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GLASS-CERAMICS: CENTER DIRECTOR'S
DISCRETIONARY FUND FINAL REPORT
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**OPTIMIZATION OF THE PROCESSING PARAMETERS
OF HIGH TEMPERATURE SUPERCONDUCTING
GLASS-CERAMICS--CENTER DIRECTOR'S
DISCRETIONARY FUND FINAL REPORT
(PROJECT #91-04)**

By E. C. Ethridge and W. F. Kaukler

**Space Science Laboratory
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E. C. Ethridge and W. F. Kaulker*

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A number of promising glass forming compositions of high T_c superconducting Ba-Sr-Ca-Cu-O (BSCCO) materials were evaluated for their glass-ceramic crystallization ability. The BSCCO ceramics belonging to the class of superconductors in the Ba-Sr-Ca-Cu-O system were the focus of this study. By first forming the superconducting material as a glass, subsequent devitrification into the crystalline (glass-ceramic) superconductor can be performed by thermal processing of the glass preform body. Glass formability and phase formation were determined by a variety of methods in another related study. This study focused on the nucleation and crystallization of the materials. Thermal analysis during rapid cooling aids in the evaluation of nucleation and crystallization behavior. Melt viscosity is used to predict glass formation ability.

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TECHNICAL MEMORANDUM

OPTIMIZATION OF PROCESSING PARAMETERS FOR HIGH TEMPERATURE SUPERCONDUCTING GLASS-CERAMICS -- CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT (PROJECT #91-04)

INTRODUCTION

It has been shown that the Bi-Sr-Ca-Cu-O (BSCCO) system contains a glass-forming region and certain compositions are reasonably good glass-forming materials.[1-4] It was quickly recognized that if superconducting materials could be melted, formed into a glass body, and subsequently crystallized, there was a possibility for having a wide range of processing methods to shape the superconductor into monolithic shapes as well as filaments and wires.[5,6] 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.

This study is a continuation of the MSFC Center Director's Discretionary Fund Project (#89-04). Some of the results from this study have been reported elsewhere.[7-11] The glass-forming ability was evaluated with emphasis on the compositional dependence of glass formation in the BSCCO system and the glass formation ability was quantified so as to find the best glass-forming compositions. Information about glass formability was obtained from quenching experiments, thermal analysis, and microstructural analysis studies of the materials. This continuing investigation examines the nucleation and crystallization with the intent of determining likely glass-ceramic processing conditions.

Glass-ceramics are fine grain polycrystalline materials that are formed from glass precursors. A distinct advantage of glass-ceramics is that traditional glass-forming methods can be utilized to prepare the body of the finished product with no subsequent machining or forming being required. After the glass article is prepared, the body undergoes a predetermined crystallization process to produce the fine polycrystalline finished product. Crystallization greatly toughens the body. Examples are Corning Glass Works' Pyroceram products. The advantage for high T_C superconductors is that fibers or films could be produced to the final shape followed by crystallization of the High T_C crystalline phases.

The glass-ceramic thermal processing procedures are dependent on the crystallization kinetics of the particular ceramic system. Figure 1 illustrates three cases based on differing nucleation and crystallization regimes. In Fig. 1a the rates of significant nucleation and crystallization are separated along the temperature line with no overlap. These conditions

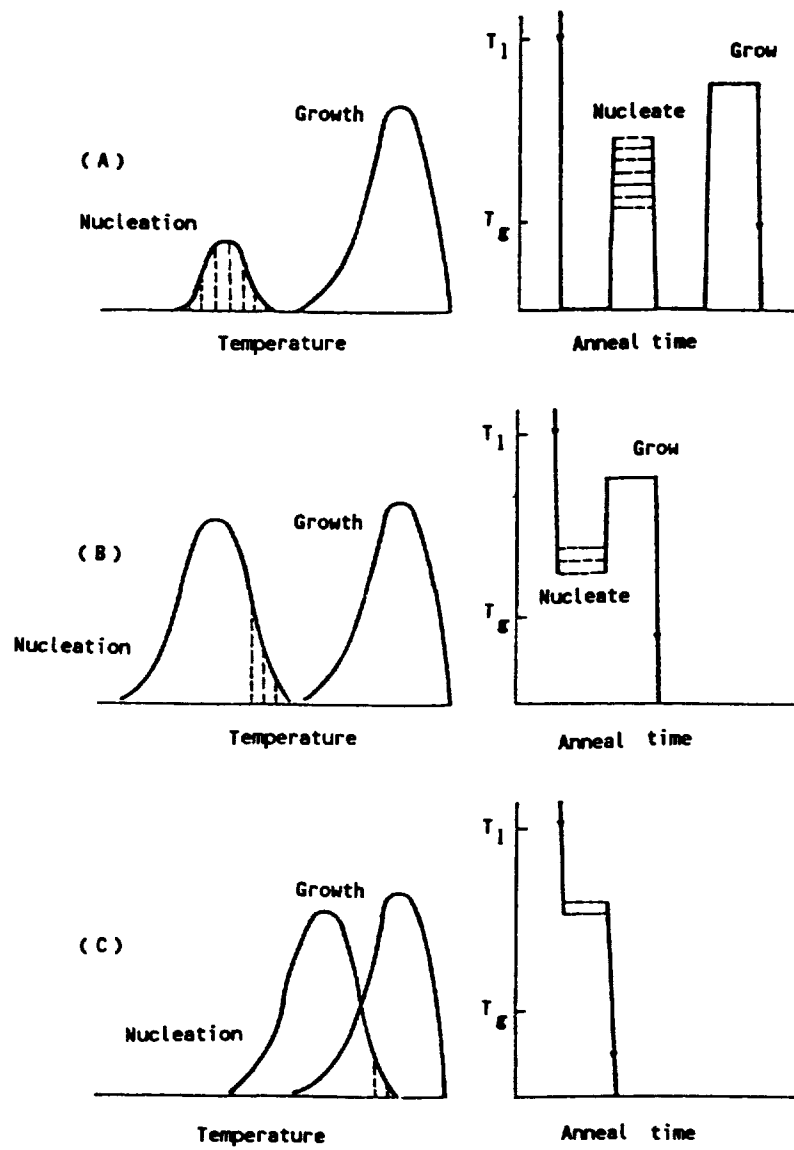


Figure 1. Schematic glass-ceramic processing cycles for three classes of nucleation and crystal growth behavior.

permit the quenching of the glass article to ambient conditions, then at convenience reheating for nucleation, followed by completion of crystallization at a higher temperature. When a significant overlap of the nucleation and crystal growth curves begins (Fig. 1b), it may become necessary to quench only into the temperature region for optimal nucleation followed by a reheat into a rapid crystal growth region to complete crystallization. When the nucleation and crystallization curves seriously overlap, it may be necessary to quench rapidly into the overlap region, hold for a short time, and then quench. The purpose of this investigation was to continue the investigation of the glass/ceramic processing conditions with emphasis on understanding the processes involved in the conversion of glass to polycrystalline superconductors.

EXPERIMENTAL PROCEDURE

Six glass forming compositions from the system Bi-Sr-Ca-Cu-O examined in this study are shown in Table 1. A literature search [2-4] indicated 2112 and 4334 were prospective good glass-forming candidates. 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 2223 and 2212 represent the stoichiometric proportions of known superconducting phases in this system with transition temperatures 110 K and 86 K, respectively.

TABLE 1. Nominal Compositions (mole fraction)

Sample	(Bi ₂ O ₃)/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 reagent grade oxides and carbonate powders calcined at temperatures higher 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 1250 °C to 1300 °C for less than 30 minutes (to avoid constituent loss due to vaporization). 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.

The research 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. Glass batches of a number of BSCCO compositions were prepared. The glass could then be transformed into the high T_c phase with the appropriate thermal annealing process. The good glasses required crystallization and annealing 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. Superconductivity properties of nominally 50 mg size samples were determined with a Quantum Design Magnetic Measurement System SQUID magnetometer using standard procedures.

Differential scanning calorimetry and differential thermal analysis are very useful methods for the investigation of nucleation kinetics. A high temperature differential thermal analysis (DTA) system was purchased with the CDDF resources and was used to correlate thermal data obtained by known methods with that obtained with the MSFC Rapid Thermal Analyzer and calculated from classical nucleation and crystallization kinetics.

RESULTS AND DISCUSSION

Glass formation in the BSCCO system was confirmed with x-ray diffraction, microscopy, and thermal analysis. The best glasses were formed from the 2112 and 4334 compositions. Glass formation was possible over a wide range of quench rates with both 2112 and 4334. The 2112 batch is the easiest glass former of the set and also appears to have the lowest melting temperature.

Depending on the batch composition, the glassy splats may show varying small volume fractions of crystalline inclusions. All splats for all recipes showed at least a tiny fraction of crystalline phase. With 4334 splats, the crystalline, acicular, needle-like precipitates were found emanating inward from the quench surfaces. This implies that with this reasonably good glass former may be quite susceptible to surface heterogeneous nucleation. Some batches, like 2212 and 4334 showed significant quantities of crystalline phases.

Annealing of the glassy specimens in oxygen or air optimizes the recrystallization of the specimen into a useful superconducting material. The as-formed glass does not superconduct. 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. With some samples phase identity becomes ambiguous and lose their identity and/or physically disappear from subsequent optical

and electron microscopy after annealing. Based on x-ray diffraction, optical microscopy and electron microscopy, it appears that most compositions contain two or more main phases after annealing as is expected from the phase rule with distinct phase species.

Critical superconductivity measurements of annealed specimens were made at the University of Alabama in Huntsville (UAH) with a Quantum Design SQUID Magnetometer. Diamagnetism is 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. The glass-ceramic produced from the good glass forming 2112 composition has only one superconducting phase transition of 82 K indicating that the glass-ceramic is predominantly the phase 2212. Glass-ceramics from batch compositions 2212, 2223, and 4334 contained two superconducting transition temperatures, 110 K and 85 K, indicating the presence of the two superconducting phases, 2212 and 2223, respectively. The best glass former, 4334, contained the largest concentration of the highest onset transition temperature for superconductivity, 110 K. Figure 2 is a representative example of the susceptibility data for these glass-ceramics. No batch formula was found to yield a specimen of single phase high T_c phase. This is due to the complex and largely unknown multiple phase fields in the phase diagrams of these systems.

DTA analysis of the quenched amorphous specimens was performed in air. Using heating and cooling cycles with rates from 2 to 10 °C/min and a peak temperature of 900 °C, the glass transition, crystallization, and melting temperatures were measured; see Fig. 3. There was little difference in the devitrification temperatures among the various compositions tested. The onset of crystallization was found to be around 400 °C. With specimens further heated to 900 °C, the cooled product shows no signs of superconductivity. It is only after a prolonged anneal at 750 °C to 800 °C that these materials show evidence of the presence of one or more superconducting phases. Although glass-ceramics are produced by a crystallization cycle, superconductors do not result. Further long-term annealing at the elevated temperature is required to form the superconductor.

Studies of single grain boundaries indicate that dislocations in the grain boundary are the weak links that limit the critical current density through the interface.[32] High temperature superconducting glass-ceramics can be prepared by a modified two-step heat treatment process, as in Fig. 1a. The first step is to heat to the temperature region above the glass transition temperature and the "crystallization" peak temperature (325 °C to 450 °C).[33] A crystal growth step is not necessary since the crystallization kinetics are fast.

Susceptibility of 4334 Glass-Ceramic

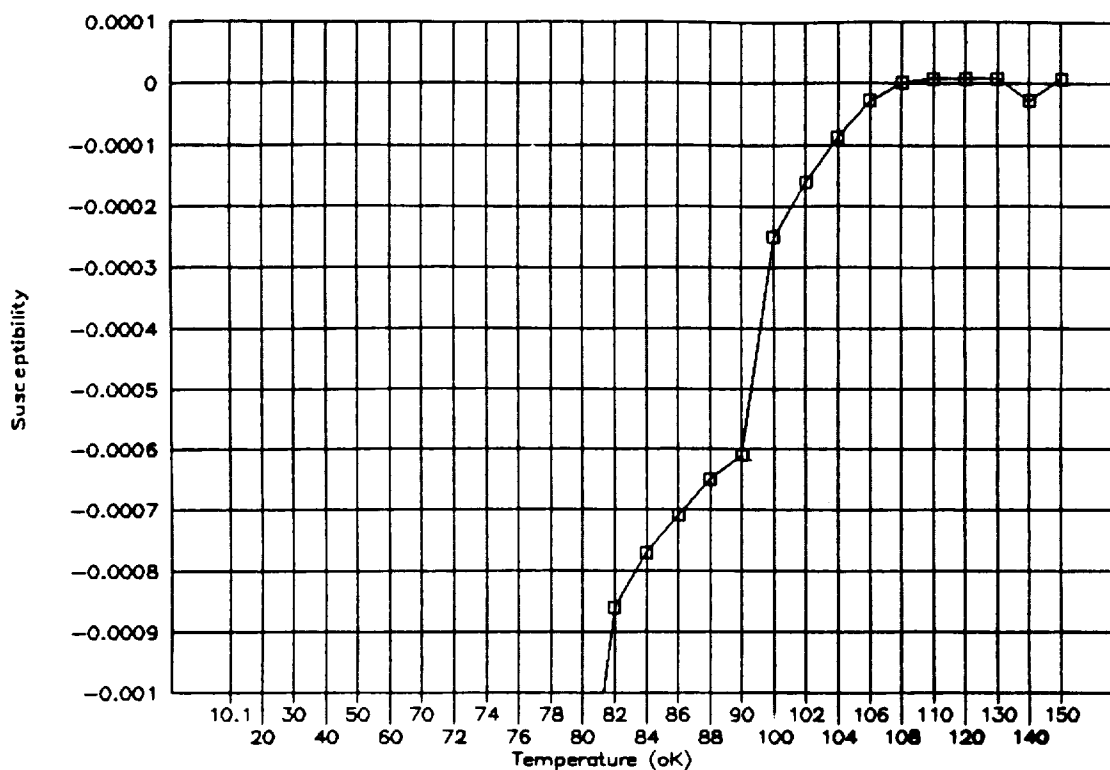


Figure 2. Magnetization vs. temperature for 4334 glass-ceramic with an initial superconducting onset temperature of 108 K and a second superconducting transition at 83 K.

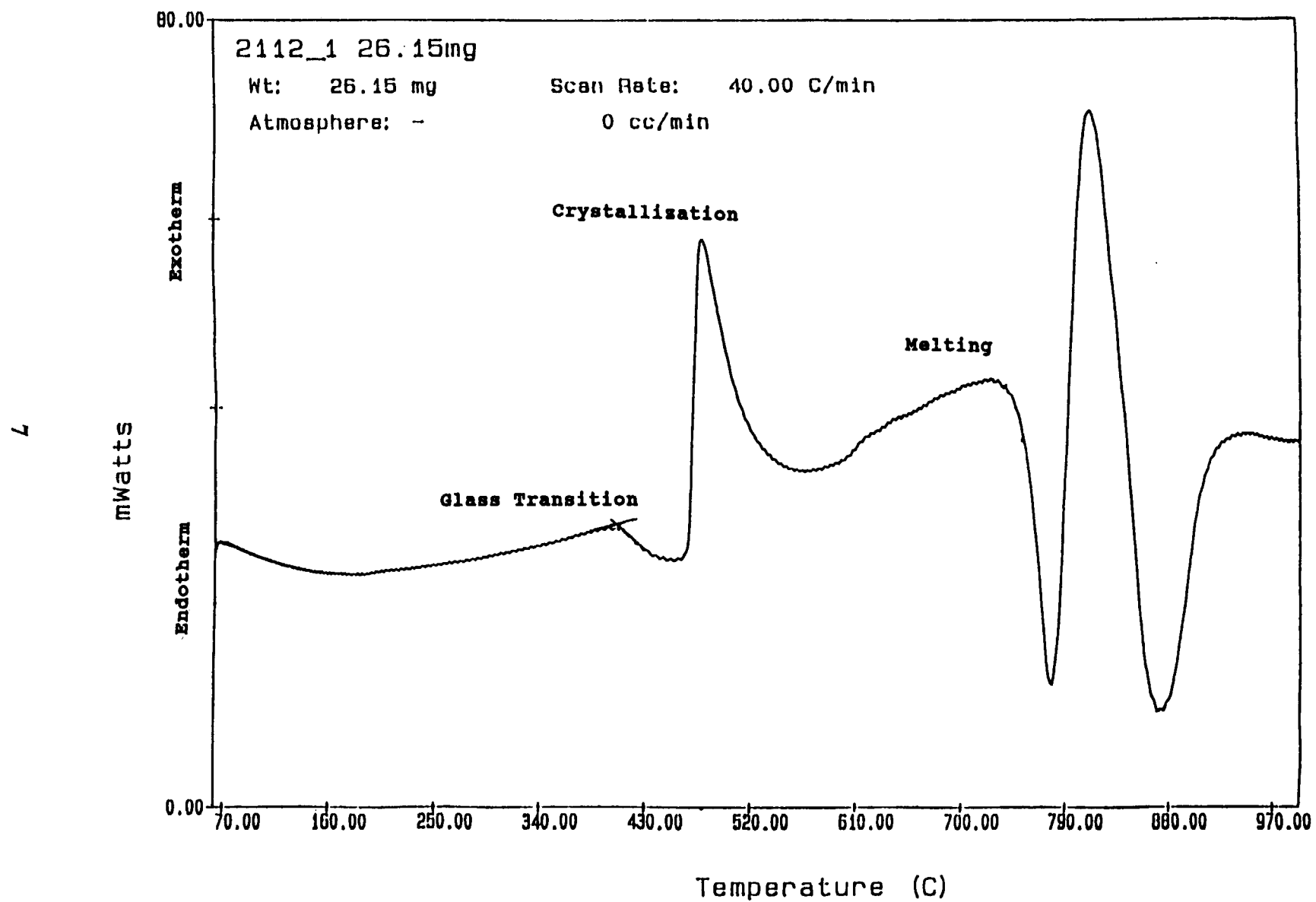


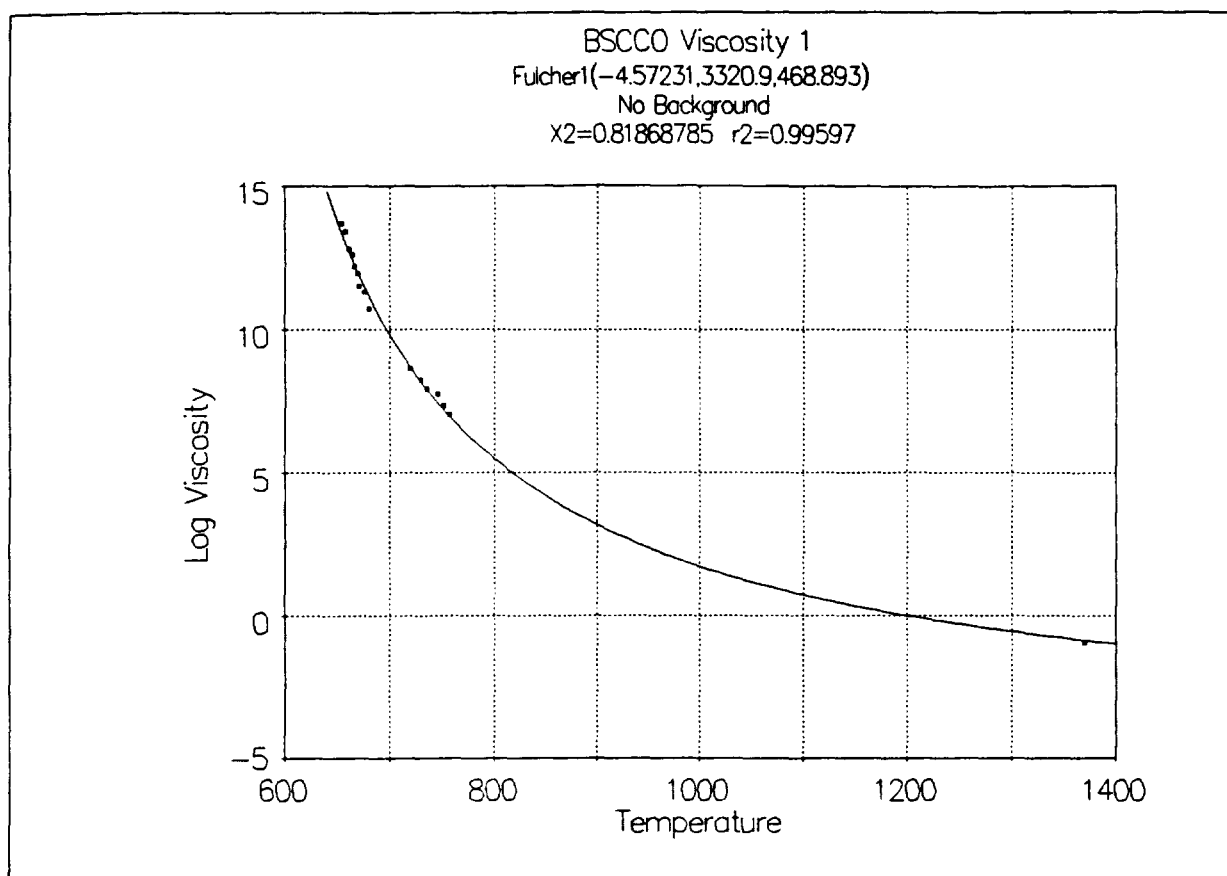
Figure 3. Differential thermal analysis data showing glass transition, crystallization, and melting.

The glass-ceramic, however, must undergo the long high temperature thermal soak at around 850 °C to form the superconducting phases. By crystallizing the superconducting glass-ceramics from fully dense glass, it is possible to reduce the extent of dislocations and possible disorder at the crystal boundaries. Glass-ceramics from 2223 have been prepared with critical currents as high as 1800 amp/cm² by a two-step process involving nucleation around 350 °C (i.e., just above the glass transition temperature) followed by high T_C transformation at 855 °C for long times.[33] Therefore, the glass precursor method is a very promising technique for producing high T_C superconductors with high critical current density J_C since crystallization is from uniform and dense glasses.

A strong exotherm over the range of 750 °C to 850 °C is seen in the DTA data. It is very difficult to attribute this peak to particular events and is, therefore, unusual. Two DTA runs were performed which tend to attribute it to oxygenation. One was performed in air and shows the peak; the other DTA was performed in argon showing no peak.[6] With thermogravimetric analysis at 10 °C/min weight gain was observed beginning at 300 °C maximizing at about 2% at 650 °C; following this was a gradual weight loss to 880 °C where a rapid weight loss occurred at the melting point. We have also shown that upon heating a sample of 2223 to 900 °C, a weight loss of 2% occurs, being consistent with Ref. [6]. Weight loss between 650 °C and 880 °C does not support attributing the broad exotherm to further oxygenation of the samples. Rather the samples should be losing oxygen. It is more likely that in the absence of oxygen in the atmosphere, the samples lose oxygen and the low oxygen content material which is known to have a lower melting temperature actually melts. When oxygen is present, the materials do not lose oxygen, do not melt, but rather recrystallize into high T_C ceramic phase.

Crystallization from glass is most dependent on the viscosity of the undercooled liquid. Viscosity data from Tatsumisago [12,13] and a value at the melting temperature were fit with a Fulcher-Volmer relationship [14,15] using PEAKFIT (Jandel software). The shape of the viscosity curve is very similar to LBN fluoride glass from which fibers can be pulled. This data is presented in Fig. 4. This fitted Fulcher viscosity relation for a composition close to 2112 was used in theoretical nucleation and crystal growth calculations.

Theoretical calculations were performed in order to evaluate the nucleation and crystal growth processes for the high T_C superconducting BSCCO ceramics. These crystallization calculations were performed using MathCad (Mathsoft, Inc.). Initial calculations of the crystallization rate and fraction crystallized at various cooling rates were performed according to the method of Barandiaran and Colmenero.[16] This model is shown in Figs. 5 and 6. The assumptions for



BSCCO Viscosity 1
 16 Active X-Y Points
 X: Temperature
 Y: Log Viscosity

Oct 5,1992 9:48 AM

Mean: 737.8952062 SD: 172.7077674
 Mean: 9.743212043 SD: 3.680113525

Curve-Fit Std Error= 0.250950171 $r^2= 0.995970004$

Curve-Fit Coefficients

Peak#	Type	#A0	#A1	#A2	#A3	#A4
1	Fulcher	-4.57231	3320.898	468.8926		

Measured Values

Peak#	Type	PkAmpl	PkCtr	Wid@HM	Area
1	Fulcher	0.886957	1370	0	1987.598

Figure 4. Viscosity data fitted with the Fulcher-Volmer relationship.

the calculation, iteration ranges, definitions, and a fit of viscosity vs. temperature are shown in Fig. 5. Figure 6 illustrates the equations and calculated plots for nucleation (I), crystal growth rate (G), combined nucleation and growth rate constant (K), crystallized fraction (X), and calculated DTA signal as functions of temperature (dX/dT). One can see from the volume fraction crystallized that at 100 °C/sec ($X_{i,2}$) some of the sample crystallizes while at a cooling rate of 1000 °C/sec the sample is virtually all glass. One can see the pronounced effect of cooling rate on the crystallization peak temperature in the calculated plots of fraction crystallized in a given temperature interval. These simple classical calculations predict glass formation and crystallization peaks in remarkable agreement with the splat quenching and RTAA experiments.[10]

A second set of calculations were performed in order to determine the effects of various assumptions used for the crystallization calculations of these materials. Of particular importance is the temperature functional relationship of the heat capacity (and Gibbs free energy) in the undercooled liquid. A number of different assumptions are assumed and identical nucleation calculations were performed; the MathCad printout is shown in Figs. 7 and 8. Figure 7 shows the assumptions for the form for heat of fusion (dH), free energy (dG), and the pre-exponential factor (A) for the undercooled liquid. The heat of fusion represented by dH_x uses the heat of crystallization where as the heat of fusion indicated by dH_f is calculated assuming a linear decrease in heat of fusion with undercooling.[17] These heat of fusion values were used to calculate the free energy of undercooling dG_x and dG after Kelton [18] and compared with the free energy as calculated by Thompson and Spaepen.[19] The corresponding work energy to form crystal nuclei using the three assumptions were calculated and two pre-exponential factors, A_a and A_{2a} , were calculated. The results of four different approaches are indicated in the plots in Fig. 8. Of the methods, the assumptions of Thompson and Spaepen with the heat of fusion calculated with a temperature dependence on undercooling [19] produced a nucleation peak most consistent with the nucleation peak from experimental DTA.

A very puzzling result of this investigation is associated with the first "crystallization" peak. In DTA analysis of BSCCO ceramics, the first large exothermic peak that occurs just after the weak endothermic glass transition temperature has been attributed by all investigators but one to the "crystallization" peak. Even though large exotherms are obtained, examination indicates that both the as-quenched glass and glass that has been processed through the "crystallization" peak are apparently amorphous as is presumed by the broad halo peaks in x-ray diffraction.[20-22] One claim is that phase separation rather than crystallization occurs (i.e., with 2212) [21] when annealing

$\pi := 3.414$	
$k := 1.38 \cdot 10^{-16}$	Boltzmann's constant, erg/K ³ molecule
$i := 1..30$	Iteration Range
$r := 0..6$	Iteration Range
$n := 1$	Iteration Range
$f_i := 1$	Avrami Index, unitless
$a := 20$	Fraction of sites for attachment
$N_v := 2 \cdot 10^{22}$	Average atomic dimension
$T_m := 701 + 273$	Number of Atoms per unit volume, 1/cm ³
$dH_m := 11.3$	Melting Point, K
$R_r := 10^r$	Heat of Fusion, kJ/mol
$T_i := 1001 - 15 \cdot i$	Cooling Rate, k/sec
$dT_i := T_m - T_i$	Temperature, K
$Tr_i := \frac{T_m}{T_i}$	Undercooling, K
$dTr_i := \frac{dT_i}{T_m}$	Reduced Temperature
$t_{i,r} := \frac{dT_i}{R_r}$	Reduced Undercooling
$\log \eta_i := \left[-4.57 + \frac{3320}{(T_i - 469)} \right]$	Quench time, sec
$\eta_i := 10^{\log \eta_i}$	viscosity

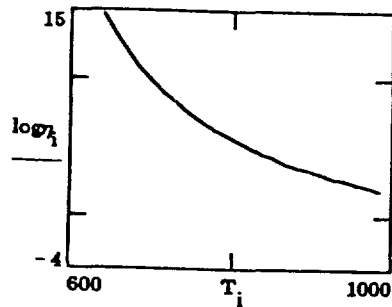


Figure 5. Values and parameters used for crystallization calculations using the assumptions of Barandiaran and Colmenero.[16]

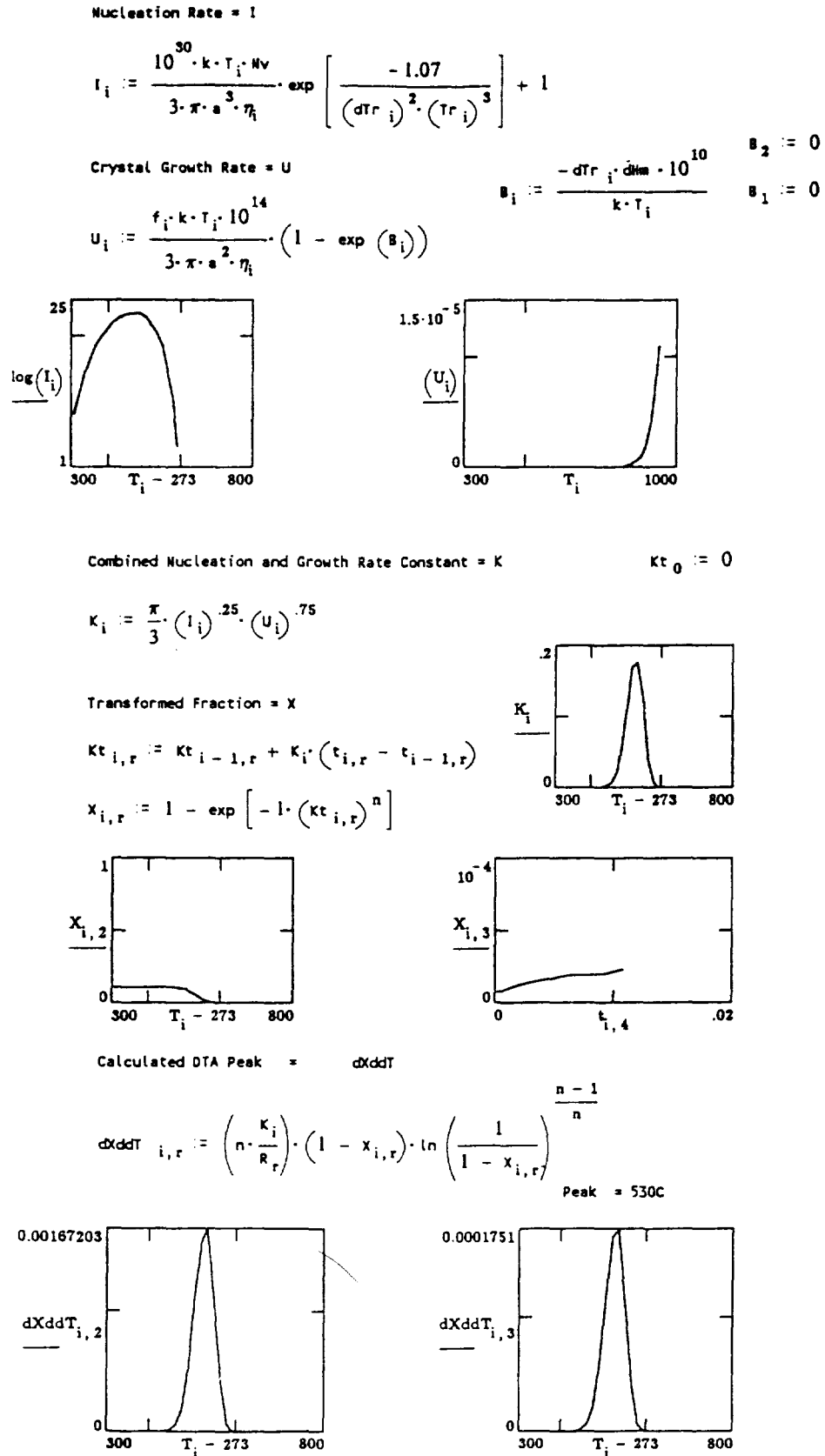


Figure 6. Calculated values for nucleation and crystallization rates, transformed crystal fraction, and calculated theoretical DTA peak according to the assumptions of Barandiaran and Colmenero.[16]

Classical Nucleation Calculations

$$\begin{aligned}
 a &:= 50..120 & T &:= 1 & \gamma &:= .051 \\
 k &:= 1.38 \cdot 10^{-23} & T_a &:= T \cdot a \cdot 10 & \lambda &:= 10^{-10} \\
 h &:= 6.63 \cdot 10^{-34} & T_x &:= 473 + 273 & n_v &:= 4 \cdot 10^{27} \\
 \Delta C_p &:= 2.43 \cdot 10^{-2} & T_m &:= 1203 & v_m &:= 1.38 \cdot 10^{-4} \\
 & & \Delta T_a &:= T_m - T_a & v &:= 5.41 \cdot 5.41 \cdot 30.81 \cdot 10^{-30} \\
 & & T_{r_a} &:= \frac{T_m}{T_a} & v &:= 9.018 \cdot 10^{-28} \\
 \pi &:= 3.142 & \text{Log} \eta_a &:= \left[-4.57 + \frac{3320}{(T_a) - 469} \right] & \eta_a &:= 10^{\text{Log} \eta_a} \\
 & & \Delta H_f &:= 3 \cdot 10^4 \\
 \text{Hoffman's Approximation} & & \Delta H_x &:= \Delta H_f \cdot \frac{T_m}{T_x} \\
 \text{Turnbull Approximation} & & \Delta G_t &:= \frac{\Delta H_f \cdot \Delta T}{T_m} \\
 \text{"Kelton"} & & \Delta G_a &:= \Delta H_f \cdot \frac{(\Delta T_a)}{T_m} - \Delta C_p \cdot (\Delta T_a - T_a \cdot \ln(T_{r_a})) \\
 & & \Delta G_{x_a} &:= \Delta H_x \cdot \frac{(\Delta T_a)}{T_m} - \Delta C_p \cdot (\Delta T_a - T_a \cdot \ln(T_{r_a})) \\
 \text{"Thompson \& Spaepen"} & & \Delta G_{ts_a} &:= \Delta H_f \cdot \frac{\Delta T_a}{T_m} \cdot 2 \cdot \frac{T_a}{T_m + T_a} \\
 \text{"Zanotto \& James 85"} & & W_a &:= \frac{(16 \cdot \pi \cdot \gamma^3 \cdot v_m^2)}{(3) \cdot (\Delta G_a)^2} & \Delta G_{ts_a} &:= W_a \\
 & & W_{x_a} &:= \frac{(16 \cdot \pi \cdot \gamma^3 \cdot v_m^2)}{(3) \cdot (\Delta G_{x_a})^2} & W_{ts_a} &:= \frac{(16 \cdot \pi \cdot \gamma^3 \cdot v_m^2)}{(3) \cdot (\Delta G_{ts_a})^2} \\
 & & \Delta G_{d_a} &:= k \cdot T_a \cdot \ln \left(\frac{3 \cdot \pi \cdot \lambda^3 \cdot \eta_a}{h} \right) \\
 \text{"Zanotto '87"} & & A_a &:= 2 \cdot n_v \cdot V^{.33} \cdot \left(\frac{T_a}{h} \right) \cdot \left[\frac{\gamma}{(k \cdot T_a)} \right]^{.5} \\
 \text{"Zanotto '87 assuming } \theta = 1 & & A_{2_a} &:= \frac{n_v \cdot k \cdot T_a}{3 \cdot \pi \cdot \lambda^3 \cdot \eta_a} & B_a &:= 2 \cdot V^{.33} \cdot \left[\frac{\gamma}{(k \cdot T_a)} \right]^{.5}
 \end{aligned}$$

"Classical Nucleation Equation in Four Forms

$$\begin{aligned}
 I_a &:= A_a \cdot \exp \left(-\frac{\Delta G_{d_a}}{k \cdot T_a} \right) \cdot \exp \left[\frac{-(W_a)}{(k \cdot T_a)} \right] & I_{x_a} &:= A_a \cdot \exp \left(-\frac{\Delta G_{d_a}}{k \cdot T_a} \right) \cdot \exp \left[\frac{-(W_{x_a})}{(k \cdot T_a)} \right] \\
 I_{ts_a} &:= A_a \cdot \exp \left(-\frac{\Delta G_{d_a}}{k \cdot T_a} \right) \cdot \exp \left[\frac{-(W_{ts_a})}{(k \cdot T_a)} \right] & I_{xA2_a} &:= A_{2_a} \cdot \exp \left[\frac{-(W_{x_a})}{(k \cdot T_a)} \right]
 \end{aligned}$$

Figure 7. Various assumptions, parameters, and equations utilized for nucleation calculations.

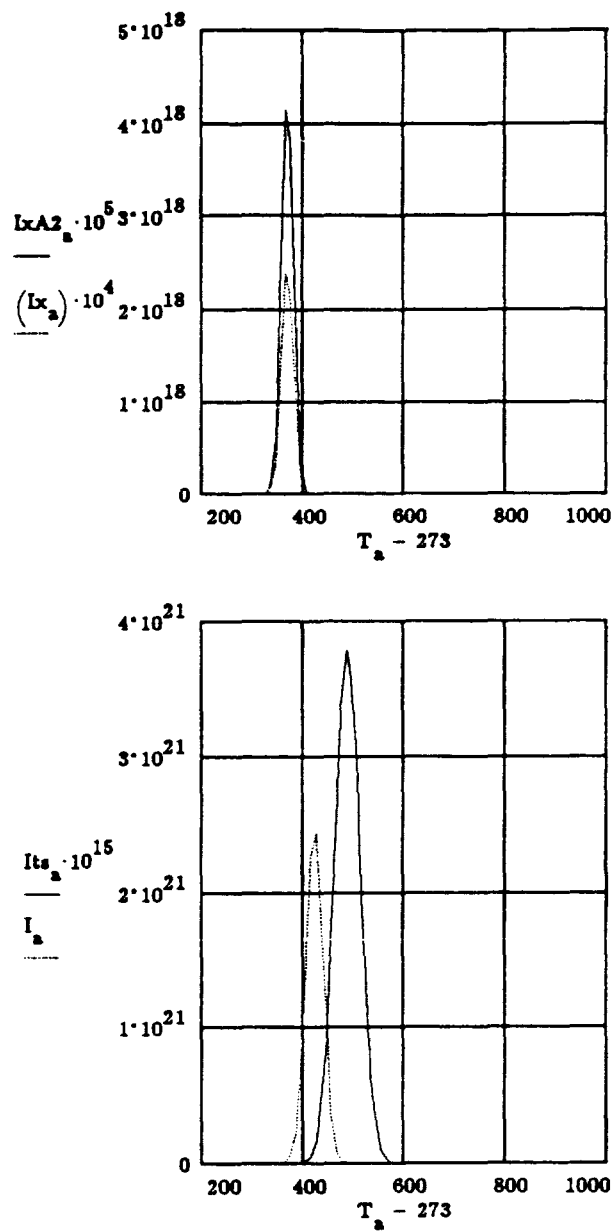


Figure 8. Calculated nucleation data for four of the crystallization models.

at just above T_g but the extent of heat evolution (exotherm peak area) that results is not fully explained.

Temperature-time-transformation (TTT) experiments have been performed on BSCCO superconducting ceramics by isothermal heating runs for given lengths of time followed by x-ray diffraction to identify the presence of crystal phases. Shi [23] (Fig. 8 of Ref. [23] with 2223) showed glass stable to 500 °C after 1 hour. This is especially puzzling since on the same page (in Fig. 7 of Ref. [23]) DTA data for the same material show a glass transition temperature of about 400 °C and a crystallization peak centered at about 495 °C. This heating rate (2 °C/min, total time to 500 °C being on the order of 4 min) is nearly 2 orders of magnitude less time than the isothermal anneal used for the TTT phase study. Similarly, Tatsumisago [24] (Figs. 3, 4, and 5 of Ref. [24]) show glass phase persisting (with some Cu₂O and CaO) for 1 hour at 500 °C. All this is very puzzling since numerous investigators report glass transition temperatures and crystallization of the glass at temperatures and times well below this.

These contradictions in the literature and our understanding of the mechanisms of crystallization indicate that some of these "glasses" may, in fact, be nanocrystalline materials (with associated nanostructure). A new category of solid materials identified as nanocrystalline materials with crystallites in the 1 to 50 nm size range were first identified and developed by Gleiter.[25] Normally nanocrystalline materials have been prepared by compaction and sintering of vapor condensed powders. More recently they have been produced by crystallization from melt quenched amorphous materials.[26-28]

Scanning tunneling microscopy (STM) has proven very useful in the confirmation of nanophase structure [27,29] in Nb-Ni amorphous alloy. Splat quenched samples were examined by x-ray diffraction and presumed to be amorphous. From the half-width of the first maximum and by means of the Scherrer [30] equation, the effective particle size was estimated to be 15 Å. This was in agreement with the particle size observed with STM where the spherical islands were on the dimension of 10 to 20 Å. Examination of the fine structure on a 30 by 50 Å image revealed rows at a spacing of 3 Å. The presence of these regularly spaced rows indicate the existence of nanocrystals.

After melt quenching of amorphous metallic alloy, nanophase material may also be produced by thermal annealing. Annealing the amorphous Ni-P alloy [28] at a temperature below the normal crystallization temperature (325 °C for 10 min) produces nanocrystalline material which upon subsequent analysis by DTA shows a slow recrystallization at a temperature higher than the normal rapid crystallization peak for amorphous material. This is entirely consistent with Kim [21] who reported a T_g of 390 °C for a BSCCO glass and a

large sharp crystallization peak at 450 °C from DSC. After annealing the amorphous BSCCO material at a temperature just above the glass transition temperature and below the crystallization peak DSC analysis was devoid of glass transition and crystallization peaks. A small broad exothermic peak centered at 490 °C, just above the crystallization temperature. These very interesting results are entirely consistent with nanophase crystallization of BSCCO ceramics and opens new very interesting processing possibilities for these high T_c materials.

Another interesting anomaly of the BSCCO material is the presence of structure in the liquid above the melting temperature. Since it is known that the liquid of these substances have pronounced structure as evidenced by strong x-ray diffraction peaks at temperatures 50 °C above the melting temperature [22] and since it is known that rapid melt processing of highly oxidized mixtures can produce high temperature superconductors, [31] further experiments on varying the temperature of the liquid are of extreme interest. New processing methods, metastable phases and other possibilities abound.

CONCLUSIONS

Results show that 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 preforms of the low viscosity fluorides. The same processing methods might be utilized to produce useful shapes from the high temperature superconductors.

The glass precursor method is a very promising technique for producing high T_c superconductors with high critical current density J_c since crystallization is from uniform and dense glasses.

The glass has a very high nucleation rate that upon subsequent reheating the material may rapidly crystallize into a nanocrystalline structure. The crystals are of such small size that the x-ray diffraction patterns are broad amorphous halos but thermal analysis is consistent with crystallization into a nanophase structure.

The STM should be used to examine for the presence of nono-structure in BSCCO superconducting glass and glass-ceramics. Confirmation of nanocrystalline structure in superconducting ceramics would be important development. Further development of these potentially high temperature superconducting BSCCO compositions as nanocrystalline ceramics could take advantage of the fact that with nanocrystalline materials the chemical composition generally remains unchanged from the amorphous state [28] so that initially prepared 2223 batch composition might be transformed into crystalline 2223 phase with a T_c of 110 K. The authors have proposed that STM should be utilized to examine the morphologies and nanostructures of rapid melt

quenched and recrystallized amorphous high temperature ceramic compositions and recrystallized glass-ceramics.

Further research of the effects of melt temperature, with resulting differing liquid structure and liquid oxidation state, on the glass-ceramics produced from the as quenched glass would be extremely interesting. It would be interesting to learn if certain stable high temperature oxygen-rich phases or crystal nuclei might be quenched into the glass structure. It is also possible that such crystal phases might be crystallized directly out of the glass at lower temperatures as nanocrystalline phases. If these nanocrystalline phases were high temperature superconductors, the properties would be very interesting.

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APPROVAL

OPTIMIZATION OF THE PROCESSING PARAMETERS OF HIGH TEMPERATURE SUPERCONDUCTING GLASS-CERAMICS -- CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT (PROJECT #91-04)

By

E. C. Ethridge and W. F. Kaukler

This report has been reviewed for technical accuracy and contains no information concerning national security or nuclear energy activities or programs. The report, in its entirety, is unclassified.



Gregory S. Wilson
Director, Space Science Laboratory