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# THE INFLUENCE OF THE SINTERING TEMPERATURE ON THE RESISTANCE AND ON THE STRUCTURE OF $YBa_2Cu_3O_{7-x}$ CERAMICS PREPARED BY THE SOL-GEL PROCESS[1])

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The article deals with the description of the microstructure development of $YBa_2Cu_3O_{7-x}$ ceramics prepared by the sol-gel process at sintering. We have observed an increase in contact quality among $YBa_2Cu_3O_{7-x}$ grains above 940 °C and a rapid grain growth at 980 °C. The unfavourable influence of the CuO phase at 980 °C is connected with its distribution along the $YBa_2Cu_3O_{7-x}$ grain boundaries. Temperature variations of resistance are discussed in the relation to the structure of these ceramics.

## I. INTRODUCTION

A high superconducting temperature has been discovered for the chemical compound Y—Ba—Cu—O system [1]. The properties of $YBa_2Cu_3O_{7-x}$ ceramics are connected with their preparation conditions. The homogeneity of the chemical composition, the density of voids, grain size and grain orientation, the quality of the contacts between grains, the secondary phases content and their distribution are the main structural parameters resulting from the preparation conditions. The ceramics prepared by the sol-gel process are of a small grain size and a high chemical homogeneity [2]. However, most workers have not investigated the sintering conditions of these ceramics systematically, thus we have tried to obtain the relation between the sintering temperature, the structure and the resistance $YBa_2Cu_3O_{7-x}$ ceramics prepared by the sol-gel process.

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## II. METHOD

Samples of nominal composition $YBa_2Cu_3O_{7-x}$ were prepared by the sol-gel process using the autocatalytic pyrolytic decomposition of Y, Ba and Cu citrates sol [3]. The interproduct was annealed at 920 °C in air for 4 h. The product (monophase orthorhombic $YBa_2Cu_3O_{7-x}$) was pressed (10 MPa) in tablets (10 mm in diameter, 1 g weight) and sintered at 920, 940, 960 and 980 °C in $O_2$ for 16 h and cooled at the cooling rate of 20 °C/min with a stop of 2 h at 450 °C. The second sintering of these samples was realised after their new grinding and pressing at 800 MPa. The structure was observed metallographically. The resistance was measured using the four point method. The mean linear grain size $\bar{l}$ was measured on light microscope photographs.

## III. RESULTS

RTG analysis showed that the material prepared by the sol-gel process is an orthorbombic $YBa_2Cu_3O_{7-x}$ monophase. Its sintering behaviour is shown in Fig. 1. The density of the samples is monotonically increasing with sintering temperature. The grain size of the $YBa_2Cu_3O_{7-x}$ phase is practically constant at 920 and 940 °C. A small grain growth is observed at 960 °C and a rapid one at 980 °C. The grain growth of individual grains is not equal, thus the structure at this sintering temperature is formed by a mixture of large and small grains (Fig. 2). Small amounts of CuO and $Y_2BaCuO_5$ present in the samples are observed on metallographic photographs (Fig. 2). The CuO phase is present as separate grains at 920, 940, and 960 °C, whereas at 980 °C it is on the grain boundaries of $YBa_2Cu_3O_{7-x}$ having an elongated form. $Y_2BaCuO_5$ (211 phase) occurs within grains.

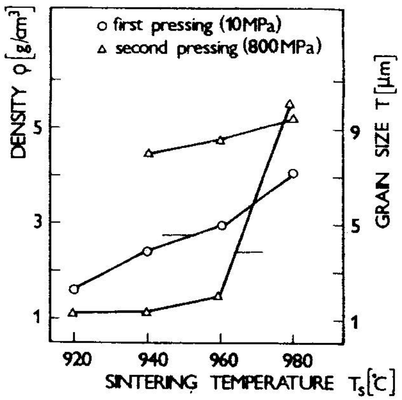


Fig. 1. Change in density and mean linear grain size ($\bar{l}$) with sintering temperature for the by the sol-gel process prepared $YBa_2Cu_3O_{7-x}$ ceramic tablets.



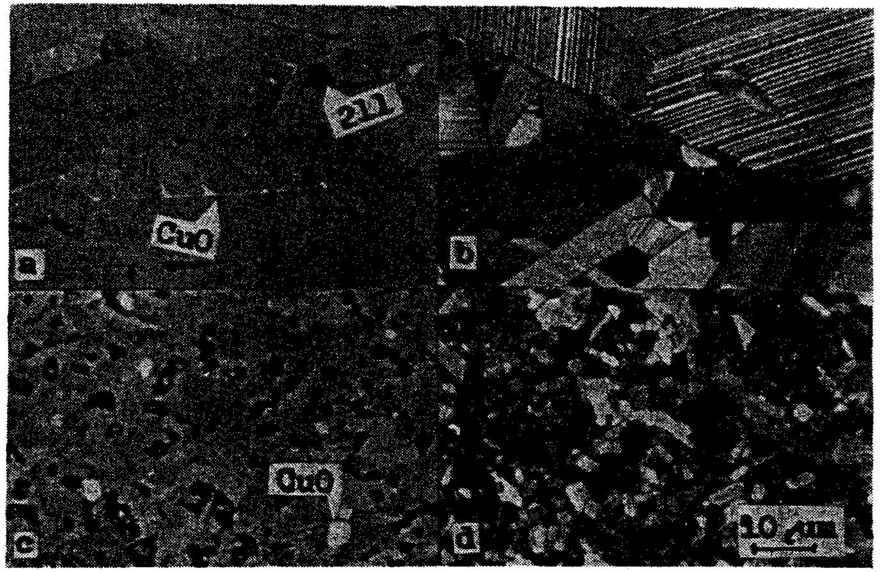


Fig. 2. Optical micrographs of polished $YBa_2Cu_3O_{7-x}$ samples in normal (a, c) and polarized light (b, c) sintered at 960° (a, b) and 980° (c, d).

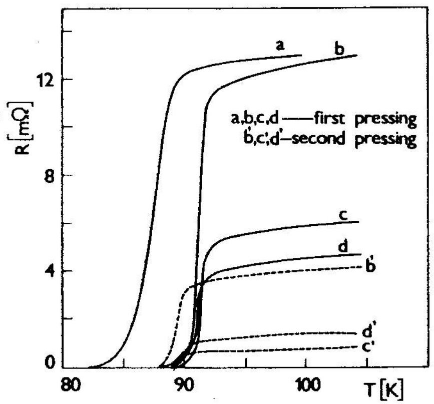


Fig. 3. Change in resistance of the $YBa_2Cu_3O_{7-x}$ cermic tablets with temperature after sintering at 920° (a), 940° (b, b′), 960° (c, c′) and 980° (d, d′).

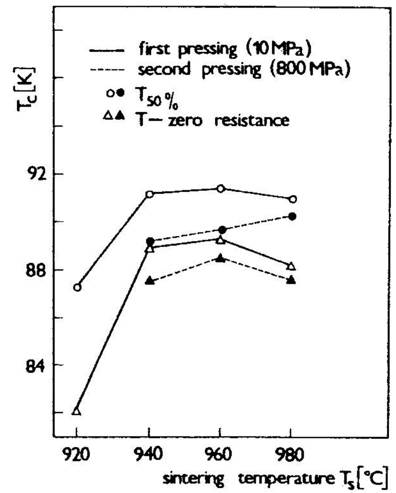


Fig. 4. Change in $T_c$ of the $YBa_2Cu_3O_{7-x}$ ceramic tablets with sintering temperature after first and second pressing.

Temperature variations of the resistance of sintered tablets are in Fig. 3. All samples show the metallic behaviour above $T_c$. Their resistance is lowered with the increase of their sintering temperature and is lower for samples after the second sintering. The highest lowering of resistance occurs between 940° and 960 °C. The relation between the sintering temperature and the critical temperature $T_c$ is shown in Fig. 4.

## IV. DISCUSSION

The resistance of the $YBa_2Cu_3O_{7-x}$ ceramic above $T_c$ can be considered as a measure of the quality of grain contacts [4]. From this point of view the quality of these contacts is rapidly increasing by sintering above 940 °C. The decrease of quality of these contacts in a sample sintered at 980 °C after the second pressing can be caused by two factors. The distribution of the high resistance CuO phase along the grain boundaries of the $YBa_2Cu_3O_{7-x}$ phase decreases the contact area among grains. The large grain size may also have an unfavourable influence. The high thermal stress occurring in large grains may lead to cracking.

The relation between $T_c$ and the sintering temperature is probably caused by the character of the grain contacts or by the structure of grain boundaries and their own critical temperatures.

Lower values of $T_c$ were observed in Y—Ba—Cu—O ceramics prepared by the sol-gel process in comparison with the ceramics prepared by the solid state reaction and are caused by some impurities in these ceramics [5]. The lowering of $T_c$ after the second pressing is not clear. Probably it will be a result of some unknown contamination of the samples during further processing.

## V. CONCLUSSIONS

1. The quality of $YBa_2Cu_3O_{7-x}$ grain contacts is rapidly increasing between the 940° and the 960 °C sintering temperature.
2. A rapid grain growth of the $YBa_2Cu_3O_{7-x}$ phase is observed at 980 °C.
3. An unfavourable influence of the CuO phase on the resistance is caused by its distribution along the grain boundaries.
4. The temperature 960 °C was estimated as the optimal sintering temperature.

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## ВЛИЯНИЕ ТЕМПЕРАТУРИ СПЕКАНИЯ НА ЭЛЕКТРОСОПРОТИВЛЕНИЕ И СТРУКТУРУ $YBa_2Cu_3O_{7-x}$ КЕРАМИКИ ПРИГОТОВЛЕННОЙ СОЛ-ГЕЛ ПРОЦЕССОМ

Мы показываем изменение микроструктури и электросопротивления $YBa_2Cu_3O_{7-x}$ керамики, приготовленной сол-гел процессом, в зависимости от температури спекания в кислороде. Из измеренных зависимостей сопротивления вытекает что качество контактов зерен фазы $YBa_2Cu_3O_{7-x}$ резко повышается выше температуры 940 °C. Розмерь зерен значительно повышается при температуре 980 °C. Оптимальное $T_c$ мы получили при тепмпературе 960 °C.