A CONTRIBUTION TO THE STUDY OF Bi—Sr—Ca—Cu—O SUPERCONDUCTORS[1])

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The influence of the preparation conditions on the phase composition of samples, morphology, and chemical composition of the superconducting phase has been studied. The best samples revealed zero resistance at 72 K. The onset of conductivity was observed at 115 K.

I. INTRODUCTION

Discoveries of 30 K superconductivity in the La—Ba—Cu—O system [1] and 90 K superconductivity in the Y—Ba—Cu—O system [2] have stimulated a worldwide race for higher temperature superconductors. Breakthroughs have recently been made in rare-earth-free superconductors by the discoveries of the 90 K Tl—Ba—Cu—O system [3, 4], the 110 K Bi—Ca—Sr—Cu—O system [5, 6] and the 120 K Tl—Ca—Sr—Cu—O system [7, 8].

In the present paper we report the behaviour of the superconducting phases observed in a material of the nominal composition $Bi_4Sr_3Ca_3Cu_4O_{16-x}$.

II. METHOD

Samples of the nominal composition $Bi_4Sr_3Ca_3Cu_4O_{16-x}$ were prepared by the solid state reaction from Bi_2O_3, CuO, $Sr(NO_3)_2$ and $CaCO_3$ (of a purity of 99.9 % or better) mixed powder pressed in pellets. After being heated at 800 °C for 4 h and at 860 °C for 64 h in air the material was ground and pressed (600 MPa) in tablets (10 mm in diameter, 1 g weight). The heat treatment of the samples was as follows:

A — at 860 °C for 16 h in air and quenching; B — at 860 °C for 16 h in air and at 860 °C for 16 h in O_2 and cooling for 0.5 °C/min.

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The materials were analysed by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffractometry with $Cu_{K\alpha}$ radiation. Resistance was measured by means of standard four-probe method.

III. RESULTS

A substantial part of the samples after the A and the B heat treatment is the $Bi_2Sr_2Ca_1Cu_2O_{8-x}$ phase. We can describe this phase in agreement with [9, 10] as a tetragonal cell with the cell parameters $a = 5.39$ Å and $c = 30.6$ Å. The peak in the X-ray diffraction pattern in Fig. 1b, marked by an arrow, indicates the presence of a small amount of the phase with $c = 37$ Å.

The plate-like crystals morphology of the $Bi_2Sr_2Ca_1Cu_2O_{8-x}$ phase was observed metallographically and on the fracture surface. Randomly oriented plate-like crystals (Fig. 2a) give a characteristic diffraction pattern shown in Fig. 1a. The preferred orientation of these crystals with c-axis perpendicular to the surface of the sample (Fig. 2b) appears as an increase of intensities of the diffraction peaks (001) — Fig. 1b.

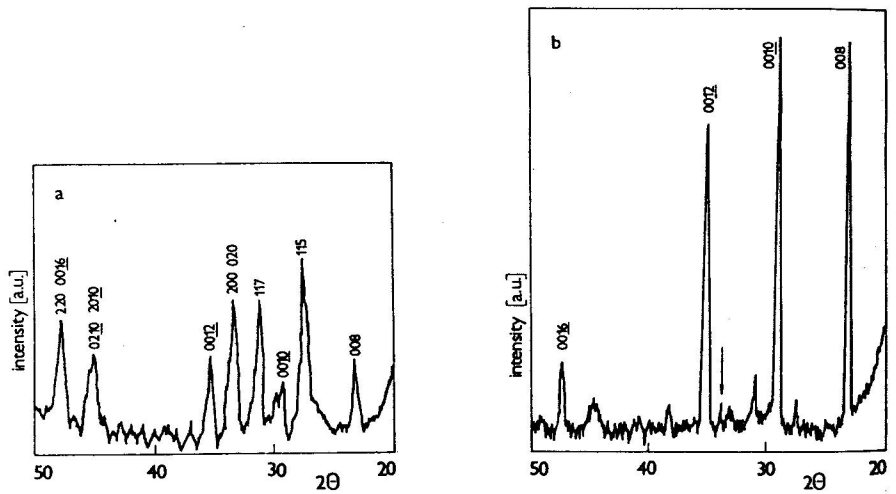

Fig. 1. X-ray diffraction pattern of the $Bi_2Sr_2Ca_1Cu_2O_{8-x}$ phase (sample B): a) taken from the surface, b) taken after the removing of the surface layer.

An oriented and a not oriented region appeared in all samples while the texture was in all cases only in the narrow region below the surface perpendicular to the axis of pressing.

A small amount of two secondary phases was present in the samples. They were analysed by EDX and their chemical compositions are Sr : Ca : Cu = 1 : 1 : 3

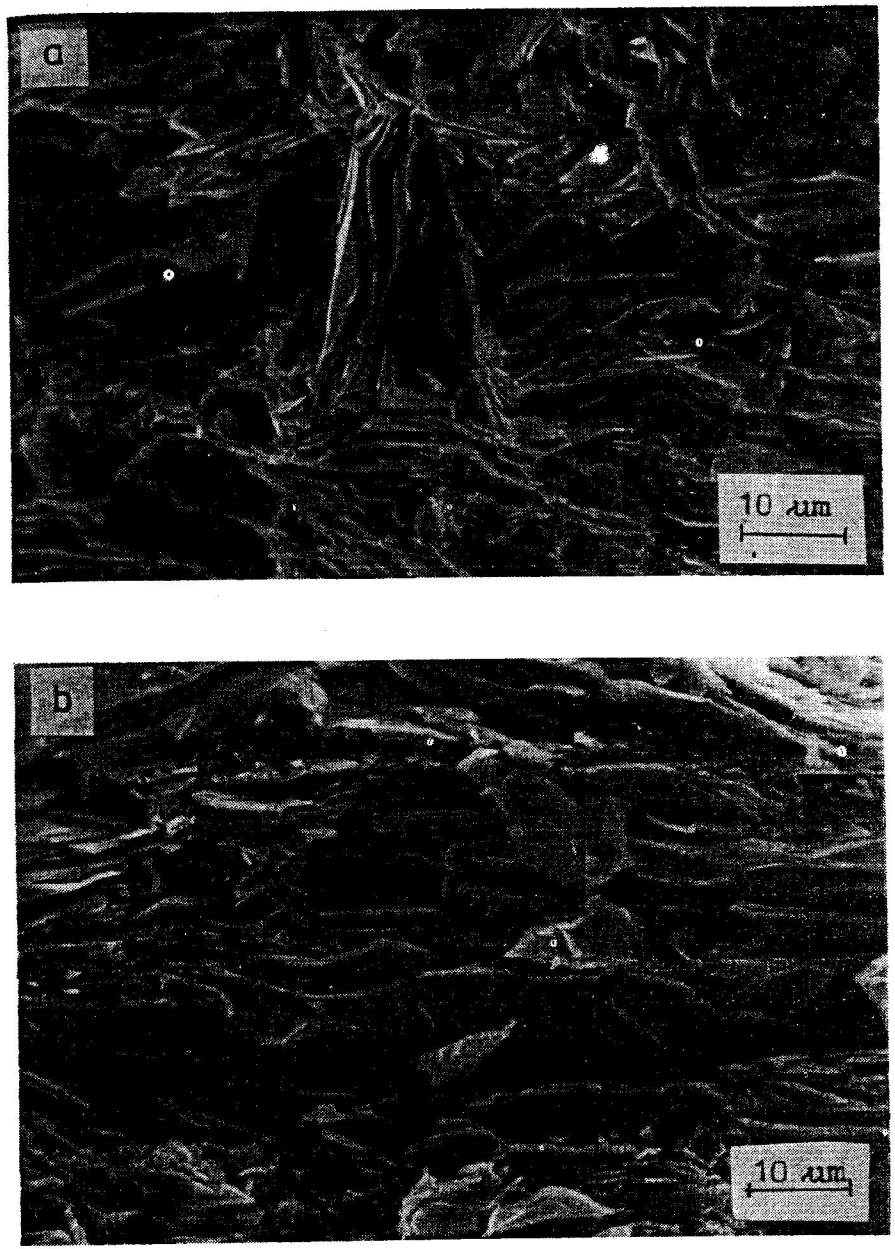

Fig. 2. The SEM image of the fracture surface of the $Bi_2Sr_2Ca_1Cu_2O_{8-x}$ phase parallel to the direction of pressing: a) the surface region of the tablet, b) the central region of the tablet.

and Ca : Cu = 2 : 1. A change in the electrical resistance of the samples A and B with temperature is in Fig. 3. Both samples show zero resistance at 72 K and small drops of resistance are located at about 115 K. The electrical resistance of sample A is higher than the resistance of sample B. The changes in resistance with temperature are different, too. Whereas sample B has a metallic behaviour, the resistance of sample A is increasing with decreasing temperature, which is characteristic for a semiconducting behaviour.

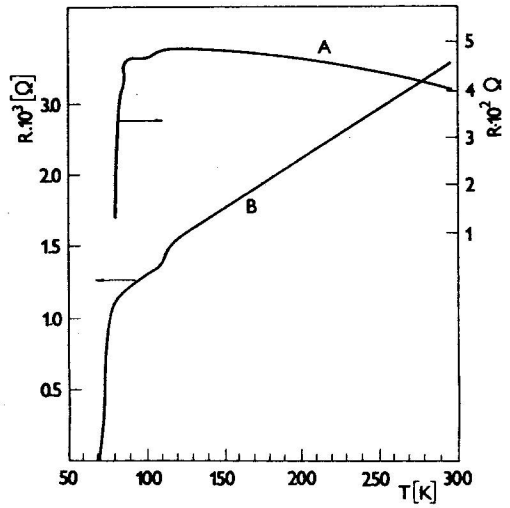

Fig. 3. Temperature dependences of electrical resistance for samples A and B.

IV. DISCUSSION

It is known that the nominal composition $Bi_4Sr_3Ca_3Cu_4O_{16-x}$ leads to a nearly monophase structure $Bi_2Sr_2Ca_1Cu_2O_{8-x}$ with a secondary phase rich in Sr, Ca, Cu or Cu, Ca [9, 11]. According to [9, 10] the transition temperature T_c of the 2212 phase is 85 K and T_c = 110 K is characteristic for the tetragonal phase with c = 37 Å. Thus both our samples are a mixture of the 85 K and the 110 K phases. Since the content of the 110 K phase does not change under the conditions of cooling we can conclude that this phase was formed during annealing at 860 °C. But the change of resistance with temperature and the resistance at room temperature are very sensitive to the cooling conditions. We believe this different behaviour to be caused by differencies in the vacancy content and vacancy ordering as observed in the $Re_1Ba_2Cu_3O_{7-x}$ systems [12, 13].

V. CONCLUSIONS

During annealing at 860 °C in addition to the 2212 phase the tetragonal phase with a cell parameter c = 37 Å and T_c = 110 K is formed and its part is not changed by the cooling conditions.

The electrical resistance and its change with temperature are sensitive to the cooling conditions.

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ВКЛАД В ИЗУЧЕНИЕ СВЕРХПРОВОДНИКОВ Bi—Sr—Ca—Cu—O

В работе изучается влияние условий при приготовлении образцов на их фазовый состав, морфологию и химический состав сверхпроводящей фазы. Лучшие образцы демонстрировали нулевое сопротивление при 72 К. Начало проводимости наблюдалось при 115 К.