CRYSTALLINE PHASES DURING THE MELTING OF $Bi_2Sr_2CaCu_2O_x$

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ABSTRACT

The melting of $Bi_2Sr_2CaCu_2O_x$ material has been studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) in order to study the phases that formed in the high temperature regions. Two distinct phases of $(Sr_{1-x}Ca_x)CuO_2$ and $(Sr_{1-x}Ca_x)_2CuO_3$ have been observed in the Bi-rich matrix depending upon quenching temperatures. Crystallization from the melt by fast cooling usually produce the co-existence of Bi (2201) and these Sr-Ca-Cu-O phases.

Introduction

High T_c Bi-Sr-Ca-Cu-O superconductors may have great potential in practical applications. Considerable interest has been raised in the many phases that form at higher temperatures in the fabrication of the high quality Bi (2212) or Bi (2223) superconductors [1-4]. In recent studies of high temperature x-ray diffraction [5-7], it has been shown that upon melting Bi (2212) material several different insulating phases appear in the liquid during the melting process. Oka et al. first reported that two phases of $(Sr_{1-x}Ca_x)CuO_2$ and $(Sr_{1-x}Ca_x)_2CuO_3$ were observed in the melted state depending upon the starting compositions of Bi (2212) and Bi (4336) [5]. But, it is unclear how these phases form. The purpose of this work is to study the crystallization behavior, the phase formation, and the factors controlling the phase growth during the melting at high temperatures in Bi (2212) system. The phases present in the melted state have been investigated by scanning electron microscopy and energy dispersive spectrometer.

Experimental

The Bi (2212) materials used in the high temperature x-ray diffraction experiments were prepared using a solid state reaction technique reported elsewhere [3]. The sample crucible is a Pt strip about 0.15 mm thick, 10 mm wide, and 100 mm long with an indentation about 8 mm by 8 mm in the center to hold the Bi (2212) powder. The samples were quenched from high temperatures by switching off the power supply, while either $(Sr_{1-x}Ca_x)CuO_2$ phase or $(Sr_{1-x}Ca_x)CuO_2$ phase diffraction

peaks was observed in the high temperature x-ray detector. More detailed description of high temperature x-ray diffraction work can be found in Ref. [8]. Microstructure and phase composition were examined by a Cambridge S-200 scanning electron microscope (SEM) equipped with a Tracor-Northern energy dispersive spectrometer (EDS) and operated at 15 kV. Chemical analysis was carried out on the EDS spectrum with standardless semi-quantitative analysis (SSQ) program.

Results and discussion

Extensive SEM and EDS studies have done on the samples quenched from high temperatures in air. The first sample was quenched from a temperature of about 860°C as $(Sr_{1-x}Ca_x)CuO_2$ or (11) phase peaks appeared in the x-ray spectrum. As can be seen in Fig. 1a, rectangular crystalline needles are embedded in Bi-rich matrix. EDS analysis in Figs. 2a and 2b reveals that the rectangular needle is the (11) phases and Bi-rich matrix is the Bi (2201) phase. From the chemical analysis, we find the ratio of Sr/Ca ($x \sim 0.33$) in $(Sr_{1-x}Ca_x)CuO_2$.

As temperature is raised to about 870°C, most x-ray peaks of (11) phase disappear and peaks belonging to $(Sr_{1-x}Ca_x)_2CuO_3$ or (21) phase appear. The second sample was quenched from these conditions. As shown in Fig 1b, there are still rectangular crystalline needles embedded in Bi-rich matrix. However, the shapes of these needle are different from the (11) phase. These needle seem to be narrower and sharper than the (11) phase as shown in Fig. 1a. EDS patterns in Figs. 2a and 2c indicate that the narrower and sharper rectangular needle belong the (21) phases and Bi-rich matrix is still the Bi (2201) phase. It should be pointed out that although the dominate phase is (21) phase, the (11) phase is still maintained as a minor phase. EDS analysis also indicate the (21) phase has a composition of $x \sim 0.55$ in $(Sr_{1-x}Ca_x)_2CuO_3$.

It should be pointed out that although both (11) and (21) phases are orthorhombic structures, they belong to different space groups. As temperature increases in the melting state, more Cu is rejected from the formed (11) phase to the Bi-rich liquid. Therefore, the (21) phase can be formed. On the other hand, the formation of the Bi (2212) phase from the melting Bi -rich liquid is inhibited by the formation of $(Sr_{1-x}Ca_x)CuO_2$ or $(Sr_{1-x}Ca_x)_2CuO_3$ since Ca is not in the Bi -rich liquid.

These EDS results are in very good agreement with the high temperature x-ray data in Ref. 8. A typical melting sequence for Bi (2212) powder shows three different phases form upon various temperatures, first (11) phase, then (21) phase, finally $(Sr_{1-x}Ca_x)O$ or (10) phase and the Bi -rich liquid. The scan pattern before melting is basically the same as at room temperature assigning as Bi (2212) crystalline phase. Once the sample began to melt, the Bi (2212) pattern starts to disappear. As the scan time develops, two strong lines grow at 44.0° and 51.3°. These two lines can be identified as the (0,8,0) and (2,0,0) lines of the orthorhombic (11) phase [9,10], where the longest lattice constant has been chosen to be the **b** -axis (the space group is CmCm). The (11) phase diminishes and the line at 54.0° grows

very rapidly at higher temperature. The lines at 34.9° and 54.0° are the (6,0,0) and (0,0,2) lines of (21) orthorhombic structure [10-12], where the longest lattice constant is also chosen as the a -axis (the space group here is Immm).

Summary

The melting of Bi (2212) occurs in several steps and two phases form in sequence upon various temperatures, first $(Sr_{1-x}Ca_x)CuO_2$ or (11) phase, then $(Sr_{1-x}Ca_x)_2CuO_3$ or (21) phase, and the Bi -rich liquid (2201). SEM and EDS studies reveal that the (11) and (21) phases are in the form of rectangular needles floating on the surface of the Bi -rich liquid and that the Bi -rich liquid crystalizes into the Bi (2201) phase by quenching in air. Both (11) and (21) phases should play an important role in the formation of the Bi (2212) phase.

Acknowledgments

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Figure captions

Fig. 1 Scanning electron microscopy photograph for quenched samples: (a) $(Sr_{1-x}Ca_x)CuO_2$ phase, (b) $(Sr_{1-x}Ca_x)_2CuO_3$ phase, both of them embedded in Bi-rich (2201) matrix.

Fig. 2 Energy dispersive spectroscopy for quenched samples indicating: (a) $(Sr_{1-x}Ca_x)CuO_2$ phase; (b) $(Sr_{1-x}Ca_x)_2CuO_3$ phase; and (c) Bi (2201) phase.

Fig. 1 Scanning electron microscopy photograph for quenched samples indicating $(Sr_{1-x}Ca_x)CuO_2$ phase (upper) and $(Sr_{1-x}Ca_x)_2CuO_3$ phase (lower) embedded in Bi-rich (2201) matrix.

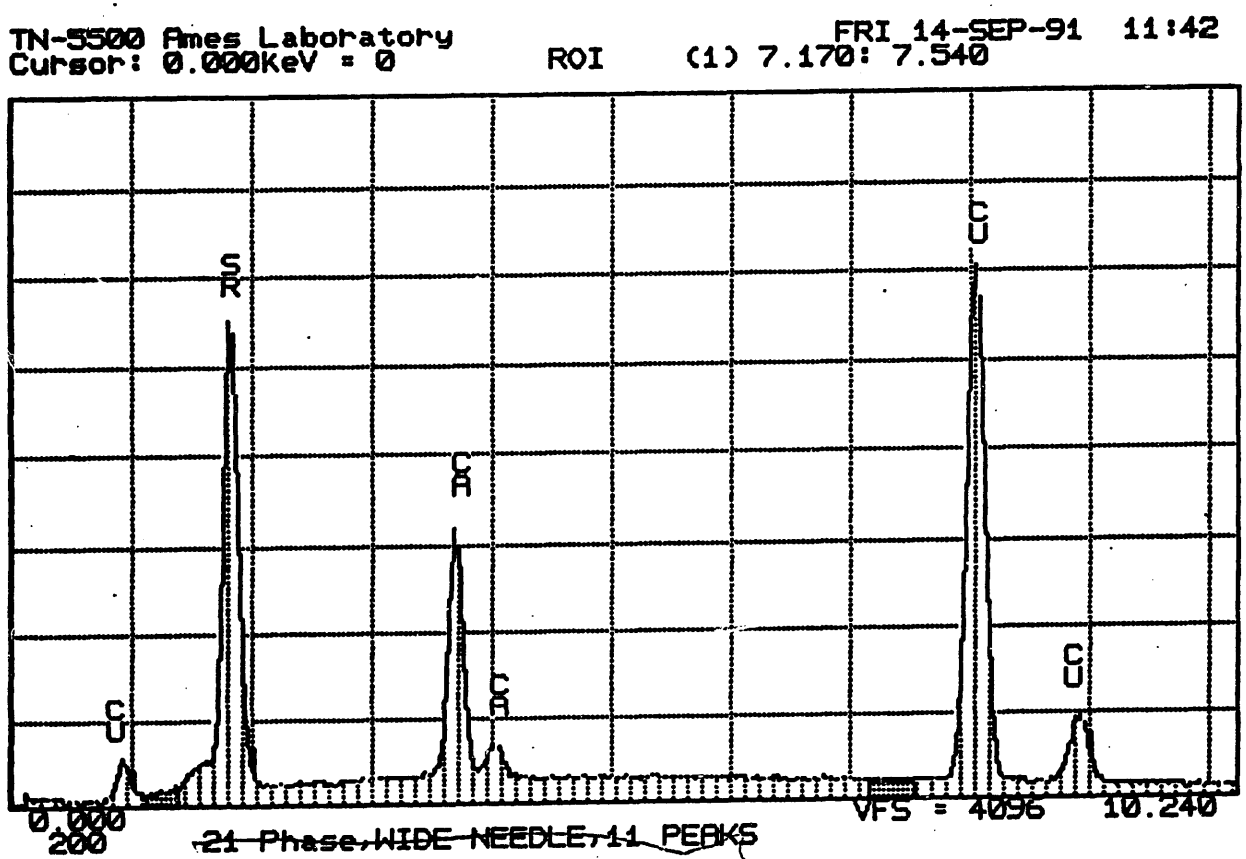


Fig 2a

MEM (12), 0.010keV LT= 200SECS
LABEL:21 Phase,WIDE NEEDLE,11 PEAKS

ROI	0 [00]	1.130: 1.380keV	GROSS=	2293	NET=	-157
ROI	1 [01]	7.170: 7.540keV	GROSS=	4030	NET=	-207

8844	33835	168
8905	4467	188

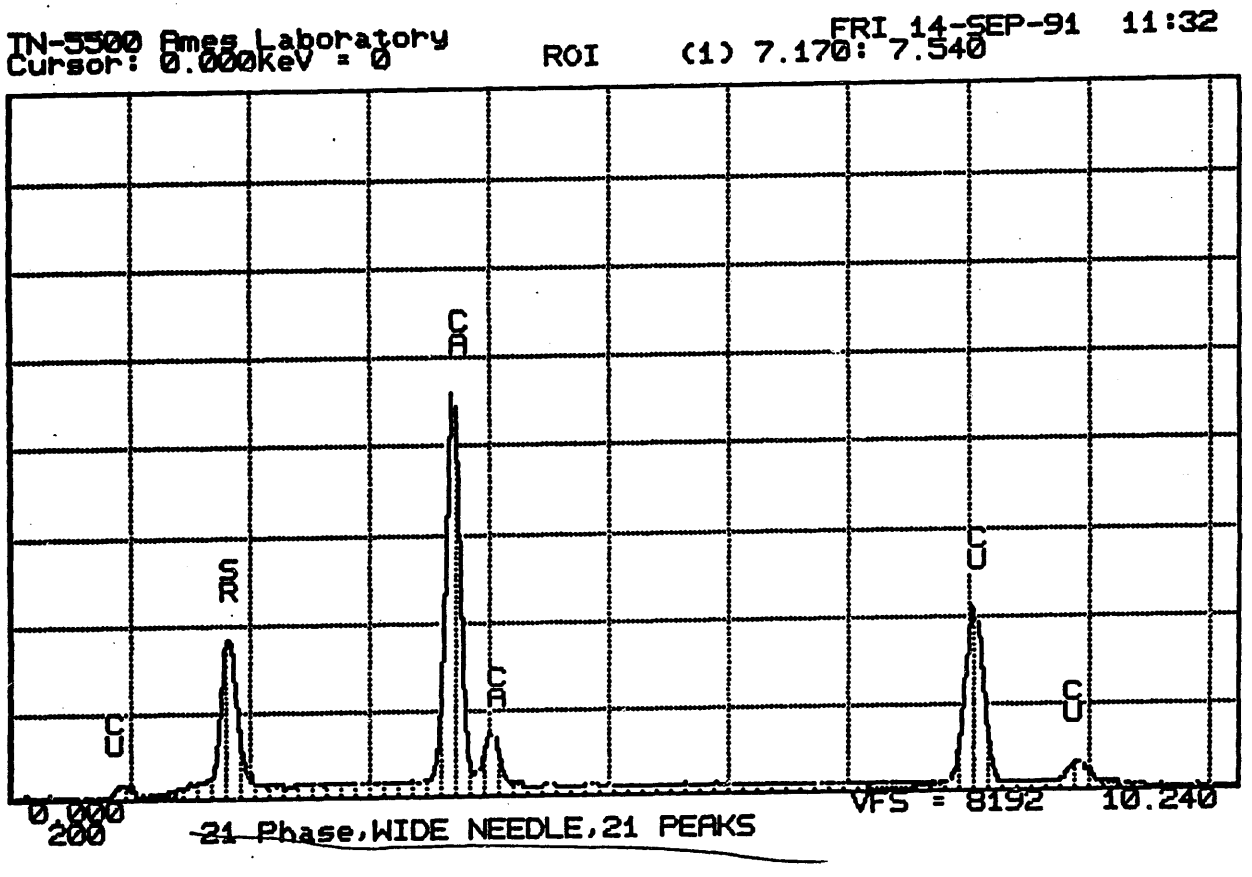
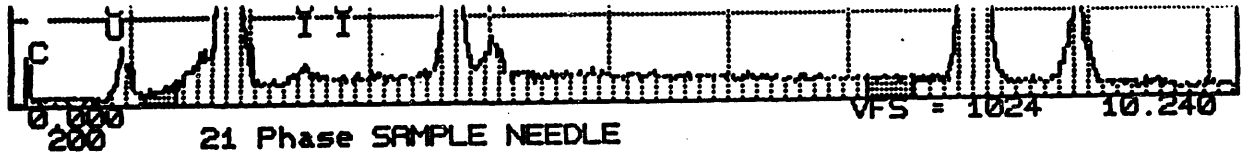


Fig 26



21 Phase SAMPLE NEEDLE

R= +212

21 Phase Matrix area 200SECS

CENTR.	AREA	FWHM	
190	296	47947	N
931	194	64883	N
1826	8208	139	
2459	15011	198	W
3693	1314	134	
8049	4759	166	
8910	629	157	

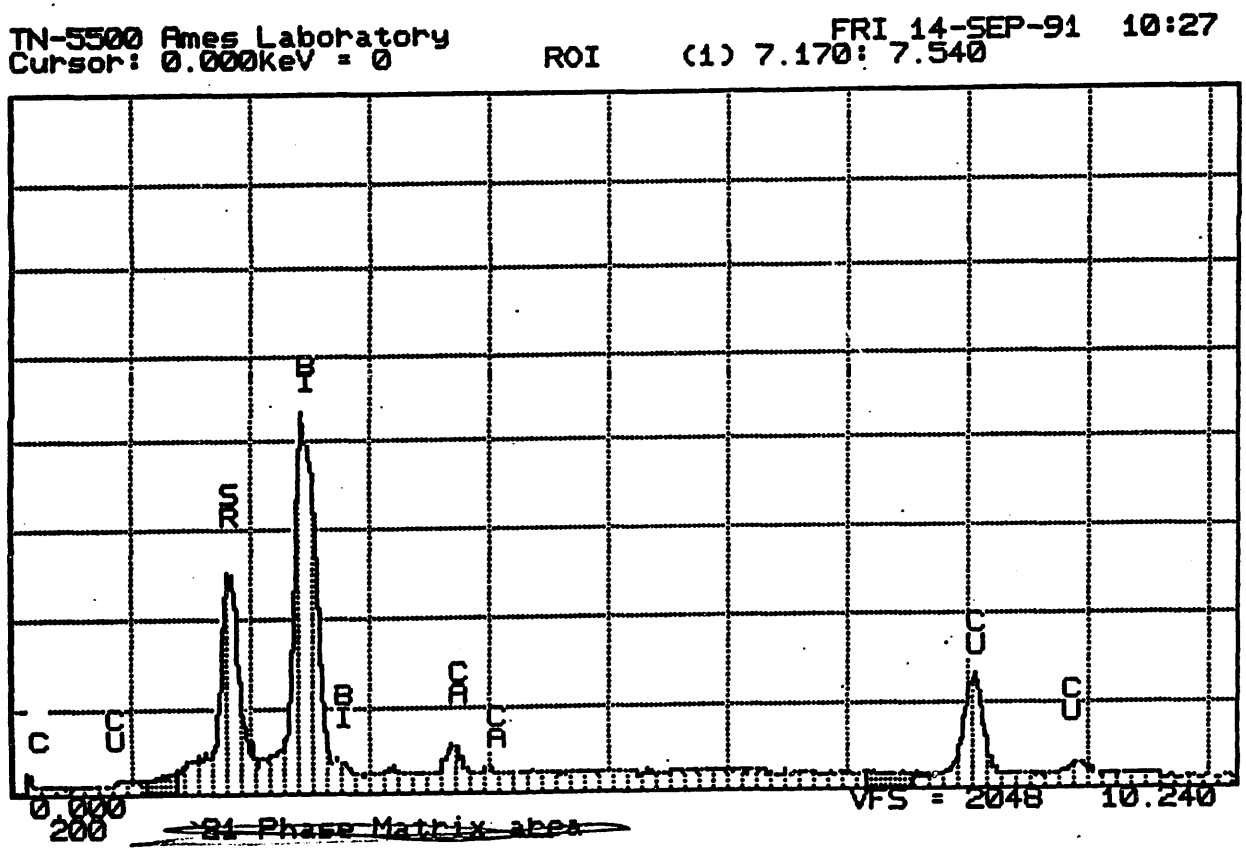


Fig 2c

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