Original Paper

Twin-roller quenching of $Bi_2Sr_2Ca_2Cu_3O_{10}$ melts

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Dedicated to Prof. Dr.-Ing. Rolf Brückner on the occasion of his 65th birthday

Melts of the target composition $Bi_2Sr_2Ca_2Cu_3O_{10}$ were produced and quenched in a specially designed twin-roller device. Quenching rates were estimated to be between about $0.2 \cdot 10^6$ and $2 \cdot 10^6$ K $\cdot$ s^{-1}. In all quenching experiments mainly three sample shapes resulted, thin slivers, fibers, and clusters of sticking droplets. Slivers and fibers proved to be glassy, whereas the bulk of the clusters was crystalline. The slivers showed surface features due to nonuniform solidification processes. Thus wavy regions could be found or the surfaces were layered because of a rupturing during quenching. It could further be shown that an Al_2O_3 content of the melts does have some influence on the glass formation.

Abschrecken von $Bi_2Sr_2Ca_2Cu_3O_{10}$-Schmelzen in einer Doppelrollenapparatur

Es wurden Schmelzen mit einer Zielzusammensetzung $Bi_2Sr_2Ca_2Cu_3O_{10}$ hergestellt und in einer speziell hierfür konstruierten Doppelrollenapparatur abgeschreckt. Die erzielten Abschreckgeschwindigkeiten lagen schätzungsweise bei ungefähr $0,2 \cdot 10^6$ bis $2 \cdot 10^6$ K $\cdot$ s^{-1}. Bei allen Abschreckexperimenten ergaben sich hauptsächlich drei Probenformen: dünne Späne, Fasern und Cluster zusammenhaftender Tropfen. Späne und Fasern waren glasig, während das Innere der Cluster kristallin war. Infolge ungleichmäßiger Erstarrungsprozesse zeigten die Späne Oberflächenmerkmale. So traten wellenartig verformte Bereiche auf, oder die Oberflächen zeigten Schichtungen infolge des Aufreißens während der Abschreckung. Weiter zeigte sich, daß der Al_2O_3-Gehalt in den Schmelzen Einfluß auf den Glasbildungsprozeß hat.

1. Introduction

The discovery of superconductivity in the system $La-Ba-Cu-O$ by Bednorz and Müller [1] evoked growing interest in other CuO-containing systems. Thus attention was drawn to the high-T_c superconductors in the system $Bi-Sr-Ca-Cu-O$. Since these materials are free both of barium and of rare earths, they show a high stability, are easier to handle and are more promising for possible applications [2]. There are at least three superconducting phases in this system. The compositions of the homologous series can be written as $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$, with $n = 1, 2, 3$ being the number of CuO layers in the unit cell.

The composition of the (2201)[2]) phase contains one CuO layer only and displays a critical temperature below 20 K. The (2212) phase, which becomes superconducting between 90 and 80 K, has two CuO layers, and the 110 K high-T_c phase with the composition (2223) has three CuO layers [3]. The exact structural analysis, however, is difficult, since the phases are changing gradually and tend to show solid solutions [4].

For practical applications the aim is to produce the material in the form of fibers, rods, tapes or in other desirable forms. Since vitrification is possible [5], the glass-ceramic route to prepare these superconductors has some advantages compared to the powder ceramic way [6],

a) production of dense, nonporous superconducting ceramics,

b) easier way to prepare more complicated bodies, and

c) control of the crystallization process.

Al_2O_3, besides PbO and other components [7 to 10], has been proved to facilitate the glass-forming tendency in this system. The resulting series can then be written as $Bi_{1-y}Al_ySrCaCuO$, bismuth being substituted by aluminum [11]. A too high Al_2O_3 content, however, inhibits the formation of the high-T_c phase [12]. Melts with an Al_2O_3 content below $y = 0.5$ tend to crystallize, if the quenching rate is too low [13]. Therefore, Al_2O_3-free melts have to be quenched more rapidly than melts containing some Al_2O_3.

In this paper the glass-forming ability of (2223) melts is investigated as a function of the quenching rate. Slow cooling between two copper plates is compared to rapid quenching by means of a twin-

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[2]) In the following code numbers will be used which refer to the system $Bi-Sr-Ca-Cu-O$. The abbreviations for the compositions of the homologous series of $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ for $n = 1, 2$ and 3 are: 2201: $Bi_2Sr_2CuO_6$, 2212: $Bi_2Sr_2CaCu_2O_8$, 2223: $Bi_2Sr_2Ca_2Cu_3O_{10}$.

roller device. The products obtained are investigated by X-ray diffraction and scanning electron microscopy. These results enable some conclusions with regard to the homogeneity.

2. Experimental

Commercially available Bi_2O_3 (ultrapure, Alfa Products, Karlsruhe (Germany)), $SrCO_3$ (analytical grade, Alfa Products), $CaCO_3$ (primary standard, Alfa Products), and CuO (reagent grade, Riedel de Haën, Seelze (Germany)) were mixed carefully according to the target composition $Bi_2Sr_2Ca_2Cu_3O_{10}$. Subsequently, the batch was calcined for 20 h at 820 °C. Then melting occurred for 90 min at 1200 °C in two ways. In one case a platinum crucible was used, in the other case melting was done in an Al_2O_3 crucible. Then the melts were cooled between two copper plates with a rate of about 10^2 K $\cdot$ s^{-1}. Already during pouring onto the copper plates the melt from the Al_2O_3 crucible behaved quite differently from that from the platinum crucible. Its viscosity was lower and it was easier to cast. After cooling the product looked glassy, whereas the sample from the platinum crucible showed small crystals on fracture surfaces.

For a more rapid quenching of the melts a twin-roller setup was used, described elsewhere [14]. The principle of this device is shown in figure 1. The speed of the rollers may be as high as 55 rps (revolutions per second). The quenching rates, $\Delta T/t$, achieved depend on geometrical conditions as well as on the materials' properties and the contact time between melt and rollers. Quenching rates between about $0.2 \cdot 10^6$ and $2 \cdot 10^6$ K $\cdot$ s^{-1} were estimated for flake thicknesses between about 65 and 15 µm, respectively, which could be measured by scanning electron microscopy (JSM-U3, Jeol, Tokyo (Japan)). For melting of the batch a furnace, shown in figure 2, was constructed. The furnace contained the crucible with an outlet. During melting the bottom outlet was closed by a fitting stopper. The best geometry for outlet and stopper proved to be that shown in figure 3. A pierced cover on the crucible served as a guide for the stopper. The stoichiometric batch was immersed into the crucible, melted there for 20 min at 1180 °C. After that the temperature was decreased to 1050 °C. Then the stopper was removed from the outlet and the melt dropped between the rollers.

3. Results and discussion

All the samples obtained were dark. The two-plate method delivered large slabs with thicknesses of about 850 µm (figure 4). The twin-roller quenching did not only produce flakes, as shown schematically in figure 1. As figure 5 demonstrates, three types of typical sample shapes were obtained, a lot of tiny
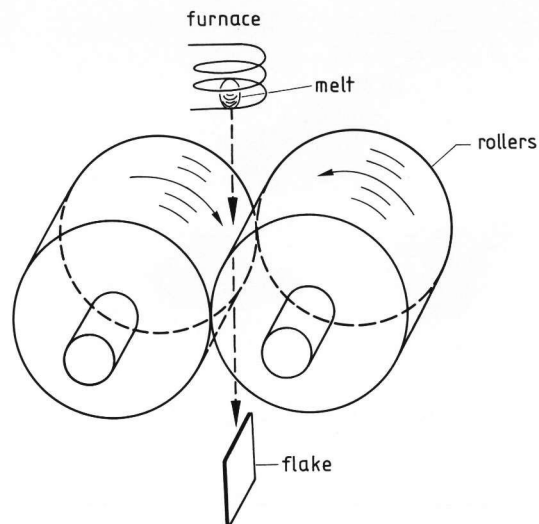

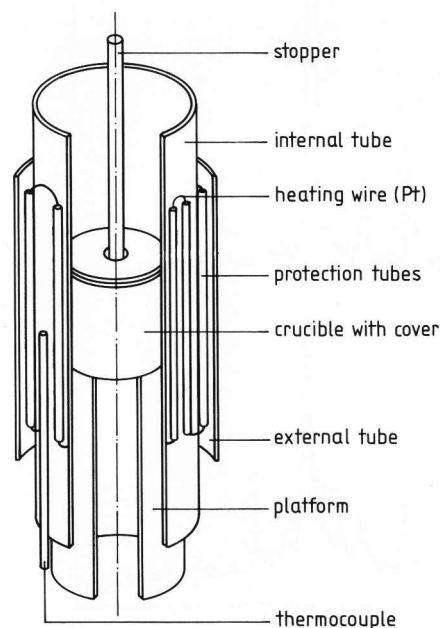Figure 1. Schematic of a twin-roller quenching setup.

Figure 2. Schematic of the furnace constructed (except heating wires and thermocouple all parts are made of alumina).
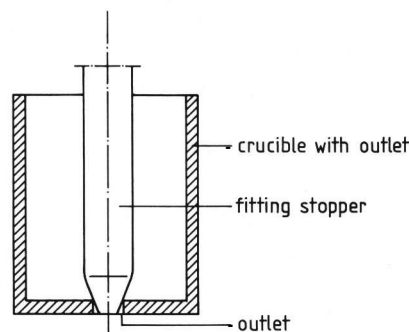

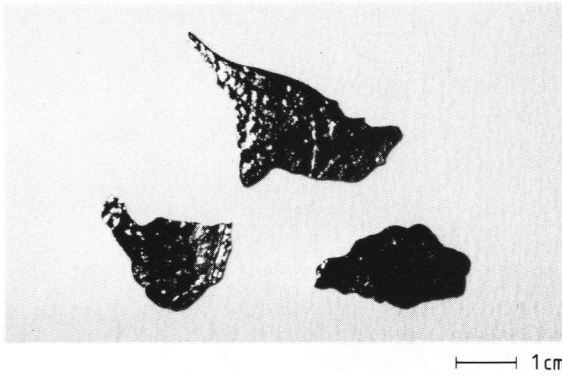Figure 3. Schematic of crucible, outlet and stopper.

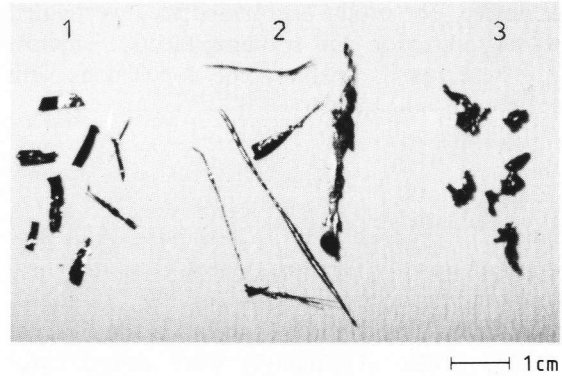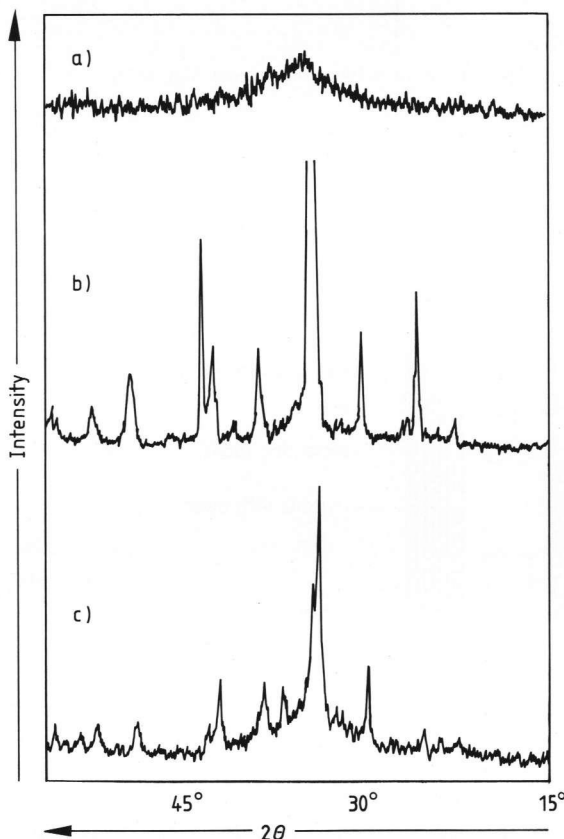Figure 4. Glass slabs produced by the two-plate quenching method.

Figure 5. Glass sample shapes produced by the twin-roller quenching method: thin slivers (no. 1), long fibers (no. 2), clusters (no. 3).

Figures 6a to c. X-ray diffraction patterns of a) glassy slivers and fibers, b) crystalline slabs cast from a melt in a platinum crucible, c) partially crystallized clusters.

slivers (no. 1), a few long fibers (no. 2), and some clusters (no. 3). These three main shapes were formed during all quenching experiments.

The slivers typically had thicknesses between 15 and 45 μm. The clusters with diameters up to a few millimeters most probably consisted of poorly quenched droplets sticking together. Fibers up to 40 mm long and about 65 μm thick were formed most frequently at a roller speed of 20 rps. For a roller speed of 55 rps and a sliver thickness of 15 μm, a $\Delta T/t$ value of about $1.7 \cdot 10^6$ K $\cdot$ s^{-1} can be estimated. For a roller speed of 20 rps and a fiber thickness of 65 μm

the $\Delta T/t$ value is about $0.3 \cdot 10^6$ K $\cdot$ s^{-1}. The quenching rate should also depend on the diameter of the crucible outlet, however, in practice the droplets rarely had the same diameter as the outlet. Either bigger drops gathered under the crucible bottom or the melt splashed onto the rollers and was torn apart into smaller droplets. Indeed, it was impossible to achieve reproducible diameters.

As X-ray diffraction (PW 1729, Philips, Kassel (Germany)) showed, most of the samples were glassy (figure 6a). One exception was the body melted in the platinum crucible. It displayed strong crystalline peaks (figure 6b). In contrast to this the sample melted in the Al_2O_3 crucible and quenched between the copper plates proved to be vitreous. The other exception were the clusters (figure 6c). As the curved baseline displays, a portion of the material is glassy. Obviously the surface part could be quenched rapidly enough to form a glass, whereas the cooling rate for the bulk material was too slow; it crystallized.

Bi_2O_3 has been shown to be a glass former [15]. Al_2O_3 acts as an intermediate glass former oxide. It is well-known that if one adds Al_2O_3 to normal silicate glass melts, e.g. of the system $Na_2O-CaO-SiO_2$, the viscosity is strongly increased, even if 0.5 wt% Al_2O_3 is added only. In that case the Al^{3+} ion substitutes a Si^{4+} ion as a network former, with Na^+ ions present for charge compensation. As mentioned earlier, in the present case Al_2O_3 acts in an opposite way. Melting in an Al_2O_3 crucible means that some minor amounts of Al_2O_3 dissolves in the melt by a corrosion process. Obviously this portion of Al_2O_3 enters the glass network as a network modifier with the consequence of lowering the overall viscosity of the respective melt. As analyses showed the Al_2O_3 contents lie below the detection limit of 0.2 to 0.4 % of the Energy Dispersive Spectrometry (EDS) system of the scanning electron microscope. Obviously traces of Al_2O_3 already have strong influence on the melting conditions.

The SEM inspection of the sliver surfaces displayed different features. Figure 7 shows that wavy
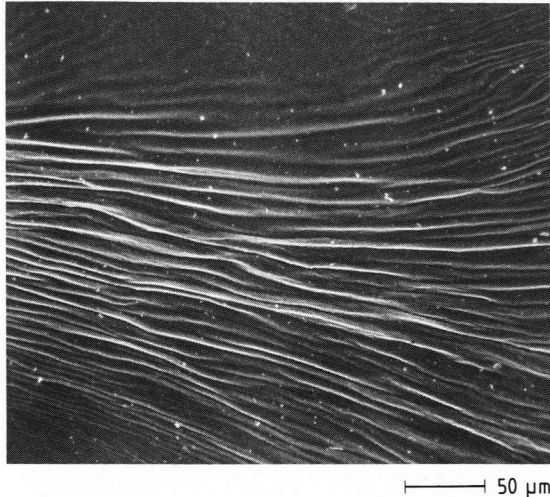
├──────┤ 50 μm

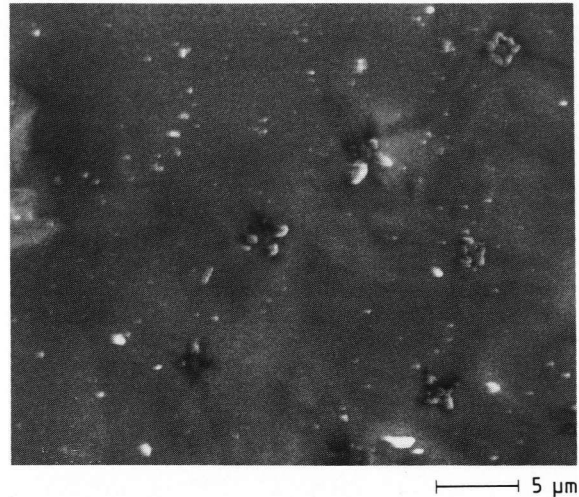Figure 7. SEM micrograph of a wavy sliver surface.

├──────┤ 5 μm

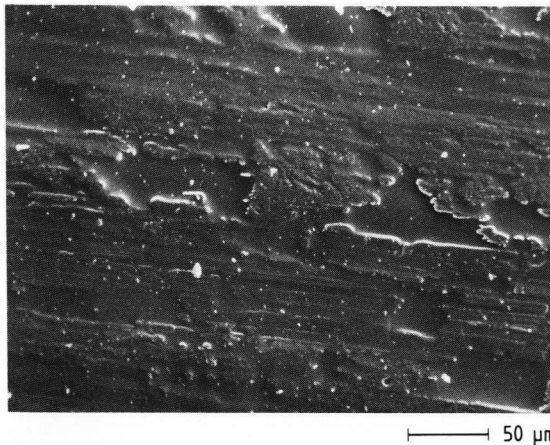Figure 8. SEM micrograph of star-shaped spots on slivers.

├──────┤ 50 μm

Figure 9. SEM micrograph of a layered surface of a sample quenched with 55 rps.

regions can be formed, giving evidence towards a nonuniform solidification process. EDS analyses resulted in enhanced bismuth contents in these regions, whereas calcium and copper showed some depletion. In contrast the surroundings of these wavy regions were depleted in bismuth and enriched in calcium. Besides these wavy regions all slivers had small star-shaped spots (figure 8). The sizes of the stars increased with decreasing roller speeds. The origin of these features is not yet clear. They could be pores because of a degassing process of the melts, they could even be metallic segregations which arise at too low roller speeds. Similar star-shaped features have also been found elsewhere [16].

Besides the mentioned surface microstructure samples quenched with different $\Delta T/t$ values may exhibit further features. Thus high roller speeds of 40 and 55 rps resulted in layered regions (figure 9), where the surfaces were cooled so rapidly that the uppermost layer ruptured partly. EDS analyses showed a good homogeneity in these layers with respect to the chemical composition. Samples

quenched at lower rates already were less homogeneous. In that case the cooling time was too long, thus the originally homogeneous melt started to develop segregated regions during the solidification process.

4. Conclusions

Slivers with different thicknesses originated from each quenching test. This means that the quenching rates varied within a certain range for each experiment. Thin slivers were cooled faster than thicker ones with rates between about $0.2 \cdot 10^6$ and $1.7 \cdot 10^6 \, K \cdot s^{-1}$. The diameter of the crucible outlet had no direct influence, as the droplet diameter is determined by other factors. The decisive influence for adjusting the quenching rate is the roller speed. High roller speeds result in well-quenched vitreous slivers. Of course, in order to obtain superconducting material these glassy slivers have to be ceramized.

5. References

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