

PHASE DIAGRAMS, MELT SOLIDIFICATION AND GLASS CRYSTALLIZATION IN THE Bi-Ca-Sr-Cu-(O) SYSTEM

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Some aspects of the preparation of oxide superconductors are discussed as concerns the problems of weak links. Known binary phase diagrams are reviewed and redrawn. Ternary compounds and glass-formation regions are included. The crystallization and formation of superconducting phases are illustrated by means of $T-T$ diagrams. The rate-controlling process of polymorphous precipitation is probably two-dimensional nucleation.

It is well known that the physical properties of the superconducting oxides depend strongly on the preparation route; therefore, dissimilar results are obtained from different processes and process conditioning, as reviewed for the already classical Y-Ba-Cu-O (YBCO) system in [1-5]. Such superconducting materials are generally fabricated through the classical sintering methods from various feed oxides and precursors [6, 7], but they are usually porous. In spite of the many attempts that have been made to synthesize and characterize superconducting phases, many problems remain unsolved. New material systems, new processes and optimized conditions for the high- T_c superconductors (abbreviated as HTS) are therefore being actively explored to increase the critical temperatures (T_c) and predominantly to uphold sufficiently high electrical currents (J_c). Studies on single-crystals and epitaxially grown thin films of $\text{YBa}_2\text{Cu}_3\text{O}_x$ (abbreviated as 123) have yielded current densities in the range 10^5 - 10^6 A/cm², whereas the conventionally prepared bulk samples have been found to exhibit values three orders of magnitude lower (a typical J_c at 77 K of as-sintered 123 being about 500 A/cm² in zero magnetic field). Several methods have been investigated with a view to improving the intergranular contact, e.g. by adding the modification oxides Ag_2O , SnO or PbO , or even elements such as Gd or Ag, in an attempt to remove the parasitic secondary phases that often enhance undesirable grain growth. Additives can be inserted mechanically or even

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segregated during the precipitation processes (e.g. during glass crystallization) and the presence of metals may cause a positive yield of the so-called proximity effect (i.e. sharing superconductivity). While the exact nature of the weak-link problems in sintered YBCO is still under intensive investigation, it has recently been demonstrated that the problem can be appreciably reduced by a new method of melt-textured growth (i.e. MTG) [8, 9], consisting of directional spherulitic solidification instead of the conventional melt-free sintering (where, in contrast, the presence of melted regions, often rich in copper oxides, was considered undesirable as reducing the good superconducting properties). Unlike metal-forming processes, the full-melting route of ceramics preparation is not generally used, since the refractory-like oxides undergo large volume changes during solidification and, in combination with the brittle nature of ceramics in the solid state, this causes cracking during the solidification process. On the other hand, the melt-processing technique has been investigated with several ideas well known from the metal production of metallic glasses [10, 11] and has the advantages of fine microstructures, reduced segregation, extended solid solubility, and, last but not least, the formation of new types of phases. Thus, it is assumed that the full-melting process allows one to fabricate materials with oriented microstructures and with tailorable solid-state properties. However, the nonequilibrium (real) conditions of solidification [14] often faced during rapid cooling demand a more extensive knowledge of the location of phase boundaries, usually to be extrapolated to the metastable regions [13] or shifted to the unstable environments [15, 16]. The extrapolation is necessary for a description of retarded nucleation, whereas the shift is required to characterize slow transport phenomena. These are linked in the recently developed field of kinetic phase diagrams [16], including the customary T - T and less conventional H - T diagrams [1, 15].

Phase diagrams

It is evident that the first step towards a better understanding of the phases and phase relations formed upon solidification is based on conventional studies of phase diagrams [12]. Metastability, parasitic reactions and, last but not least, the experimental difficulties, how to preserve the high-temperature state down to the room-temperature investigation by quenching [17-20] for example, are the major reasons why the HTS phase compatibilities are not fully understood as yet. The most intensive studies have been devoted to the already classical system Y-Ba-Cu-O, as reviewed in [21-

28], which can be best analysed in terms of a partially open system Y-Ba-Cu-(O) [28]. For the system Bi-Ca-Sr-Cu-(O) (abbreviated as BCSCO), the situation is even more complicated due to the presence of an additional cation. Known binary edges [29-34] are collectively shown in Figs 1 and 2 and complemented by the only known pseudobinary cut [35]. The ternary system SrO-CaO-CuO [32, 33] exhibits three solid-solution series, which extend from the SrO-CuO edge towards that of CaO-CuO, Ca^{2+} being substituted for Sr^{2+} , Sr_2CuO_3 and Ca_2CuO_3 being essentially isostructural. The 14:24 ratio of the solid solution extends from the compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ to about

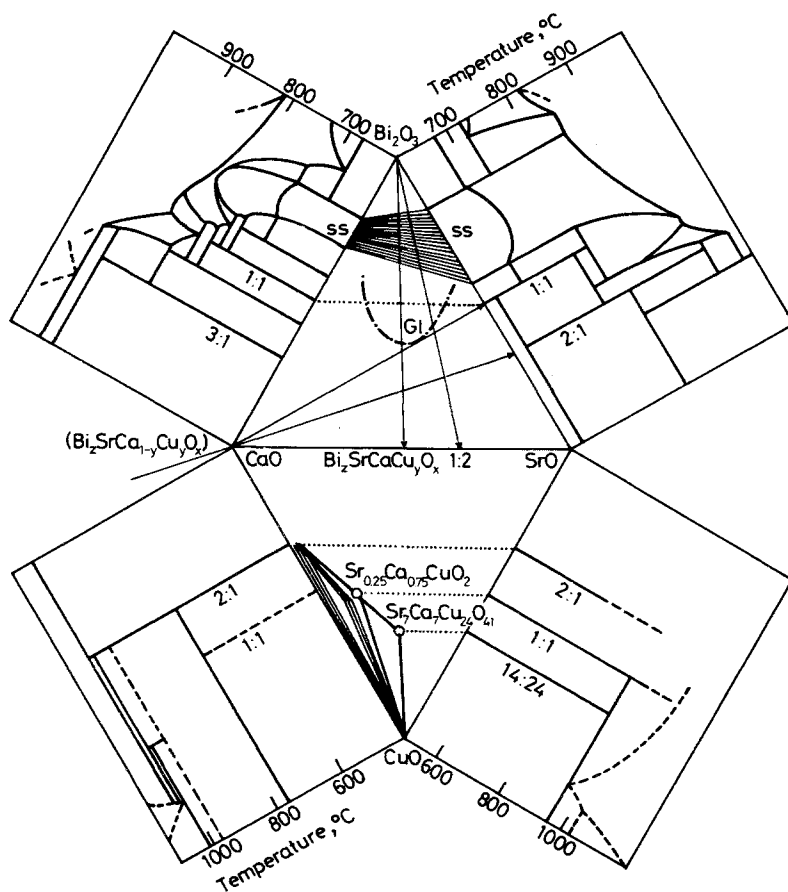


Fig. 1 The binary edges of CaO-Bi₂O₃, CaO-CuO, SrO-Bi₂O₃ and SrO-CuO including the glassforming region (dashed-and-dotted), isostructural joins (dotted) and major superconductive compositions Bi₂SrCa_{1-y}Cu_yO_x [29-34]

(Ca_7Sr_7). There is a ternary phase with a very limited homogeneity region of $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$. This can be regarded as the end-member of the homologous series $(\text{Tl}, \text{Bi})_2(\text{Ba}, \text{Sr})_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4-2n}$, in which all the Tl and Bi layers have been removed, leaving only Cu-O layers alternating with those of (Sr, Ca)-O. The compound $\text{Sr}_2\text{Bi}_2\text{CuO}_6$ should nominally be the phase with $n = 1$ [34] having no Ca-O layers. Instead, however, a different phase is formed, exhibiting a gross deficiency in SrO content [34] (about $\text{Sr}_{16}\text{Bi}_{17}\text{Cu}_7\text{O}_x$). The only pseudobinary cut was reported on the line $1 < n < 2$ of the system $\text{Bi}_n(\text{SrCa})\text{Cu}_{3-n}\text{O}_x$ [35], locating the HTS phase 2(3)2 (i.e. $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_x$) and the semiconductor phase 2(2)1. The liquidus line of the HTS phase was found to lie in the region $1.6 < n < 1.875$, possibly allowing single-crystal growth. It was conjectured that the amorphous

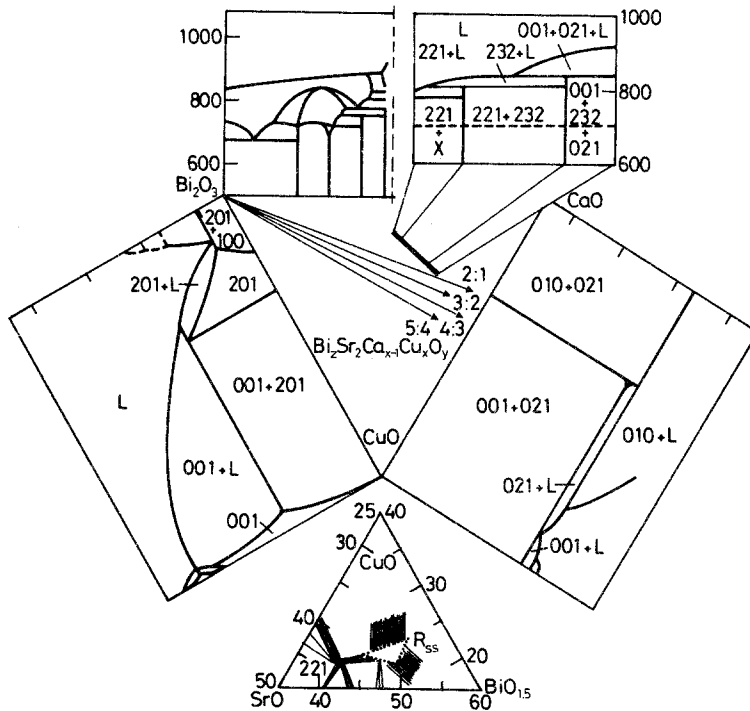


Fig. 2 The binary system of Bi_2O_3 , CaO and CuO end members covering the only known pseudobinary cut [35] $\text{Bi}_y\text{SrCa-Cu}_{3-y}\text{O}_x$ ($1 < y < 2$) and the subsolidus region (at about 900°C) of the ternary diagram [34] (top corner corresponding the composition 40 CuO -25 SrO -35 $\text{BiO}_{3/2}$) around the two important phases $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (221) and Raveau-type solid-solution (R_{ss}).

phase first formed from the melt undergoes crystallization of the 2(2)1 phase below 700°.

Solidification studies

The comparatively easy and most convenient technique of splat-quenching between two copper block surfaces to press plates about 0.5-3 mm thick was transferred [11, 12]. The resulting cooling rate of about 10^2 - 10^3 deg/s, however, was too low to stop nucleation-growth processes allowing the formation of low-temperature phases below the peritectic melting of the 123 phase [19]. Although the as-quenched samples from above the peritectic temperature cannot exhibit the desired superconducting properties because of the absence of the 123 phase, they do not show the presence of the more stable 211 phase (disregarding some traces of Y_2O_3). The latter oxide is possibly left due to its incomplete dissolution and/or partial precipitation during the manual time delay caused by pouring the melt out of the crucible; it is worth noting that reactions between the sample and crucible materials [24] appear to be negligible in contrast to the prolonged time of conventional firing. Fast quenching methods, however, did not produce a completely noncrystalline phase [36-42] when the same 123 starting material was used. From the samples obtained by melt-quenching methods, it is evident that the valence state of copper ions [20, 27] is essential for the subsequent formation of a superconductive phase, which can be achieved only by secondary firing, similarly to the ordinary ceramic processing [38, 39]. Oxide additives in the melt can either increase or decrease the dissociation stability of Cu ions. Easy melt vitrification was indicated for the composition Y:Ba:Cu:B(P) = 1:2:3:4 which, however, produced upon reheating YBO_3 instead desired 1:2:3 [17]. For doped solidified melts, the good crystal contacts of superconductive components are unable to retain superconductivity; according to percolation theory, the amount of the non-superconductive matrix should not exceed 2/3 of the total. Bulk samples containing a glassy matrix have to be annealed for longer times, which indicates that oxygen diffusion through the entire sample is crucial for desirable superconducting properties; EMS reveals the formation of holes several microns in diameter within the originally dense matrix, as a necessary passage for oxygen intake.

The early-studied BCSCO compositions of (1, 5)112, (1,5) (1,5)12 and 1112 (doped by 0.3 Al) [43, 45] exhibited a glassy state for splat-quenched samples. After annealing for 24 hrs at 820°, these showed a higher T_c and a sharper transition than those of the slowly cooled samples exposed to com-

parable conditions [69, 70]. The molten 2223 mixture was splat-quenched onto copper surfaces preheated to about 200°, which helped to improve the mechanical integrity of the glass [46], the initial crystallization of which occurred at temperatures of about 450 and 650°, producing identifiable phases of CuO, CaCu₂O₃ and BiCaSrO_x. The superconducting phase was not formed at temperatures below 800°. The standard melt-quenching between the copper slabs and rotating twin rollers was found to produce a near-non-crystalline material with the following nominal compositions, 2223, 2324 and 2425, the latter yielding after annealing a substantial amount of the high-*T_c* phase. In all cases, small amounts of extraneous phases were present. Glass-formation for the sample with the 2212 composition with the low-*T_c* phase has been reported by several research groups [44-49]. The 2212 amorphous films were prepared by twin-roller quenching [50]. Bi₂Pb_{0.5}Sr_{1.9}Ca_{2.2}Cu₄O_x was melt-pressed between steel plates to 1 mm thickness and, after annealing at 840° for 120 hrs in O₂, provided fibrous crystals up to 300 μm long (*T_c* about 105 K and *J_c* about 550 A/cm²). The glass-forming region was examined in the BiO_{3/2}-(Ca,Sr)O-CuO system [51, 52], a relatively wide interval of glass-formation being reported, including the 1112 and 2223 compositions of interest. The single and twin-roller techniques have become popular [53-59], including other nonconventional methods, such as pumping up the 1112 melts at 1150° into quartz tubes to form glassy rods and coils [54].

Crystallization and superconductor formation

The formation of superconducting phases during BCSCO glass annealing, however, is as difficult as that already found for the quenched YBCO systems [36-42]. The splat-quenched glassy 2122 [19] showed a gradual build-up of crystallinity when heated at 2 deg/min up to 700°. However, this was followed by a distinct loss of crystallinity, in accordance with the indistinct melting indicated by DTA above 750°. It can be anticipated that the low-temperature crystallization yields non superconductive phase(s), which latter reacts with the remaining glassy matrix to form first the low-*T_c* and then the high-*T_c* phases. The 2(3)2 roller and water-quenched samples [53] produced glasses which appeared to be heterogeneous and exhibited two glass-transformation and crystallization temperatures as well as a weak superconductivity. The heat-treated 1112 (including its partly Pb-substitutes) showed a low-temperature crystallization (600°) of (Sr, Ca)₃Cu₅O_x (together with some impurity phases such as Ca₂PbO₄), which latter reacts

to form the low- T_c phase. The rapidly solidified 2425 composition [59] showed the evolution of the high- T_c phase out of the 2122 phase, which in turn develops from the 2021 phase (exhibiting as low a T_c as 12 K). The high- T_c phase is formed at 865° in the presence of a liquid phase rich in copper and calcium, as verified by the presence of CuO and (Ca, Sr)₂CuO₃ phases at the solid-liquid interface [59]. An investigation of Pb-doped Bi-based glasses [51] confirmed that the first phase to precipitate at around 500° is Bi₂(Ca, Sr)₂CuO_x, which on further annealing produces the low- T_c phase at around 800°. The DTA exothermic effect observed just prior to the endothermic peak of partial melting at around 870° is assumed to be related to the formation of the low- T_c phase [60].

The superconducting properties of the resulting glass-ceramics were comparable with those of classically sintered ceramics, whereas the density was found to be higher, i.e. 5.91 g/cm³ [48] for the 4334 glass and 6.42 g/cm³ [61] for the 0.4 Pb-doped 2223 glass ceramics (closely approaching the theoretical values). The T_c value for the Y112 glass ceramics was found to decrease with increasing content of Bi (= Y) [44]. Several authors have succeeded in preparing Pb-doped 2223 glass ceramics with T_c above 100 K [55-62], but the value of J_c did not exceed 100 A/cm². A detailed analysis of glass ceramic HTS was given in [51].

Description of nucleation-growth processes

Since the noncrystalline structures are thermodynamically unstable [12], they undergo crystallization at elevated temperatures. If such a structure crystallizes into merely a single phase without any concentration changes, this is called polymorphous crystallization. However, in many cases, crystallization occurs through complicated decomposition reactions such as eutectic crystallization, resulting in various products with different physical properties and microstructures. From the standpoint of material synthesis, the fabricated materials ought to possess properties such as phase purity, freedom from defects, high density, chemical stability and controllable microstructures. These goals cannot be achieved until the crystallization, phase transformation, diffusion and crystal-chemistry of the materials in general are fully understood. This is particularly important in HTS in order to produce Bi-based high-density single-phase superconductor samples routinely. The nucleation-growth processes of both the low and high- T_c phases are not yet clear. It is difficult to study these mechanisms with ceramic-sintered samples, since the microstructures are not easily control-

led. In melt-quenched samples, on the other hand, the starting material is a highly uniform and dense amorphous structure, so that the crystallization can be carefully controlled by adjusting the annealing parameters, allowing observation of the whole phase change by various characterization techniques [17, 18, 44, 51, 53].

The DTA curves of the powdered 2122 splat-quenched samples with different surface areas [19] showed no identical reactivity, probably due to the different abilities to precipitate, the surface and bulk nucleation possibly producing crystalline phases with different compositions and at different rates. The kinetics of nonisothermal crystallization studied for the Y112 glasses [63] prepared by both the twin-roller and splat-quenching methods indicated that the apparent activation energy of the assumed surface nucleation decreases with increasing Bi (= Y) content; SEM studies suggest that surface crystallization is the predominant mechanism [63]. Two-dimensional nucleation [64] appears to be a rate-controlling process even for other processes associated with the layered perovskite structures, e.g. for the oxygen intake of the standard 123 structure at low temperatures [65] investigated by thermogravimetry, or for the face build-up observed optically during the growth of HTS single-crystals [66].

It has been shown [57, 67] that the high- T_c phase does not crystallize directly from the amorphous phase; it can form only during prolonged annealing. Eutectic crystallization is likely to occur as the composition of the matrix reaches the eutectic point, which is close to that of the 2223 glass. In such a case, interfaces are therefore created between the low- T_c phase and mixed calcium copper oxides, these probably having a morphology similar to that known from the crystallization of metallic glasses [16]. Because of the high concentration differences in calcium and copper across the interface, a kind of balancing diffusion must take place. The high- T_c phase will thus form at these interfaces after certain amounts of calcium and copper have diffused in the low- T_c phase, adding one more Ca-O and Cu-O planes in its unit-cell structure (syntactic intergrowth). At higher temperatures, the atomic diffusivities are high enough, so the largest contribution to nucleation comes from the term containing the Gibbs energy, to form a nucleus of critical size. This term is then dependent on the interfacial energy, the molar volume and the Gibbs energy difference between the amorphous and the crystalline phase, usually proportional to the degree of undercooling. Obviously, a smaller critical Gibbs energy is expected for a larger difference, which implies a lower Gibbs energy of the crystalline phase with respect to that of the noncrystalline one. The low- T_c phase has a smaller unit cell c -axis value of 31 Å, thus having a lower free energy than that of the high- T_c

phase (with $c = 38 \text{ \AA}$). The free-energy increase is also associated with the insertion of two extra planes, which could explain the fact that the low- T_c phase always crystallizes first from the amorphous matrix. It has been observed [57] that the diffusion process is enhanced by increasing initial calcium and copper contents, as for example starting from the 2234 composition. For the 2223 samples, the growth is limited by the insignificant amounts of Ca and Cu. However, the time required to form the high- T_c

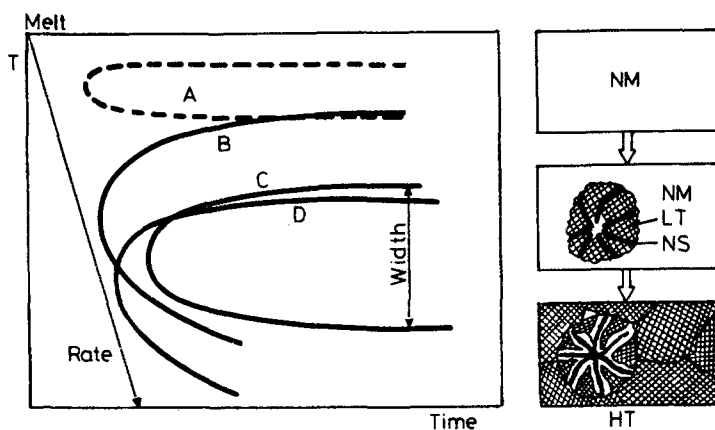


Fig. 3 Schematical time-temperature-transformation (T - T - T) diagram proposed for the rapidly quenched HTS assuming the critical cooling rates of vitrification (rate: K/s), melting temperatures (melt: °C), temperature width of the superconductor possible occurrence (width: °C) and following phases

phase is as much as 10 days, this being essentially shortened to 3 days for the 2245 starting composition with the highly advanced diffusion process [67]. According to the compiled data [57] and our own experience [19, 39], we may attempt to construct the T - T - T diagram for the glass-formation and crystallization boundary (Fig. 3).

HTS	Comp.	Rate	A	B	C	Width	D	Melt
YBCO	123	10^7	(001) (100)	211	123	~200	011 (0201)	>1400
BCSCO	2223	10^{2-3}	(001)	2212	2223	(?) < 10	2021	~900

Right: a hypothetical process of eutectic-like BCSCO crystallization is illustrated where the noncrystalline matrix, first developing nonsuperconductive, low- T_c and high- T_c phases are marked as NM, NS, LT and HT, respectively [57]

Conclusion

The glasses in the BCSCO system are easily formed at a critical cooling rate of from 10^2 to 10^3 deg/s by using the conventional splat-quenching technique. The glass-formation ability decreases with increasing CuO and decreasing Bi₂O₃ contents. Formation of the high- T_c (2223) phase is favoured by the presence of noncrystalline phases, probably within a very small temperature region (as narrow as about 5 deg). In general, the splat-quenched glasses first precipitate the 2201 phase, this developing fully at about 650°. This is then transformed to the 2212 phase, which is further converted to the desired 2223 phase only after prolonged heating at about 865°. The inherent polymorphous crystallization is in agreement with the proposed T - T - T diagrams [57]. More data are needed for a better understanding of the nonisothermal processes associated with HTS formation [68] and the possible existence of superconductivity in noncrystalline structures [69].

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Zusammenfassung — Es wurden einige Aspekte der Herstellung von Oxidsupraleitern bezüglich der Probleme schwacher Bindungen besprochen. Existierende binäre Phasendiagramme wurden kritisch besprochen und unter Berücksichtigung von ternären Verbindungen und Glasbildungen neu erstellt. Die Kristallisierung und Bildung von supraleitenden Phasen wurde mittels $T-T-T$ -Diagrammen illustriert. Der geschwindigkeitsbestimmende Schritt der polymorphen Präzipitation ist wahrscheinlich eine zweidimensionale Kristallkeimbildung.