

INFLUENCE OF THE SIZE AND DISTRIBUTION OF THE PORES ON THE PROPERTIES OF THE HIGH TEMPERATURE SUPERCONDUCTORS Bi(Pb)–Sr–Ca–Cu–O

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The influence of the porosity of bulk high temperature superconductors Bi(Pb)–Sr–Ca–Cu–O on superconducting properties was investigated. Samples were prepared using the standard solid state reaction. The material having higher porosity was prepared by the addition of the noncalcined material into the samples before sintering. Low-porous sample was repeatedly sintered. It has been found that samples with bigger pores have lower critical current densities than samples having smaller pores. Critical temperatures of all samples were practically the same. In addition, the phase composition of the samples determined by XRD shows no fundamental differences.

INTRODUCTION

Superconducting materials show electric resistance at temperatures close to zero Kelvins and they are able to transport electric current without losses. These materials are divided into low and high temperature superconductors. The high temperature superconductors work beyond the boiling temperature of the liquid nitrogen. Limiting factors of all superconductors are critical temperature (T_c), critical current density (i_c) and critical intensity of outer magnetic field (H_c). Among the high temperature superconductors widest focus is on the cuprate superconductors.

Cuprate superconductors, ceramic multiphase materials, are a subject of studies for a long time. The widest focus is on superconducting filaments and tapes used in current transports and similar applications. These are also mainly produced and investigated in industry. Another form of this material are bulk superconductors. It can be used like magnetic field shielding, levitation kits and systems [1] etc. Their main advantages are low cost and simple preparation. Main disadvantages are low superconducting properties, low corrosion resistance [2] and mechanical properties. Superconducting properties can be improved by changing the phase composition, by variation of the quality of grain boundaries but also and mainly by changing the macroscopic and microscopic ordering of grains, their sizes and orientation. Another way of improvement is addition of microscopic particles to the material as possible magnetic-flux pinning centers [3, 4].

There are three superconducting phases in the Bi(Pb)–Sr–Ca–Cu–O superconductors marked according to their stoichiometry as 2201, 2212 and 2223 - with critical temperature of about 107 K [4]. An influence of the addition of noncalcined portion of the mixture to the calcined mixture before sintering on the superconducting properties, phase composition and porosity of the samples was investigated in this work.

EXPERIMENTAL

Two sets of samples were prepared. The first set of the samples was prepared by standard solid state reaction with Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO as starting compounds. Mixed powder was divided into two parts and one of them was twice calcined at 800°C for 24 hours and mixed. After that 0, 5, 10, 15 and 20 (S, P5, P10, P15, P20) weight percent of noncalcined powder was added into calcined part. Final powder was pressed into pellets of diameter about 1.5 cm and weight about 1.0 g. Pellets were sintered in tube furnace for 168 hours at 840°C . Another sample (2S) was prepared in the same way but without noncalcined powder and after the first sintering sample was milled, pressed into pellets and sintered again under the same conditions. The preparation process is summarized in Figure 1.

The superconducting properties of the samples were characterised by measuring of the temperature dependence of resistivity and of the critical current density. The critical current densities (i_c) were determined

as a current per cross-section area with extended voltage of $1 \mu\text{V}/\text{cm}$ at temperature of 77 K using standard four contacts method which was protected against overheating. The critical temperature was measured using current 10^{-3} A .

Porosity, bulk density and distribution of the pores of the samples were measured using mercury pressing method by porosimeter Poresizer 9320.

Phase composition of the samples was identified using XRD on instrument X'Pert Pro Panalytical (Cu-K α). The volumes of the phases 2223 and 2212 were calculated from the peaks intensities using X'Pert High Score Plus software.

The estimated volume of the closed pores from the theoretical densities of the 2223 and 2212 phases was calculated. The densities of both phases are nearly the same ($6.27 \text{ g}/\text{cm}^3$ and $6.54 \text{ g}/\text{cm}^3$) and were obtained from crystallographic parameters.

SEM images of all samples for visual examination of structure, pore sizes, grain sizes and illustration were made.

RESULTS AND DISCUSSION

The pore distribution of the samples was compared. In the first set of samples (S, P5, P10, P15 and P20) distribution of the pores clearly depended on the amount of noncalcined addition into the sample. Occurrence of the pores with the greatest radius increased with addition of noncalcined powder. Two areas of the pores were observed. Most of pores have radius $0.2\text{--}1 \mu\text{m}$; sample P20 has the greatest pores and standard sample the smallest ones (Figure 2). The occurrence of small pores decreased with addition of noncalcined powder. Larger amount of the small pores (about $0.01 \mu\text{m}$) in this set has standard S and lowest amount in the sample P20 (Figure 3). Total porosity of the samples of this set was very similar about 30 %. Total porosity of samples P15 and P20 (36 %) was little higher (Table 1). This shows how the sizes of the pores could be increased by the addition of the noncalcined powder. The creation of bigger pores is caused by the carbon dioxide evolution from the carbonates decomposition.

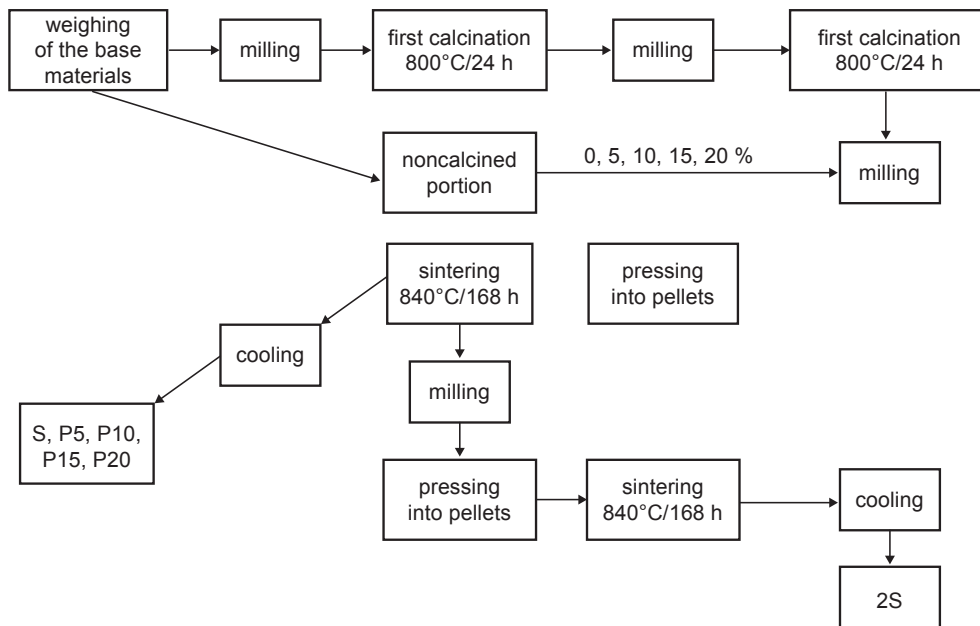


Figure 1. The schematic of the samples preparation.

Table 1. Properties of the samples.

Sample	i_c (A/cm 2)	ρ (g/cm 3)	Total porosity (%)	Volume of 2223/2212	Volume of closed pores (%)	i_c eff. (A/cm 2)
S	149	3.4	30.0	56/44	17	281
P5	111	3.3	29.3	50/50	19	213
P10	124	3.7	28.8	51/49	14	217
P15	89	3.3	36.9	47/53	12	173
P20	73	3.2	36.5	54/46	14	147
2S	272	4.4	16.7	63/37	14	390

Sample 2S pore distribution was more different from the first set of samples. The large pores in this sample disappeared (Figure 2), this sample had the smallest pores of all samples, pores have radius mostly less than 3 nm (Figure 3). 2S sample diversity is due to difference in the technological procedure of preparation. This sample confirmed that the large pores decreasing i_c of the samples (Table 1, Figure 2).

The superconducting properties of prepared samples were characterised by the temperature dependence of the resistivity and the critical current density. The critical temperatures (T_c) of all five samples were identical, about 107 K. The critical current densities decreased with increasing amount of the large pores in the samples from 272 A/cm² (2S) to 73 A/cm² (P20) (Table 1).

Total porosity of this sample was 16.7 %, much lower than total porosity of the samples of the first set. Other characteristic of the samples measured using mercury pressing porosimetry was density. The amount of the closed pores was in range from 12 % to 19% in all samples, it was calculated from the density and the phase composition of the samples (Table 1). Theoretical (skeletal) densities were calculated from the theoretical densities of the 2223 and 2212 phases and are 6.4 g/cm³ for all samples.

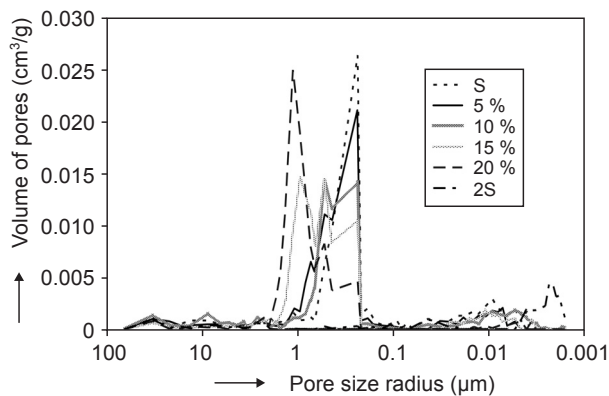


Figure 2. Pore distribution of all samples.

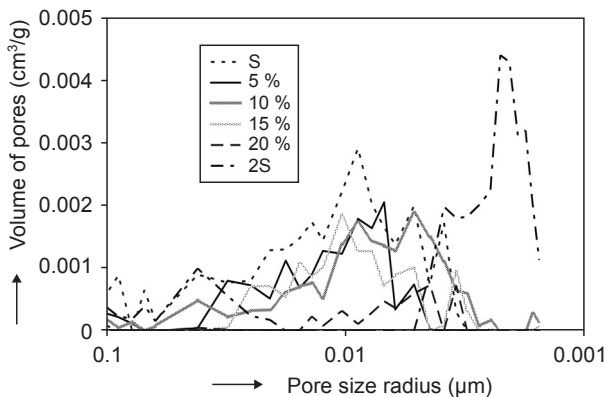


Figure 3. Pore distribution of the small pores.

Phase composition of the samples was identified using XRD. All major peaks were identified. The amount of superconducting phases 2223 and 2212 were determined (Table 1). All other phases were too minor to take into account and were ignored. No differences between volumes of these phases significant for the large variation of the i_c were observed. The larger volume of the 2223 phase in the 2S sample is due to additional sintering process. The variations in the 2223/2212 ratio are usual in the Bi(Pb)–Sr–Ca–Cu–O samples prepared by solid state reaction because the metastable 2223 phase is sensitive to the temperature changes.

The effective cross-section area could be calculated from the summation of the estimated closed porosity and the measured porosity. The current densities calculated from effective cross-section areas (i_c eff.) of the samples shows then the i_c is not commonly dependent on the total porosity of the samples (Table 1) and the pore sizes distribution must be considerate. Increasing

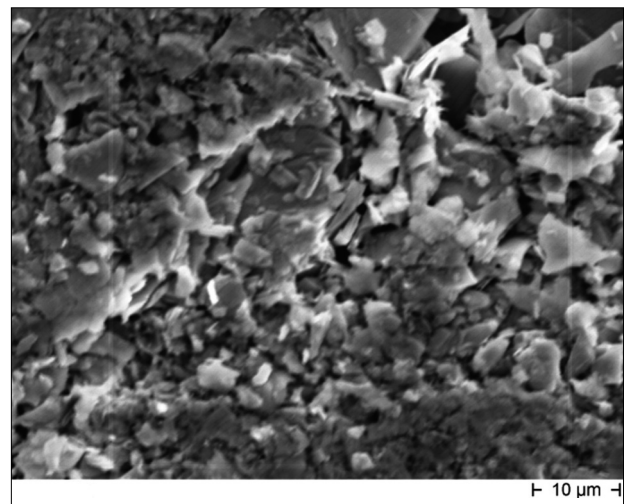


Figure 4. SEM image of the sample S.

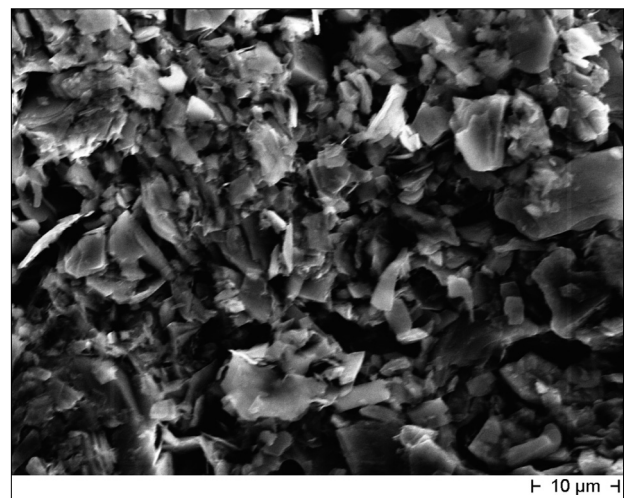


Figure 5. SEM image of the sample P20.

pore sizes decreasing the critical current densities of the samples (Figure 1). The electric properties of the high temperature superconductors depend on many other relevant facts like the grain boundaries and the magnetic-flux pinning, too. For this reason the critical current densities cannot be simply predicted from the total porosity or density of the samples and the dependences of the electric properties of the Bi(Pb)–Sr–Ca–Cu–O superconductors have to be measured.

The destruction of the grain boundaries important for the superconducting properties caused by noncalcined addition of the samples is not too large and the material is still usable as a superconductor.

SEM images of the first set samples illustrated microstructure, pore sizes and grain sizes. The differences were found mainly between standard sample and the sample with the largest amount of added noncalcined powder (Figures 4 and 5). These visible differences are in agreement with graphs of the pore distribution.

CONCLUSIONS

The results showed that by the addition of noncalcined portion containing carbonates into the sample superconducting material with greater pores can be prepared at the cost of relatively small decrease of the current densities. This can be useful for preparation of special composite materials in the future. The porosity of the 2S was much lower than porosity of the samples of the first set and pores were smaller. This is probably reason of the higher current density of this sample. Large pores in the structure of the material act as the barriers for the current and increase the local density of the current in neighborhood. Very little pores could act as the magnetic-flux pinning centers in superconductors of second kind because their diameter is comparable with the coherence length and can be considered as suitable defects [3, 4].

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VLIV ZMĚNY VELIKOSTI A ROZLOŽENÍ PÓRŮ NA VLASTNOSTI Bi(Pb)–Sr–Ca–Cu–O SUPRAVODIČŮ

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V této práci byl zkoumán vliv pórovitosti na supravodivé vlastnosti vysokoteplotních objemových supravodičů Bi (Pb)–Sr–Ca–Cu–O. Vzorky byly připraveny standardní metodou reakce v pevné fázi. Více porézní materiál byl připraven přidáním nekalcinovaného podílu do směsi před sintrací, méně porézní materiál byl připraven opakovanou sintrací vzorků. Bylo zjištěno, že vzorky s většími póry měly nižší proudové hustoty než vzorky s oblastí pórů posunutou k nižším poloměřům. Kritické teploty všech vzorků byly prakticky stejné. Také fázové složení určené RTG fázovou analýzou nevykazovalo u jednotlivých vzorků podstatné rozdíly. Tato zjištění mohou být užitečná při aplikacích vysokoteplotních supravodičů a také při budoucím vývoji speciálních kompozitních materiálů.