QUENCHING EFFECT ON THE Pb-SUBSTITUTED Bi-BASED BULK CERAMIC SUPERCONDUCTORS

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Abstract The effect of cooling process for the synthesis and the superconductivity properties of Pb-substituted Bi-based materials, has been investigated. The preparation condition for the formation of (2,2,2,3) phase has been examined. The influence of thermal condition of the synthesis and quenching on the critical temperature and the content of 110K phase was investigated. Results of the ac-susceptibility, resistivity measurements, XRD, and SEM are given. Analysis is made of the effect of processing on the properties of grain boundaries in these materials.

Key Words Superconductivity, Bi-based Compound, Grain Effect

چکیده در این پروژه اثر سرعت خنک کردن بر خواص ابررسانایی و ساخت ابررساناهای بر پایه بیسموت که به سرب آلاییده شده اند، مورد بررسی قرار گرفته است. شرایط آماده سازی نمونه ها برای تشکیل فاز (۲،۲،۲،۳) آزمایش شده، و اثرات نحوه پخت و شرایط خنک کردن بر دمای گذار و میزان حضور فاز ۱۱۰K نیز مطالعه شده است. نتایج اندازه گیری پذیرفتاری و مقاومت ویژه ,XRD, SEM داده شده اند. اثر فرایند پخت بر خواص دانه بندی و مرزهای بین دانه ای این مواد، تحلیل شده است.

INTRODUCTION

Since the discovery of high temperature superconductors, a number of these materials based on copper oxide have been found [1,2]. All of these contain the square network of the planes composed of copper and oxygen. Empirically, the superconductivity transition temperature T_c becomes higher with increasing number of Cu-O layers up to three[3]. Attention has been paid to the preparation and the physical properties of materials with a larger number of Cu-O layers [4,5,6].

The detection of high temperature superconductivity in the bismuth copper oxides, $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ (n =1, 2, or 3) [7, 8, 9] has led to much interest in these series of compounds. This behavior has quite naturally led to the speculation that significantly higher values of T_c might be achieved by adding more Cu-O layers to the unit crystals. The reality, however is not as simple as such a picture predicts. The coherent growth of perovskite lamellae with one, two and three Cu-O layers would correspond to the pure bulk phase of (2,2,0,1), (2,2,1,2) and (2,2,2,3) respectively. The transition temperatures for these phases are 20, 80, and 110K respectively.

It has been found that Pb doping can greatly reduce the fine intergrowth defects which is commonly observed in undoped BSCCO superconductors[10]. It is now well established that Pb-doping can significantly raise the zero resistance superconductivity transition temperature. This improvement in T_c could be due to the minimization of intergrowth. The intergrowth defects in the undoped BSCCO sample cause the appearance of steps in the resistivity versus temperature plots. Of course, some degree of intergrowth is always present in the Pb-doped sample. The Pb-doping drastically reduces the density of the fine intergrowth defects (<100°A). So that, within a grain, almost no intergrowth defects are present. Hence, the electrical conductivity is enhanced in the Pb-doped BSCCO superconductors due to their more homogeneous microstructures, giving rise to higher T_c and disappearance of the steps in the resistivity plots.

Extensive studies have been conducted to single out the (2,2,2,3) phase of T_c=110K with ideal composition of $Bi_2Sr_2Ca_2Cu_3O_X$ [5,6,11]. The focus of the present work is to understand the thermal process for the formation of the high temperature (2,2,2,3) phase, to study the effects of small fields in the susceptibility measurement, the electrical conductivity, and the identification of the pahses of the system.

EXPERIMENTAL DETAILS

In order to avoid formation of unwanted impurity phase during the preparation of the (2,2,2,3) phase, certain preheat procedures must be followed. From 600°C to 860°C temperature range, a low heating rate must be implemented to ensure the decomposition of nitrite precursors used. However, once the superconducting phase is formed, the cooling down time in 860°C to 750°C region must be minimized to avoid the re-oxidation of the Pb that has been incorporated into the compound (later, we will discuss this part in more details). The purity of the starting materials: Bi_2O_3, PbO, CaO, $Sr(NO_3)_2$, and CuO, all from MERK company, were of at least 99.99%. These constituents were mixed in stoichiometric amounts with the molar ratio Bi: Sr: Ca: Cu of 2: 2: 2: 3. Pb substitution for Bi was around 10%. To increase sample homogeneity, after weighing, the initial powders were mixed and finely ground, placed into a ball mill with ethyl alcohol and ground for several hours. The alcohol was evaporated at 200°C. The remaining sediment was heated in powder form to 830°C for 24 hours, reground, and pressed into pellets of 12mm diameter and 2mm thickness under 10Ton/cm^2.

To achieve a good quality sample, subsequent grindings and preheating were necessary. The heating rate up to 700°C was 10°C/min, from 700°C to 800°C was 2°C/min and from 800°C to 860°C was 1°C/min by holding the temperature at each 5°C increment for 10 minutes. The samples were heated in the air at 860°C for 155 hours, the (NEPB2A) samples were quenched to room temperature and the (NEPB2N) samples were quenched to liquid nitrogen. The bulk densities of the samples were 3.6 and 4g/cm^3 respectively.

To characterize the specimens, the electrical transport properties were measured with the current density of 0.5 A/cm^2 on samples of $1\times 2\times 7$ mm^3 size, using a four-probed dc technique. The resistivity meausrements were made from room temperature down to 10K with the accuracy of 0.1K. The temperature stabilization was established by using a Pt resistor sensor to better than 10mK. For the ac magnetic susceptibility, we have used the Lake Shore Susceptometer (model 7000) at 333.3Hz and rms fields of 50 and 0.8 A/m. The susceptibility measurements were made from 77 to 150K, with increasing temperature rates of 0.2 K/min from 77 to 120K and of 3K/min from 120 to 150K.

The phase identification was carried out by using standard powder X-ray diffraction with CuKα radiation.

The microstructure of sintered specimens was observed by examining polished surface with Philips Scanning Electron microscope.

RESULTS AND DISCUSSION

The results of ac susceptibility measurements (real, χ', and imaginary, χ'',) on two typical samples with the same preparation procedure except for quenching (NEPB2A in air and NEPB2N in liquid nitrogen) are presented in Figure 1. Both measurements were made at 50A/m and a frequency of 333.3Hz. Although the results give different behavior for the susceptibility, both samples show a plateau in the real part of the susceptibility, indicating the presence of two superconducting phases in the samples. To check this we measured the susceptibility of both samples in the field of 0.8A/m and 333.3Hz. The results for (NEPB2A) are given in Figure 2. It shows a relatively sharp transition at 111K, which is expected for a single phase sample. The results of ac susceptibility of (NEPB2N) in the field of 0.8A/m and 333.3Hz given in Figure 3, shows two distinct transition temperatures.

It should be noted that, the plateau in the real, χ', part of susceptibility of the plot of 50A/m (NEPB2A) sample in Figures 1 and 2 is believed to be due to the grain boundaries. The resistive or imaginary, χ'', part of the susceptibility goes from almost zero just below T_c through a peak near T_c, to zero in normal state. This χ'' signal is usually associated with resistive losses occuring in the vicinity of T_c as the superconductor is composed of multiconnected superconducting and normal regions. Both the inductive χ' and resistive χ'' components of the susceptibility were very sensitive to ac magnetic field. The transition width of χ' broadened as the magnitude of the field increased, although the onset temperature didn't change. The χ''

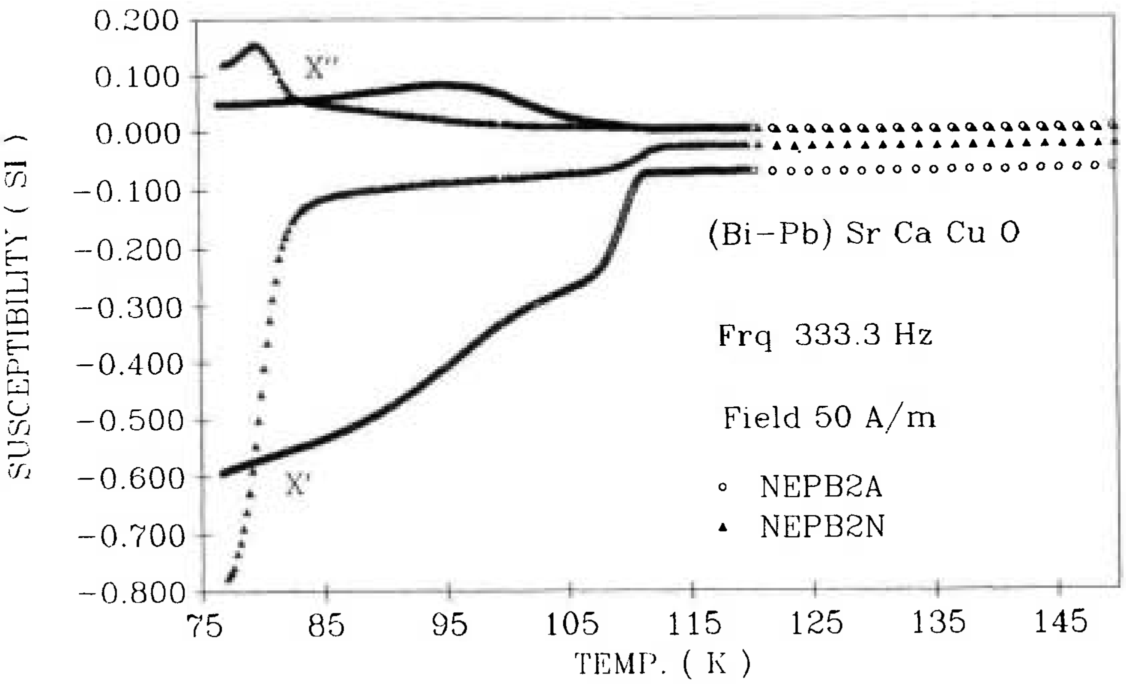

Figure 1. Ac-susceptibility of (NEPB2A & NEPB2N) Air quenched and Liquid Nitrogen quenched in a field of 50A/m as a function of temperature.

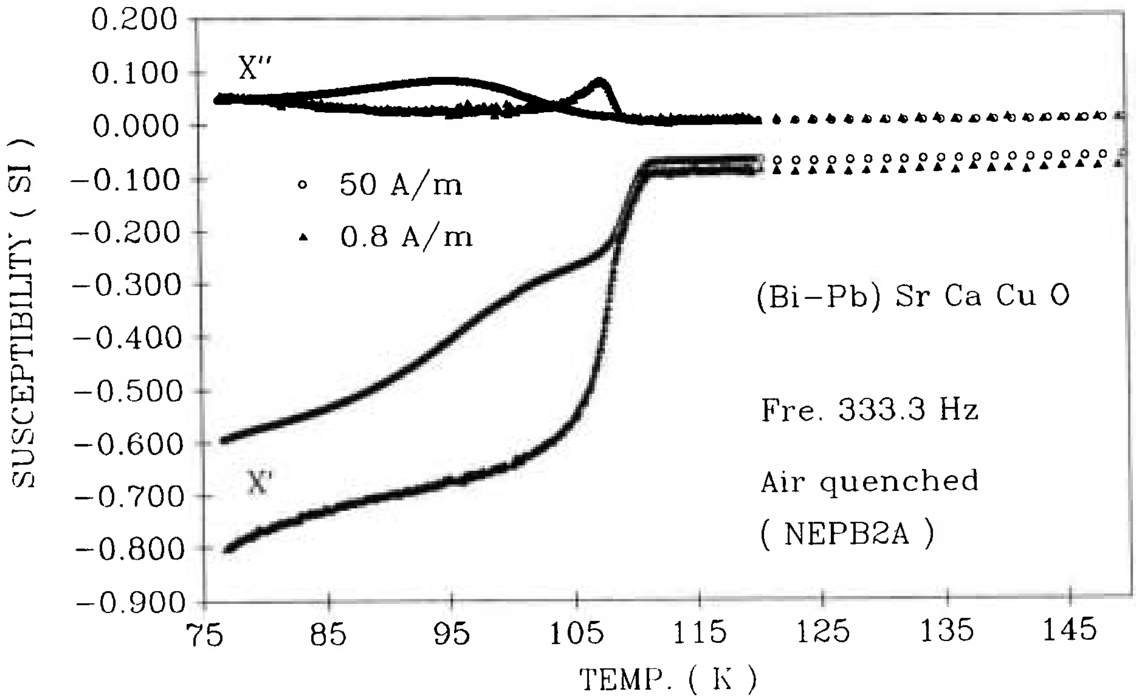

Figure 2. Ac-susceptibility of (NEPB2A) in a field of 0.8A/m and 50A/m as a function of temperature.

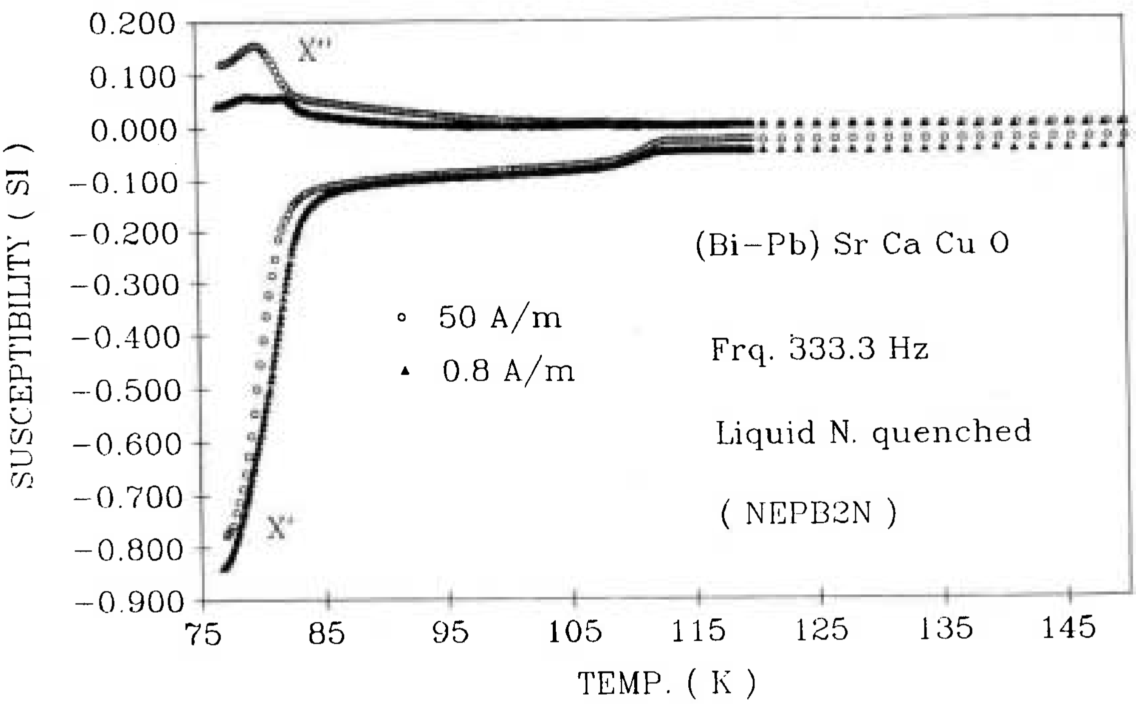

Figure 3. Ac-susceptibility of (NEPB2N) in a field of 0.8A/m and 50A/m as a function of temperature.

had an asymmetric peak which shifted to lower temperatures as the field increased[18]. As we see from both components of the susceptiblity measurements of air quenched samples, there is a first stage fall-off just below T_c which indicates the superconducting transition intrinsic to the grain, and the subsequent stage showing a spatially extending process of a network consisting of weak links at the grain boundaries.

Sintered high-T_c superconductors and composite low-T_c superconductors with closely spaced filaments exhibit two critical temperatures, one is intrinsic to the superconductors and the other is the characteristic of the coupling between either grains[12,13] or filaments[14].

Because of the large change in shielded volume that occurs at T_c of the coupling components, there is a striking change in the susceptibility. The change in resistivity, in comparison, is minor because of the coupling components form a small part of the conduction path[15]. To see these effects, we have made the resistivity measurement on both samples. The result of resistivity measurements of (NEPB2A), presented in Figure 4, shows a single transition at 111K. In the resistivity of (NEPB2N) we see two distinct transition temperatures. these results show that there are a good quality and coupled sintered samples. The room temperature resistivity for both samples is 30 m-Ohm-cm. The existence of two phases in (NEPB2N) samples are observed in both the resistivity and the susceptibility measurements.

Figure 5 shows the XRD patterns for the samples **a)** NEPB2A and **b)** NEPB2N. The analysis shows that the content of (2,2,2,3) phase in the air-quenched samples is much higher than that of the liquid nitrogen-quenched samples. The peaks at 4.89, 19, 23.9, and 33.75 degress which correspond to the (2,2,2,3) phase have been magnified in the air-quenched sample.

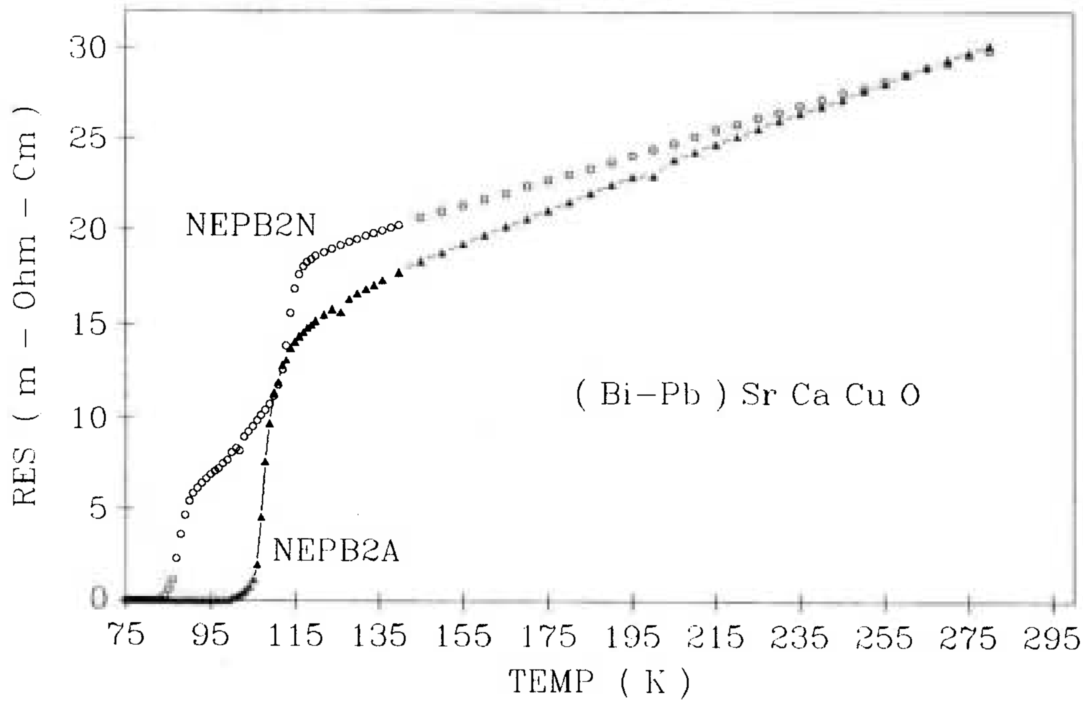

Figure 4. Resistivity of (NEPB2A & NEPB2N) as a function of temperature.

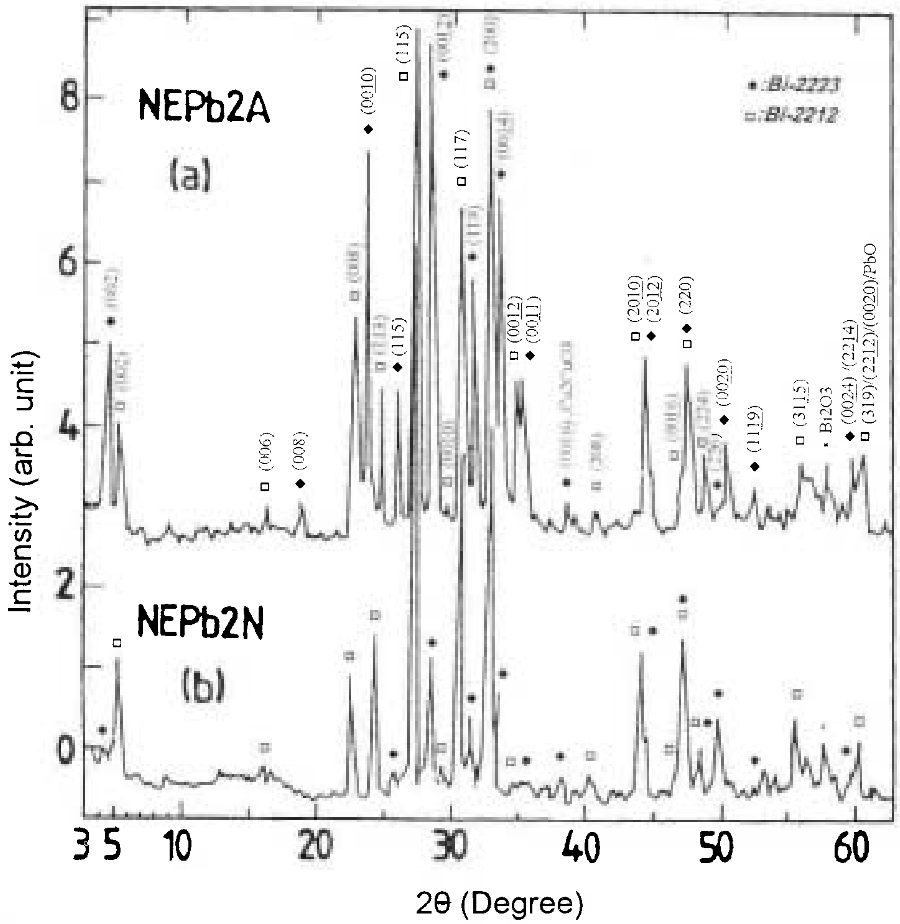

Figure 5. Powder XRD patterns for samples after heat treatment and subsequently quenched: **a)** to room temperature, **b)** to liquid nitrogen temperature.

Analysis of both samples show that there is no trace of PbO or negligible trace of other starting materials in the sintered samples. So, as expected, the reoxidation of Pb didn't take place during the cooling process.

Figure 6 shows the microphotograph of NEPB2A (a) and NEPB2N (b). The ubiquitous platelets in (a) micrograph indicates the presence of a higher volume fraction of the (2,2,2,3) phase in the air-quenched samples[19].

CONCLUSIONS

Although there have been many reports on the process optimization of Bi-based (2,2,2,3) ceramic superconductors [6,16,17,18,19], among other factors the heat treatments still play an important role in the formation of (2,2,2,3) phase. The cooling process (between 860-750°C) must be minimized, but if it happens in a very short time, it will increase the content of the (2,2,1,2) phase. The dependence of the real part of susceptibility in the air quenched sample on the field is believed to be associated with the weak-link structure. In summary, we can draw these conclusions:

a) Ac susceptibility could be used in characterizing the samples.

b) The formation of the (2,2,2,3) phase is more

a

b

Figure 6. Scanning electron micrographs depicting the microstructure of pellets of **a)** NEPB2A, **b)** NEPB2N.

readily possible in the air-quenched processed materials.

c) Liquid nitrogen quenched samples result in a mixed-phase state.

d) The plateau in the susceptibility measurements in air quenched samples is associated with the weak-link structure.

In order to be able to characterize these systems more, further study on the susceptibility measurements at different fields, frequencies, and critical current densities and their comparison with different phenomenological models which assume the multiconnected network behavior is underway.

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