0.58	g
2112	0.66	vg
2112	0.67	g
2112	0.82	vg
2112	3.87	vp
4334	0.49	g
4334	0.55	vg
4334	1.44	vg
4334	2.12	p
4334	3.22	p
2212	0.49	g
2212	0.51	vg
2212	0.56	g
2212	1.25	vp
2212	1.80	p
2212	3.23	p
2223	0.68	vg
2223	0.70	vg
2223	0.71	vg
2223	0.76	vg
2223	0.92	vg
2223	1.13	vg
2223	1.22	vg
2223	1.29	g
2223	1.35	g
2234	0.59	vg
2234	0.63	vg
2234	0.94	g
2234	0.99	g
2234	1.4	g
2234	1.56	g
2245	0.2	-
2245	thin	-
2245	0.91	p
2245	0.94	p
2245	1.41	p

*vp = very poor; p = poor; g = good; vg = very good



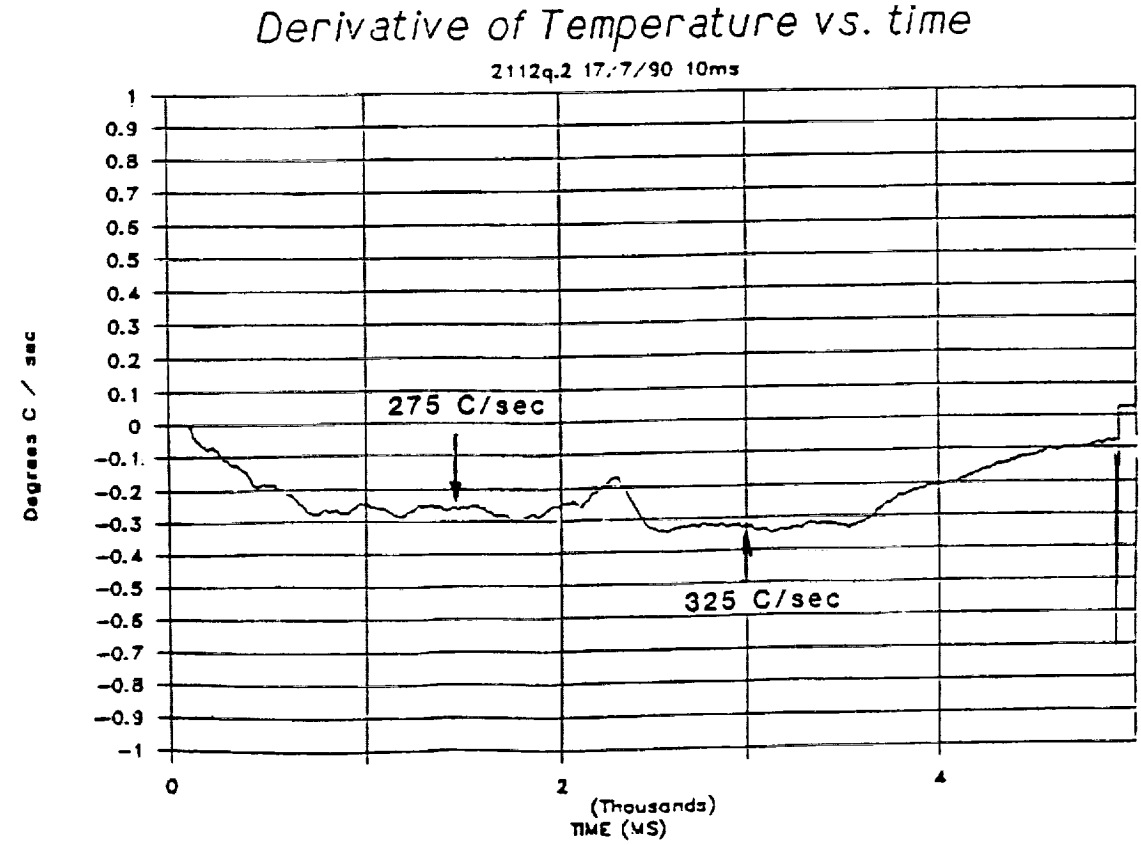
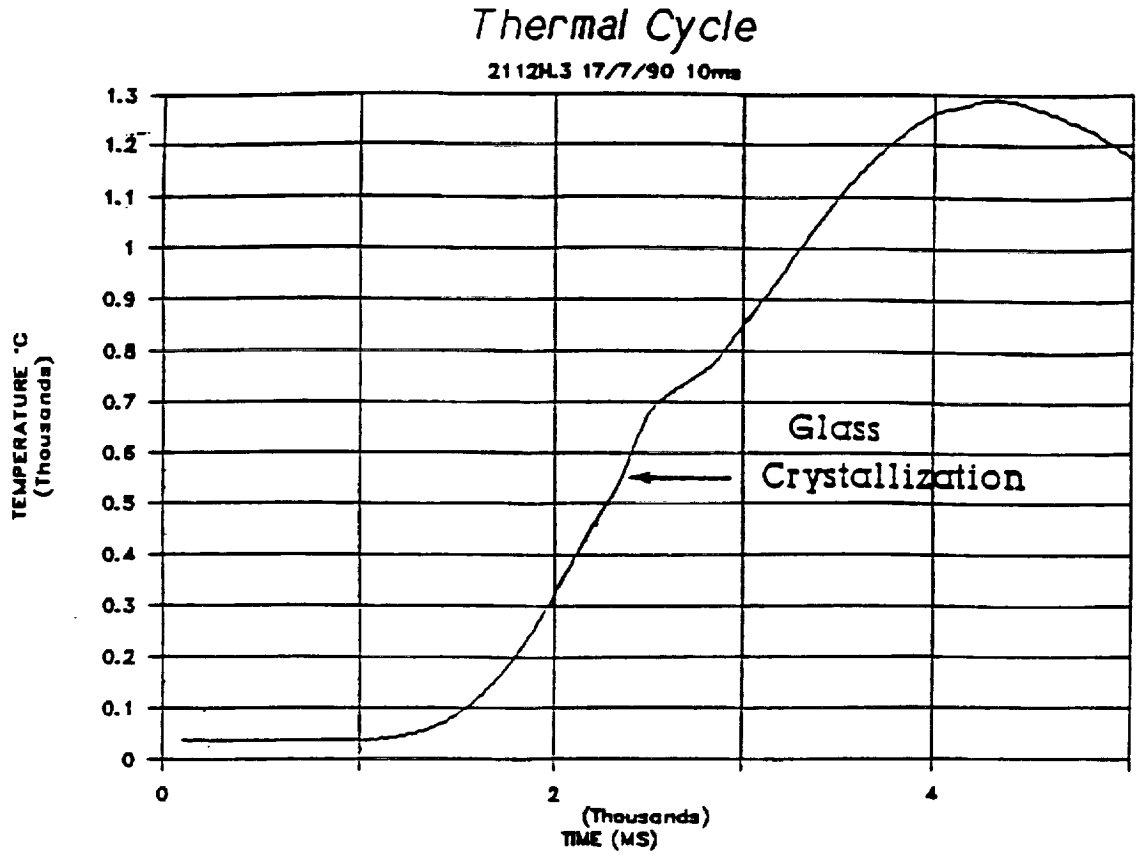


Figure 7. Rapid thermal analyzer quenching data from sample 2112 using the automatic rapid thermal analyzer. Figure 7a is the temperature data; Fig. 7b is the derivative of the temperature data calibrated in °C/sec being equivalent to an uncalibrated plot of heat capacity.



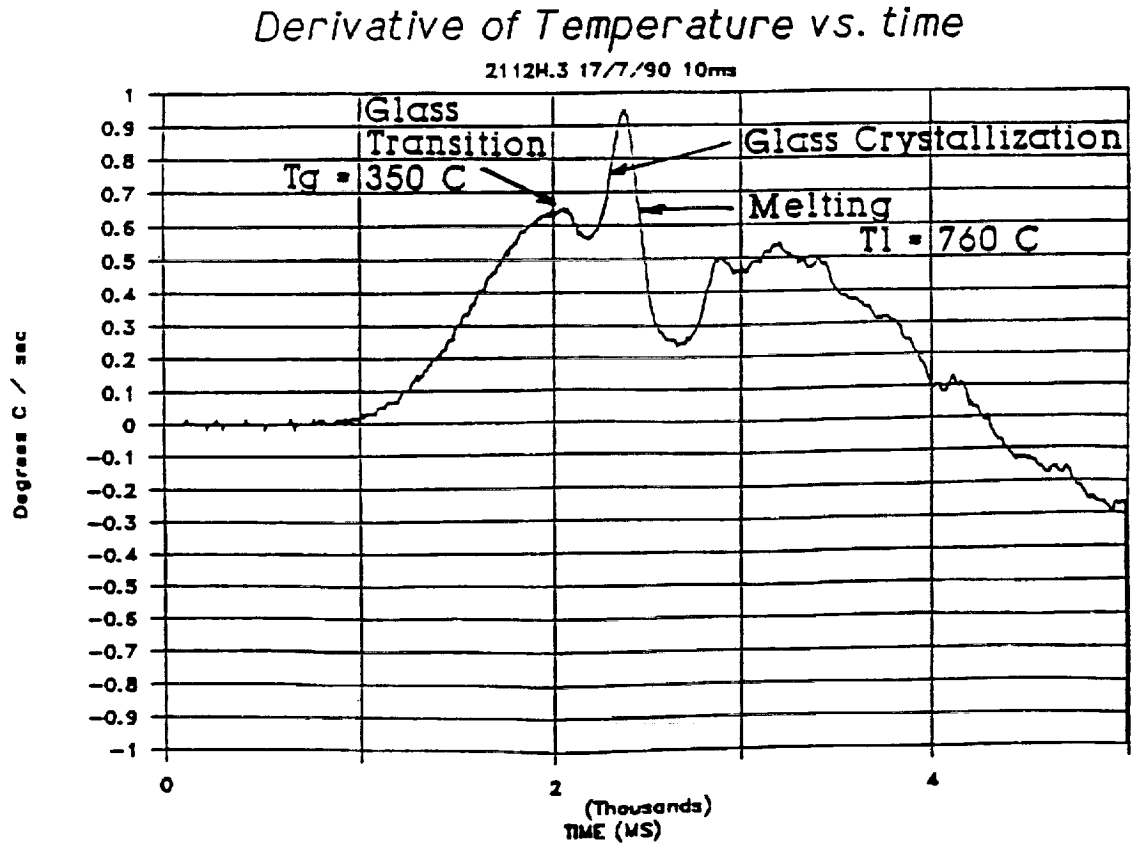


Figure 8. Reheating data from the rapid thermal analyzer for a glass sample of 2112 (8a) and the calculated delta temperature data (8b).

Annealing of the glassy specimens in oxygen or air is required to recrystallize the specimen into a useful superconducting material. Broken, bulk pieces were annealed in air at 800 °C for 20 hours followed by soaking at 825 °C for 86 hours in oxygen. Since 2112 showed signs of melting at the above conditions, the annealing was performed at 775 °C in air for 20 hours and then in oxygen for 72 hours. Some measurements of annealed specimens have been made at UAH with the Quantum Design SQUID Magnetometer, a JEOL SEM, and a Norelco X-Ray Diffraction Analyzer. Optical microscopy was performed on polished sections of both splatted and annealed specimens. Based on these observations, it appears two main phases are forming in these materials after annealing. Depending on the batch composition, the glassy splats show varying small volume fractions of crystalline inclusions, as may be seen in Fig. 3. All splats for all batches showed at least a tiny fraction of crystalline phase. Some, like 2212 and 4334, showed significant quantities of crystalline phases. These phases lose their identity after annealing. With 4334 splats, the crystalline, acicular, needle-like precipitates were found emanating inward from the quench surfaces indicating a susceptibility for surface heterogeneous nucleation.

The magnetization vs. temperature of the resulting glass ceramics for four of the samples is shown in Figs. 9, 10, 11, and 12. Diamagnetism as indicated by a negative value for magnetization on this plot is confirmation of the presence of superconducting phases in the sample. The extent of diamagnetism is proportional to the volume fraction of superconducting phase. Figure 9 shows that the glass ceramic produced from the good glass forming 2112 composition contained primarily one superconducting phase, 2212 with a T_c of 82 K. As can be seen in Figs. 10, 11, and 12, glass ceramics from the glass batches 2212, 2223, and 4334 contained the same two superconducting phases, 2212 and 2223, with superconducting transition temperatures of 110 K and 85 K, respectively. One of the best glass formers, 4334, contained the largest concentration of the highest onset transition temperature for superconductivity (110 K); see Figure 12.

DTA analysis of the quenched amorphous specimens was performed in air using heating and cooling rates of 2 °C/min. Glass transition temperatures, crystallization temperatures, melting points, etc. were obtained for a number of samples. The glass transition, crystallization, and apparent de-oxygenation temperatures were measured. There was little difference in the devitrification temperatures and de-oxygenation temperatures among the various compositions tested. The onset of devitrification was found to be around 400 °C and oxygen uptake by the devitrified material becomes significant in this same general temperature range (Minami et al., 1989; Yoshimura et al., 1988). But, it is only after annealing at 750 °C to 800 °C that these materials show evidence of the presence of one or more superconducting phases. The details of these important oxygenation and glass ceramic crystallization studies are to be reported in a subsequent NASA Technical Memorandum [13].

CONCLUSIONS

Glass formation in the BSCCO system is relatively good. High T_c crystalline ceramics can be produced from glass ceramics produced from these glasses. The glass ceramics contain significant volume fraction of high T_c superconducting phases. These results are supportive proposals to produce high T_c glass ceramics from glass preform monolithic bodies and fibers. More work is indicated for examining the oxidation reduction behavior of glass formation and the effects on high T_c phase production.

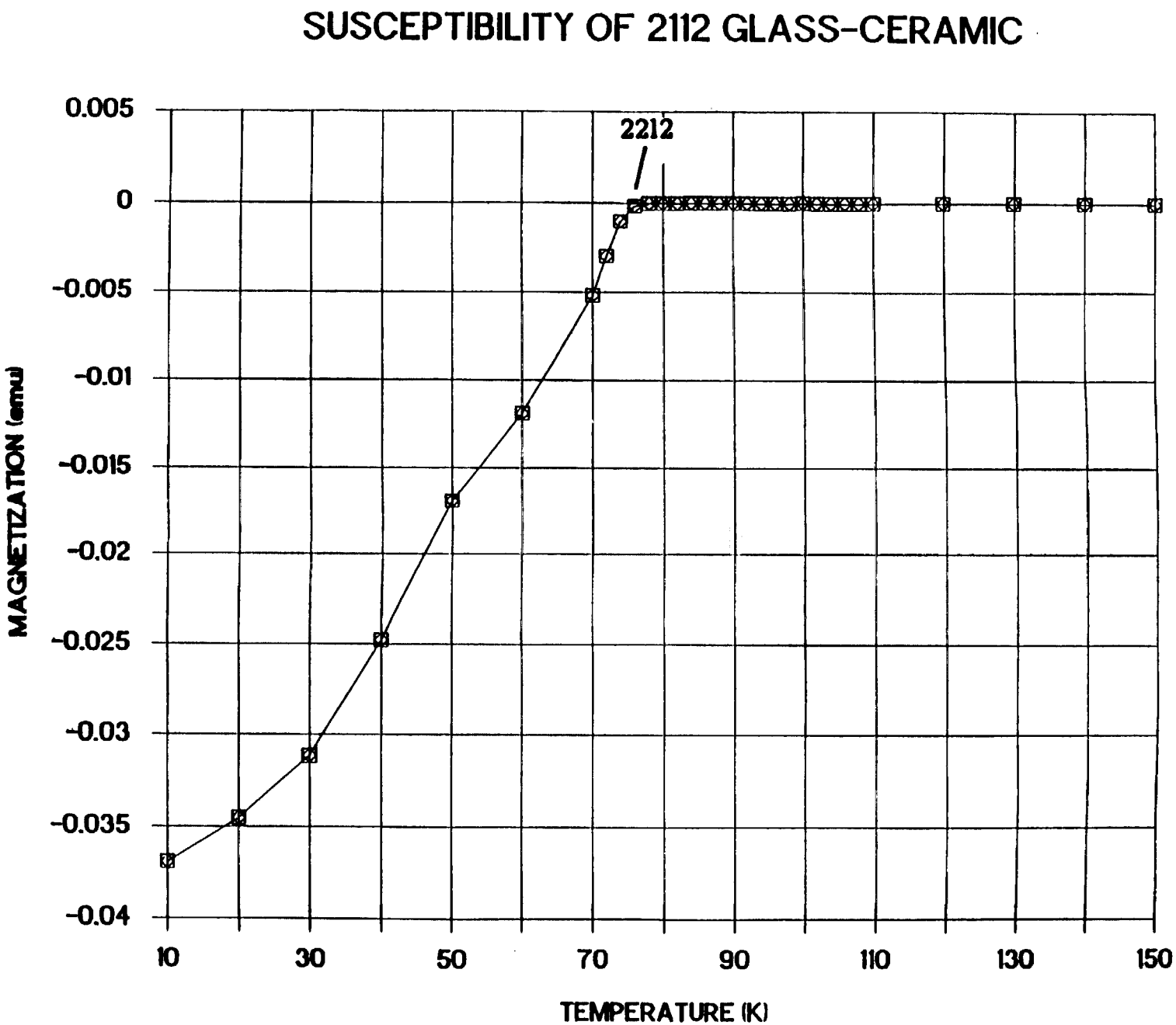


Figure 9. Magnetization vs. temperature for 2112 glass ceramic. Onset of superconductivity at 76 K is indicative of a single superconducting phase of 2212.

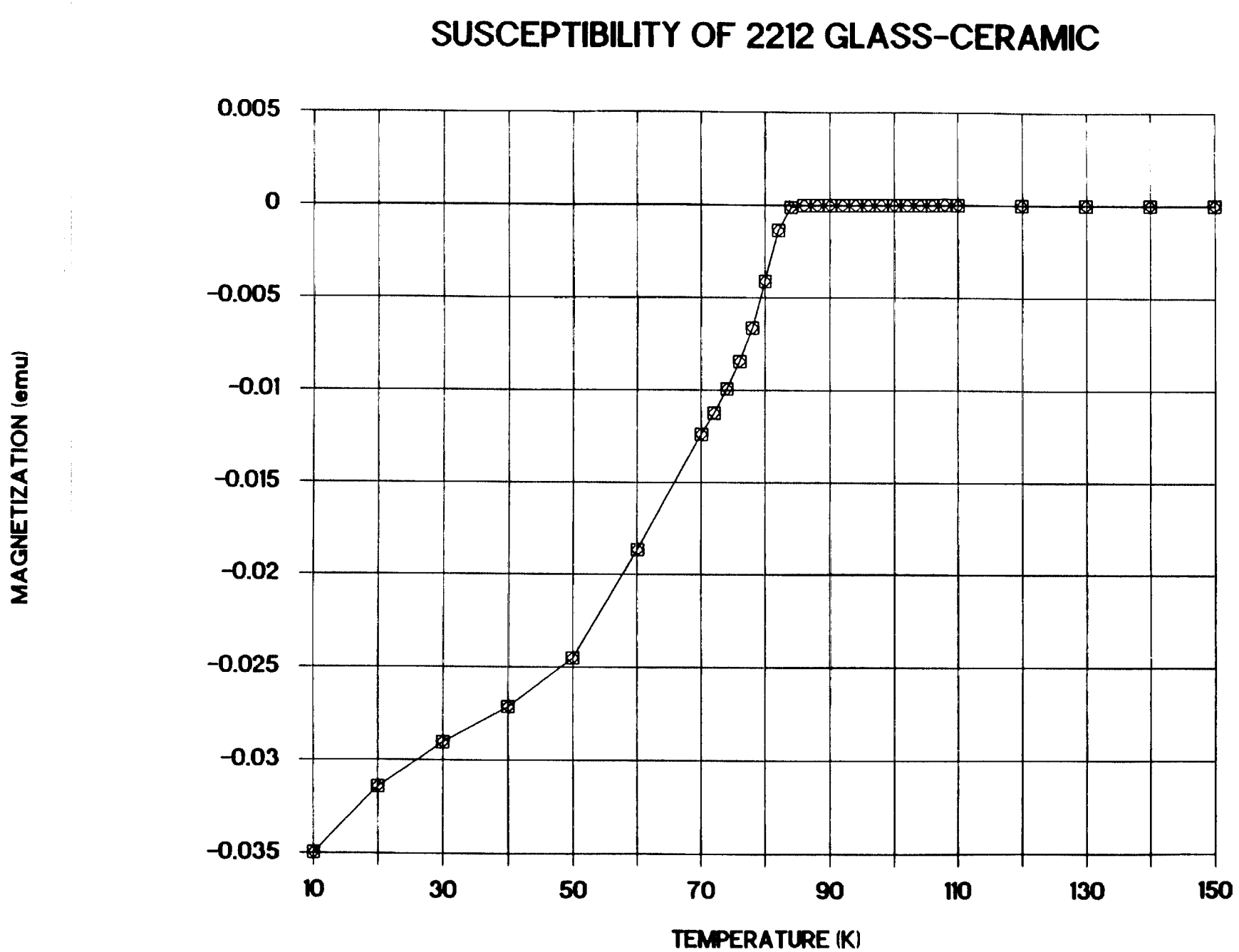


Figure 10. Magnetization vs. temperature for 2212 glass ceramic. Onset of superconductivity at 84 K is again indicative of a single superconducting phase of 2212.

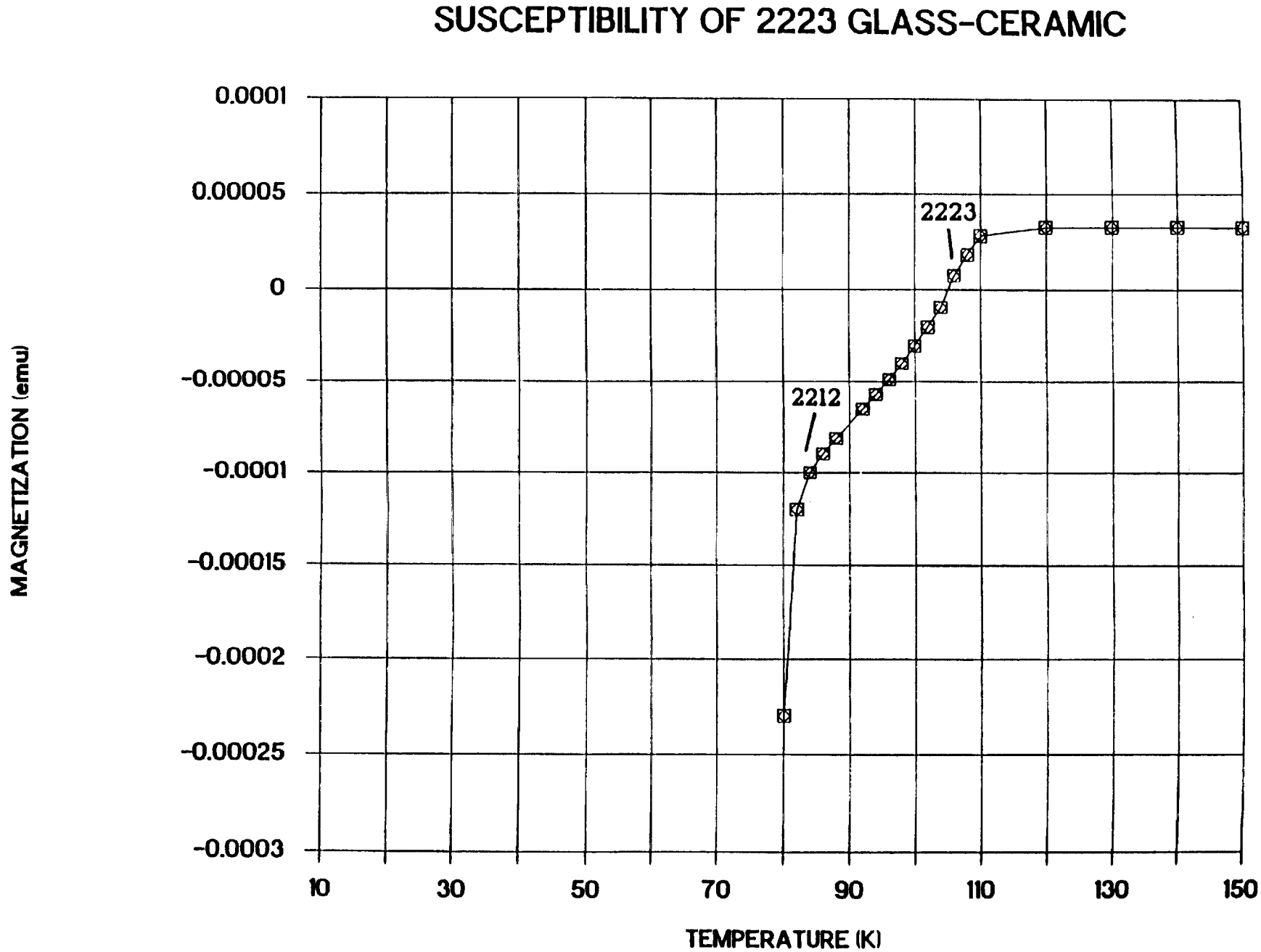


Figure 11. Magnetization vs. temperature for 2223 glass ceramic. Two superconducting onset transitions at 105 K and 83 K indicate the presence of the two superconducting phases 2223 and 2212.

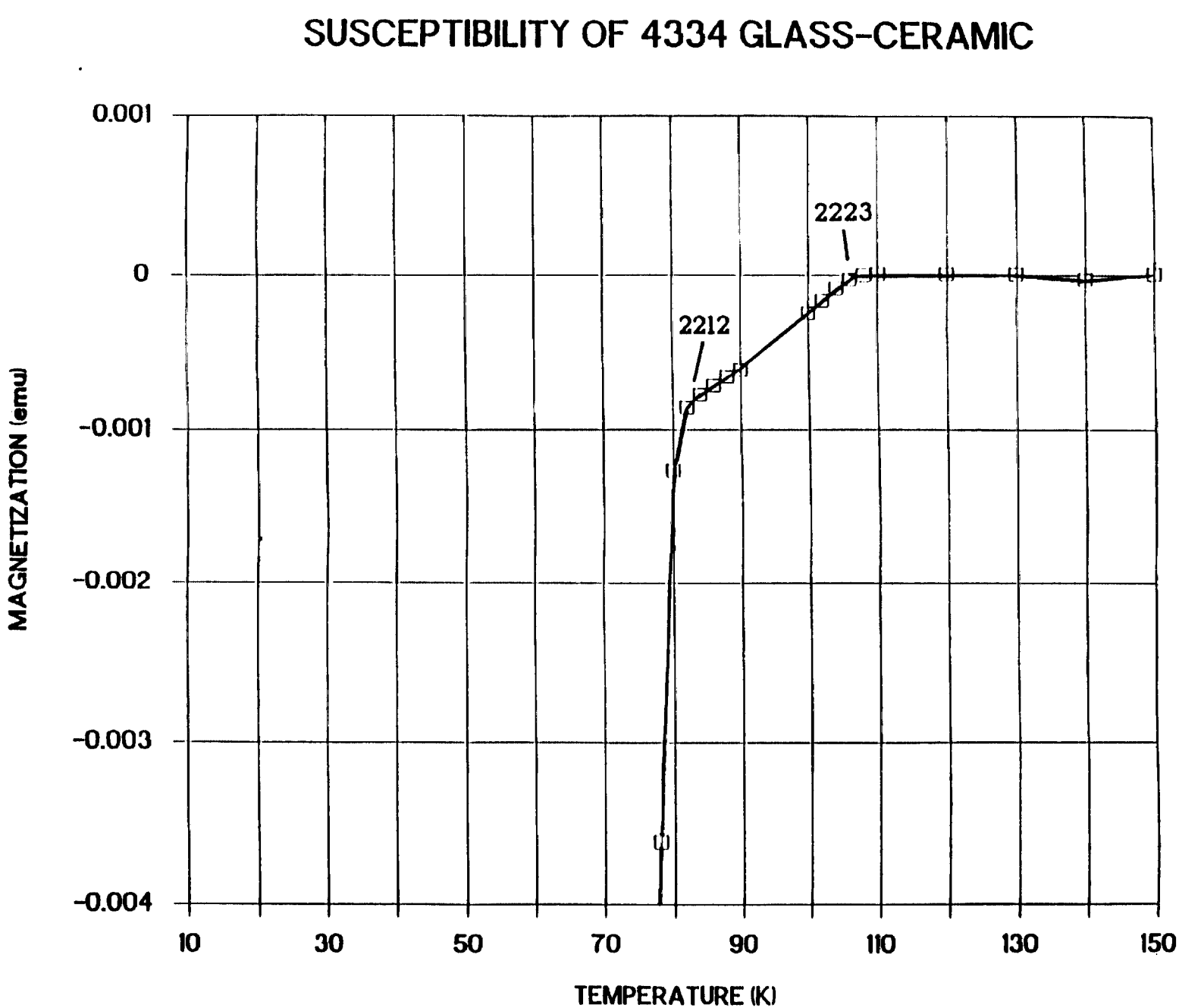


Figure 12. Magnetization vs. temperature for 4334 glass ceramic with an initial superconducting onset temperature of 108 K and a second superconducting transition at 83 K.

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APPROVAL

STUDY OF THE GLASS FORMATION OF HIGH TEMPERATURE SUPERCONDUCTORS--CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT (PROJECT #89-04)

By

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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