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Melt-texture processing and high-temperature reactions of Bi-2212 thick films

D.P. Matheis[1], S.T. Misture and R.L. Snyder

Institute for Ceramic Superconductivity, New York State College of Ceramics at Alfred University, Alfred, NY 14802, USA

The optimum melting temperature and the phases which form on cooling from the melted state during melt-texturing $Bi_2Sr_2CaCu_2O_8$ are investigated. Nearly phase-pure and highly c-axis-oriented thick films are produced under these optimum conditions. The highest-quality films are produced by melting above 955°C, where the $(Sr,Ca)_xCu_yO_z$ phases melt to form $(Sr,Ca)O$ and liquid. The heat-treatment schedule after melting includes rapid cooling to 880°C, followed by slow cooling at 0.8 K/min to 775°C. In addition to the reactions which occur on cooling, an overview of the peritectic phases which form on heating is given. The principal tools used in these investigations are dynamic observations with high-temperature powder XRD (HTXRPD) and optical microscopy, which are complimented by DTA and electron microprobe EDS.

1. Introduction

The value of a liquid phase in sintering and microstructure control of ceramics has been well established. It is imperative that the nature of the liquid, and the order in which phases precipitate out of the liquid phase be understood in order to take advantage of the liquid present during the sintering process to optimize the microstructure. This is especially true in the case of ceramic superconductors, where the current-carrying capability may be dramatically enhanced by properly aligning the grains using the melt-texture process. Melt processing has been shown to improve the current density, J_c, and decrease the magnetic field degradation of J_c in $YBa_2Cu_3O_{7-\delta}$ by Jin et al. [1].

The melting and recrystallization sequences of $Bi_2Sr_2CaCu_2O_8$ (Bi-2212), which are of prime importance in melt-texturing, have been investigated by several groups using HTXRPD. Oka et al. [11, 12] investigated the partially melted states of Bi-2212 having nominal compositions 2212 and 4336. For a sample with nominal composition 2212, a partial melt forms at 890°C resulting in the formation of

$Sr_{1-x}Ca_xCuO_2$ ($x < 0.51$), and on cooling the Bi-2212 phase recrystallizes by 850°C with the $Bi_2Sr_2Cu_1O_6$ (Bi-2201) phase forming at 730°C. With the 4336 sample, a partial melt was achieved at 880°C resulting in $(Ca_{1-x}Sr_x)_2CuO_3$ ($x < 0.1$) crystals and on cooling the Bi-2212 phase forms at 840°C, and at 720°C the Bi-2201 phase forms.

In more recent studies using high-temperature XRD, Polonka et al. [13] and Xu et al. [14] have investigated the melting of Bi-2212 with and without the addition of silver powder. On heating a sample of Bi-2212 powder, the Bi-2212 peaks disappear and are replaced by the 080 and 200 peaks of $(Sr,Ca)CuO_2$ at 870°C. At this temperature, the 002 peak of the $(Sr,Ca)_2CuO_3$ phase is also present, and this peak grows in intensity at 880°C as the $(Sr,Ca)CuO_2$ peaks diminish. Above 890°C, the $(Sr,Ca)_2CuO_3$ peaks diminish, and are replaced by the peaks of $(Sr,Ca)O$, with a Sr/Ca ratio of $\frac{1}{3}$. On cooling, the $(Sr,Ca)_2CuO_3$ phase reforms but no evidence of Bi-2212 formation was seen at 870°C.

2. Experimental procedures

Bi-2212 powders were prepared by devitrification of melt-quenched glasses. Glass samples have been

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[1] Current address: Philips Semiconductors, 811 E. Arques Ave., M/S 76, Sunnyvale, CA 94088-3409, USA.

Fig. 1. Scanning electron micrograph of Bi-2212 powder heated through the first melt and quenched. The needle-like phase is a strontium calcium copper ternary in a quaternary matrix.

prepared with the Bi:Sr:Ca:Cu stoichiometric ratio 2212 by batching the proper amount of high-grade Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO, then melting and quenching to form a glass. This glass was then ground and heated in ambient atmosphere at a rate of 10 K/ min to the crystallization temperature, ~870°C, holding for 8 h, and then cooling at 10 K/min to produce phase-pure Bi-2212. The details of this glass-ceramic process are given in a separate paper [6].

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) was performed using a Setram TAG24 simultaneous thermoanalyzer. Samples were contained in platinum crucibles, and heated under oxygen using heating and cooling rates of 10 K/min. High-temperature optical microscopy was used to follow the morphological development during the reactions of the crystalline Bi-2212 sam-

ples. A resistively-heated Pt strip was used to control the sample temperature, a Leitz reflected-light microscope was used for imaging at a magnification of about 100×, and a video camera was used to record a real time representation of the reactions. EDS analysis was performed using an ETEC Autoscan with a PGT system 4 plus EDS attachment.

Ambient-temperature XRD data were collected using a Siemens D500 diffractometer with copper Kα radiation and a diffracted-beam graphite monochromator. In-situ HTXRPD was performed on a Philips diffractometer using a scanning position sensitive detector which allows for rapid data collection [7–9]. This system uses copper K radiation with a Ni beta filter. Sample heating and temperature control were achieved using a metal ribbon furnace, Model X86-N from Materials Research Corp. In both the high-temperature XRD and optical-microscopy experiments, the sample was loaded on a single-crystal MgO substrate. Samples were ground in cyclohexanone to form a slurry, and applied to the surface of the substrate dropwise. This sample-mounting procedure results in a sample film which is ~100 μm thick before melting.

3. Results and discussion

DTA analysis of Bi-2212 samples under oxygen shows that three endothermic reactions occur on heating with onsets of 892, 940, and 955°C. Previous work [13, 14] indicates that two ternary $(Sr,Ca)_xCu_yO_z$ phases form in the partial melt of Bi-2212, which accounts for the three endotherms in the DTA. The phases present after these three reactions, as well as the crystal morphologies, were confirmed by correlating high-temperature XRD, optical-microscopy, and quenched-sample results.

The high-temperature XRD patterns are shown in fig. for Bi-2212 heated in air. These patterns were collected every 50 K, from 800 to 1000°C. Note that the first pattern after melting, at 900°C, contains oriented reflections of two phases, $(Sr,Ca)CuO_2$ and $(Sr,Ca)_2CuO_3$, with $(Sr,Ca)CuO_2$ in the largest quantity. In the next pattern, at 950°C, the $(Sr,Ca)CuO_2$ peaks have decreased in intensity while the $(Sr,Ca)_2CuO_3$ peaks have grown, indicating that the $(Sr,Ca)_2CuO_3$ phase forms at higher tempera-
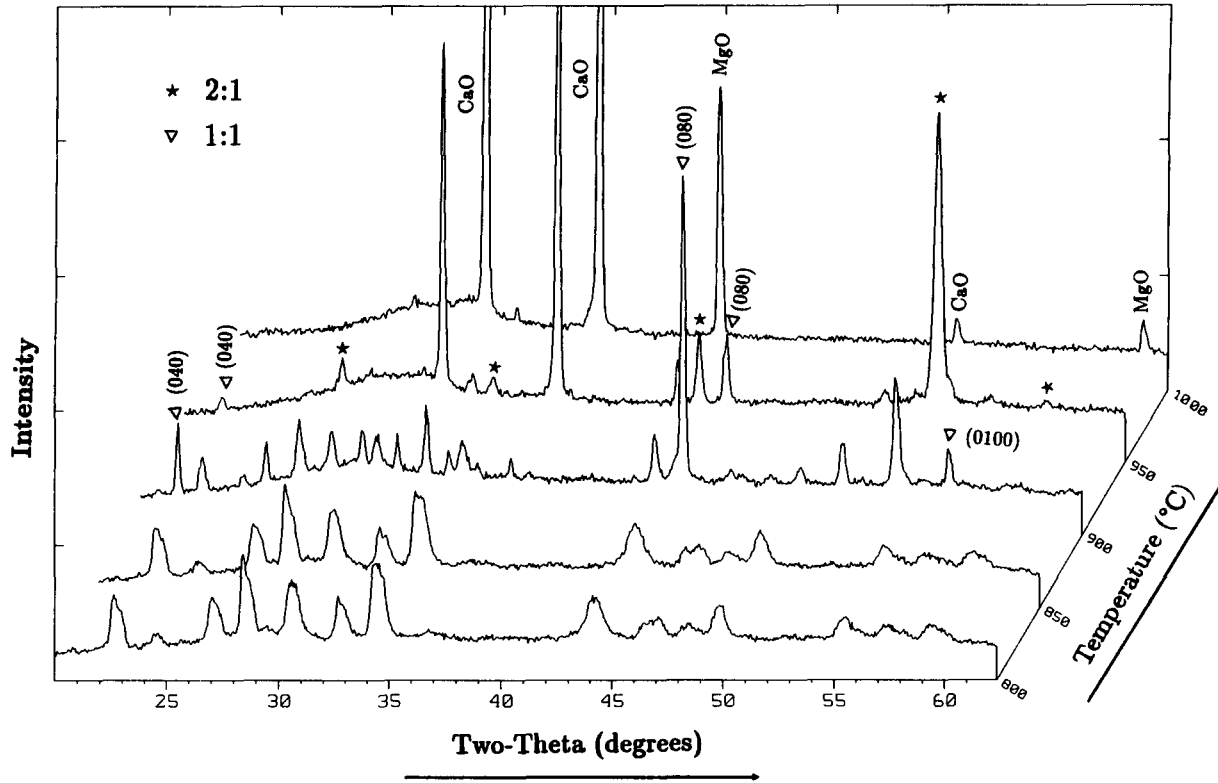
Fig. 2. High-temperature diffraction patterns of Bi-2212 powder heated in air.
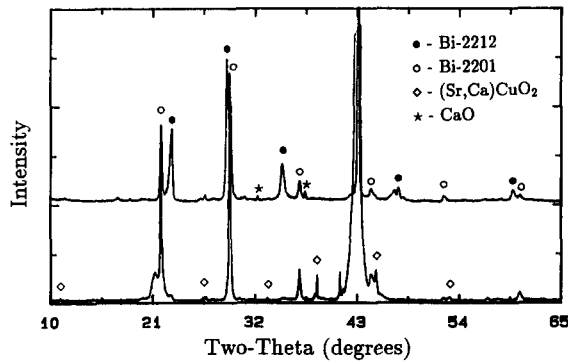

Fig. 3. X-ray diffraction patterns of high-temperature optical microscopy samples quenched after the first and second melting reactions.

tures. These results are also in agreement with the results of Polonka et al. [13] and Xu et al. [14]. CaO reflections are also present in the diffraction pattern at 950°C, which results from the final peritectic re-

action. By 1000°C, all of the Cu-containing intermediate phases have melted, leaving CaO and liquid.

In addition to the in-situ phase analysis, high-temperature optical microscopy was used to observe the morphological changes. On heating, the sample melts quickly at 880°C and the $(Sr,Ca)CuO_2$ phase grows out of the melt in the form of needle-like crystals. The $(Sr,Ca)_2CuO_3$ phase also forms as needles while heating further. At 950°C, the needle-shaped $(Sr,Ca)_xCu_yO_z$ crystals melt, leaving liquid with spherical grains of $(Ca,Sr)O$.

Samples were heated to several temperatures in the melt, and then quenched for SEM analysis to identify features which were possibly not observed in the low-magnification images from the optical microscope. Semi-quantitative EDS analysis was performed on these quenched samples in an attempt to identify each of the $(Sr,Ca)_xCu_yO_z$ phases. The EDS results indicate that the ternary needle-shaped crystals can be described by the formula $(Sr,Ca)_xCu_yO_z$

with $x:y$ ratios near 1:1 and 2:1, which has been observed previously [13, 14]. There is no correlation, however, between the size and shape, needle versus plank, of the ternary crystals and the observed stoichiometries. The highest-temperature phase, which occurs as spherical grains, is $(Ca,Sr)O$. The measured stoichiometries for the matrix phase in the two samples indicates that Bi-2201 crystallizes on quenching from 900°C, just above the first melt, and a combination of Bi-2201 and Bi-2212 form when quenching from 960°C, above the melting point of the ternary cuprate needle phases.

Figure 3 shows the XRD patterns of these quenched microscopy samples. The pattern for the sample quenched from the first partial melt is dominated by the 00l peaks of the Bi-2201 phase, and the peaks of the $(Sr,Ca)CuO_2$ phase are also present. The pattern for the sample quenched after the second melt contains the 00l peaks of both the Bi-2201 and Bi-2212 phases, as well as small, slightly shifted peaks of CaO. This corroborates the EDS results indicating Bi-2212 forms from the melt only after the sample has been heated above the melting points of the cu-

prates. Based on these results, the remaining melt-texturing runs were made by melting at or above about 960°C.

Using HTXRPD, the optimum temperature for Bi-2212 formation was found to be 880°C. Figure 4 shows the typical results for melting at 960°C and cooling to 880°C. Note that during repeated scans at 880°C, only the Bi-2212 00l lines are present, but upon cooling further, Bi-2201 forms beginning at ~825°C. This observation indicates that by holding below the Bi-2212 recrystallization temperature, but above that for Bi-2201, the sample should completely convert to Bi-2212. The cooling rate in this temperature region of 880–800°C has a significant effect on the final phase content.

Several cooling schedules were used to find the optimum cooling rate for forming phase-pure Bi-2212 after melting at 960°C. The best results are shown in the XRD patterns in fig. 5. The temperature profile used in this experiment included heating at 5 K/s to 960°C, then cooling immediately to 880°C at 5 K/s, where data collection started. Diffraction patterns were collected every 5 K during cooling, and
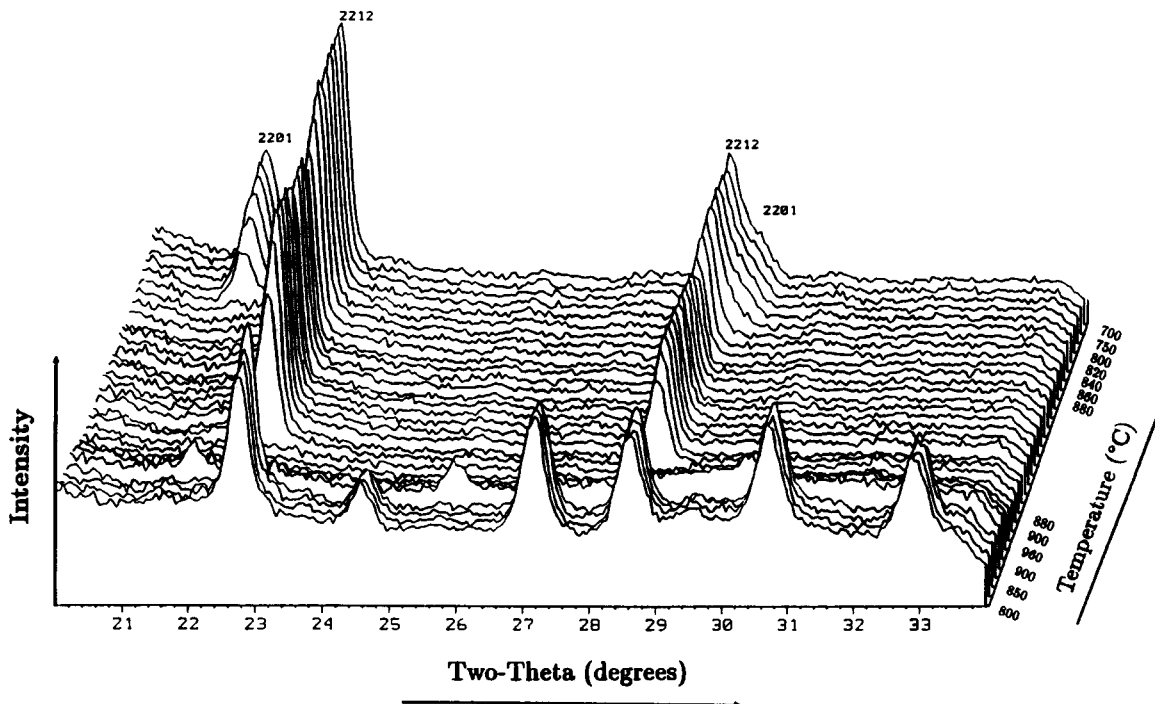

Fig. 4. HTXRPD patterns of Bi-2212 powder heated in air, with a soak at 880°C on cooling from 960°C.
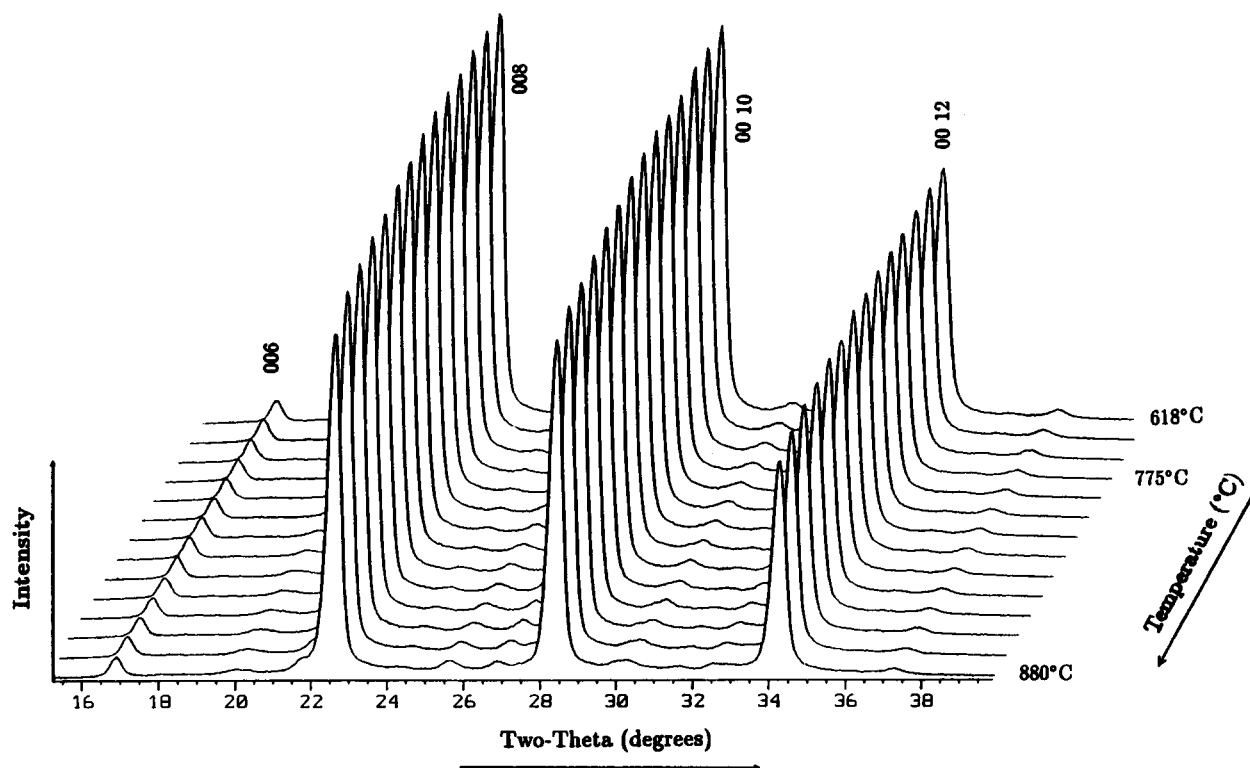
Fig. 5. High-temperature diffraction patterns of Bi-2212 powder melted in air at 960°C, then quickly cooled to 880°C. Cooling from 880 to 775°C required 130 min.

each scan required 6 min for collection. The total time to cool from 880 to 775°C, which is the temperature range shown, was 130 min, so the average cooling rate was 0.8 K/min. The first pattern, collected at 880°C after rapidly cooling from 960°C shows that nearly perfectly oriented Bi-2212 has formed during the rapid cooling stage. The 00l lines of Bi-2212 increase in intensity during the first four scans, but remain constant on further cooling. All of

Table 1
Summary of differential thermal analysis of Bi-2212 powder run in oxygen

	Temp. (°C)	Heat flow
Heating	892	endo
	940	endo
	955	endo
Cooling	945	small exo
	870	exo
	760	exo

the reflections present in the first scan at 880°C remain until 775°C, but no new phases evolve. In particular, this cooling schedule has inhibited Bi-2201 formation, yielding a highly oriented, phase-pure Bi-2212 film.

When cooling from the first molten state the presence of the $(Sr,Ca)_xCu_yO_z$ phases causes the liquid to be deficient in copper and the alkaline earths, which results in Bi-2201 crystallizing more prominently than Bi-2212. When cooling from the second molten state the presence of $(Ca,Sr)O$ inhibits $(Sr,Ca)_xCu_yO_z$ formation and so the liquid remains rich in copper allowing Bi-2212 crystallization to occur. Rapid cooling from 955°C to below 880°C will cause the liquid to remain deficient in calcium because dissolution of CaO crystals is kinetically limited. Bi-2212 growth will eventually be inhibited because insufficient Ca is present, and the remainder of the melt will crystallize as Bi-2201. If the temperature is held above the Bi-2201 crystallization point for a sufficient length of time, the CaO will dis-

solve in the liquid and increase the Ca content so that further Bi-2212 crystallization may proceed. Unfortunately, while soaking in this temperature region, more of the ternary needle phase can form which consumes copper and alkaline earths which are necessary for continued Bi-2212 formation. Slow cooling allows any ternary crystals to react with the remaining liquid to supply the Cu and alkaline earths needed to provide the proper stoichiometry liquid to allow further Bi-2212 crystallization. Of course, the solid and liquid phases must remain in contact for these reactions to occur. Further work is currently under way to determine the details of the peritectic reactions, including solid-solution phases, temperatures, and kinetics of formation.

4. Conclusions

Melting reactions and sequences of Bi-2212 have been investigated, which aid in determining the optimum melting temperatures and cooling schedule for melt-processing. Recrystallization of the Bi-2212 phase was found to be more complete after melting above 955°C, where (Ca,Sr)O and a liquid are present.

The optimum heat-treatment schedule for forming highly oriented and phase-pure Bi-2212 thick films has been determined, as well as the reaction path which produces Bi-2212 from a partially melted state containing (Sr,Ca)O and liquid. Samples should be heated above 955°C to produce the melt plus (Sr,Ca)O, then cooled to the Bi-2212 crystallization temperature of 870–880°C. The cooling rate used from above 955 to 880°C was 5 K/s. After cooling to 880°C, (Sr,Ca)O is still present, and $(Sr,Ca)_xCu_yO_z$ crystals will form. Dissolution of the (Sr,Ca)O and $(Sr,Ca)_xCu_yO_z$ crystals will adjust the stoichiometry of the melt toward 2212 to allow spinodal growth of Bi-2212 crystals. Slow cooling from 880 to below about 800°C is necessary to keep the stoichiometry of the liquid near 2212 by dissolution of both (Sr,Ca)O and $(Sr,Ca)_xCu_yO_z$. Complete conversion to Bi-2212 is dependent on slow cooling and contact between the liquid and solid phases. The

optimum average cooling rate for complete conversion to Bi-2212 was determined as 0.8 K/min. Cooling too rapidly from 880°C will cause the liquid to become deficient in Cu or the alkaline earths, resulting in Bi-2201 formation.

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