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Addition of Li-based salts into superconducting $Bi_{1.8}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_x$ ceramic

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Li-based salts M such as LiF, LiCl and LiI were introduced into $Bi_{1.8}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_x$ superconducting ceramic. Samples were prepared by solid state reaction route using a precursor, (Sr, Ba)$CaCuO_z$, and were characterized by ac susceptibility, resistivity and structural measurements. Imaginary part of the magnetic susceptibility allows observation of two different Bi2223 superconducting phases with different intragranular properties. Two intragranular peaks in χ''(T) are also observed in the Ba-free and M-added samples. On the other hand, in the M-free samples with Ba only one peak is detected. Although samples with Ba and M-compounds introduced separately are showing some improved properties comparative with the un-added samples, for the samples with double addition (Ba and M) most of the superconducting characteristics are suppressed comparative to the best samples with only one addition of Ba or M. Of interest is that for these double added samples (with Ba and M), the tendencies of the superconducting characteristics vs. M-concentration are, in most cases, similar to Ba-free and M-added samples, but some differences were also noted. This result suggests that: (1)- the influence of M-addition is very strong, (2)- double addition might be useful for independent tuning of some properties while maintaining the tendencies of the others, and that (3)- the optimization process should be adjusted for each composition to keep the maximized overall characteristics.

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1. Introduction

High T_c superconductors (HTS) in the Bi-based system (Bi-Pb-Sr-Ca-Cu-O or BSCCO) are attracting much attention from fundamental as well as from applications points of view. For both situations optimized samples with maximized and controlled properties are necessary. However, preparation of such samples is a difficult task due to high sensitivity of the system to the external factors, as well as due to high complexity of the system. To solve this problem several methods are available. Among them, introduction of additions and substitutions is frequently used. However, relatively rare are the cases with addition of two or more compounds. This approach is of interest to search for methods that allow a better control of the properties and their improvement.

In this work we present some aspects for superconducting BSCCO bulk samples substituted by Ba for Sr and added with Li-based flux-like salts (M= LiF, LiCl and LiI) at different concentrations.

2. Experimental

Samples of BPSCCO substituted by Ba for Sr (denoted BPSBCCO) were prepared by conventional solid state reaction. Raw materials were high purity powders (Merck Co, 99.999% purity) of Bi_2O_3, PbO, $SrCO_3$, $BaCO_3$, $CaCO_3$ and CuO. Cation composition was Bi:Pb:Sr:Ba:Ca:Cu=1.8:0.4:1.8:0.2:2:3.

In the first step, a precursor powder $Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_z$ is obtained by subsequent annealing at 924°C for 85h, 947°C for 70h and 950 °C for 75h with intermediate grindings. The precursor is mixed with Bi_2O_3 and PbO, and heated at 820°C for 20h in the air. The optimum amount of Ba/Sr ratio was determined according to literature data and our experiments [1-3].

In the second step, as-prepared powder is mixed with M to obtain compositions $(BPSBCCO)_{1-y}M_y$, y=0.02, 0.05, 0.07, 0.10, 0.12 and 0.14. Pressed pellets (3mm x 3mm x 10mm) at 0.75GPa of each composition were heated at 834°C for 320 h in the air. Notation of the samples is: F, C and I for samples with LiF, LiCl and LiI, respectively. Heating temperature of 834°C is selected based on our previous results, high quality M-added samples without Ba being obtained for 828-835 °C. The best our Ba-added sample (up to now), $Bi_{1.8}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_y$, denoted N, was obtained for a final heat treatment in the air at 847°C, a value that is higher than for the samples with M-addition (with or without Ba) of 834 °C.

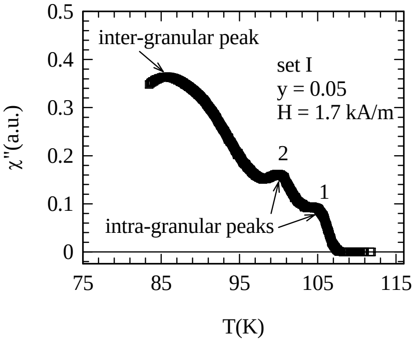

Fig. 1. Example of a χ''(T) curve showing two intragranular peaks P1 and P2 and one intergranular peak. Sample, concentration of the addition, y, and applied dc magnetic field are indicated.

Samples were characterized by *ac* susceptibility measurements using a lock-in amplifier. Amplitude of the *ac* field was usually H_{ac}=100A/m. A dc field was superimposed (up to H_{dc}= 20000A/m). An example of a typical curve measured on F, C or I samples of the imaginary part of ac susceptibility, $\chi''(T)$, is presented in Fig. 1. Peaks 1 (P1) and 2 (P2) at higher temperatures are ascribed to intragranular regions and the peak at lower temperature to the intergranular regions. Peaks P1 and P2 are both ascribed to phase Bi2223 [4]. The position of the peaks, T_p, corresponds to full penetration of the magnetic field into the grains and can be used as a relative measure of the intragrain critical current density. As an exemple, in Fig 2a are presented $T_p(H_{dc})$ curves for C-samples. In a similar way, intergrain regions can be also evaluated. From the relationship for full penetration H_p and critical current density J_c, $H_p(T)$=d x $J_c(T)$, d=sample diameter, J_c can be determined. Occurrence of the P1 and P2 indicate that sample is not homogeneous and there are grains of Bi2223 with a different quality (grains with P1 are of better intragrain critical current density than the grains with P2).

Measurements of resistivity (R) vs. temperature (T) were performed in zero-field by the standard four-probe method. Critical temperature T_c was taken for the maximum dR/dT.

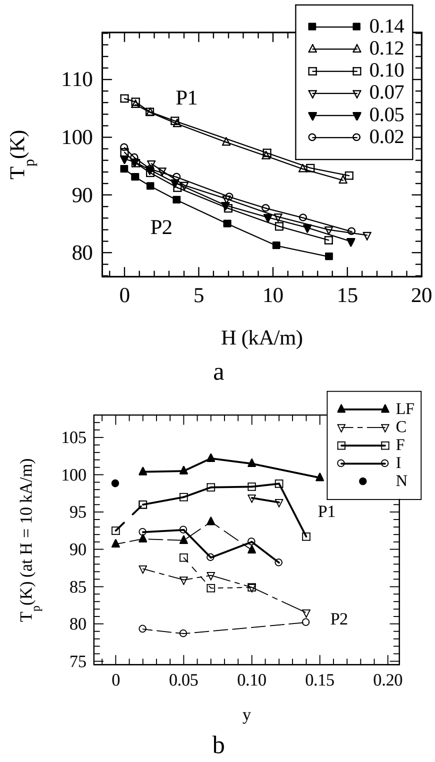

Fig. 2. a) Temperature T_p for peaks P1 (continuous line) and P2 from Fig. 1 vs. applied magnetic field for C-samples with a different concentration of LiCl. b) Temperature T_p vs. y for the samples N, C, F, I and LF taken at an applied magnetic field of 10 kA/m.

The amount of Bi2223 superconducting phase was estimated from X-ray diffraction patterns as $f\% = [A(0010)Bi_{2223}/(A(0010)Bi_{2223}+A(008)_{Bi2212})] x100$, where $A(0010)_{Bi2223}$ and $A(008)_{Bi2212}$ represent the peak area for reflections $(0010)_{Bi2223}$ and $(008)_{Bi2212}$, respectively.

3. Results and discussion

In the literature one can find many studies on the influence of additions on the structural, microstructural and superconducting properties, but not rare are the cases when results are in contradiction and a general trend cannot be easily revealed. Raw materials, technological route and growth conditions, starting composition, when and how addition is introduced in the material and so on are interdependent parameters influencing the final characteristics of the superconductor. In such circumstances knowledge of the samples history in detail is mandatory, but unfortunately in many cases it is impossible to extract this information from the literature reports. Due to that we shall compare in this article only our samples and results using as a starting point for this work also our data.

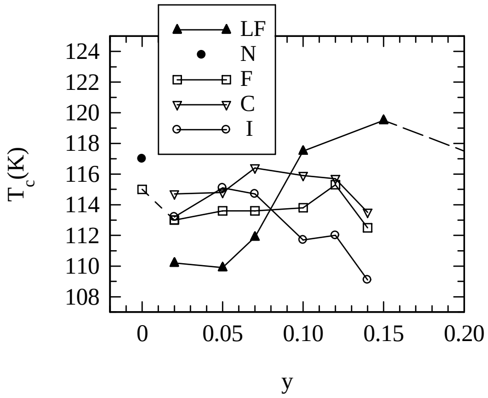

Fig. 3. Critical temperature T_c vs. y of flux-type M-addition for I, C, F, N and LF samples.

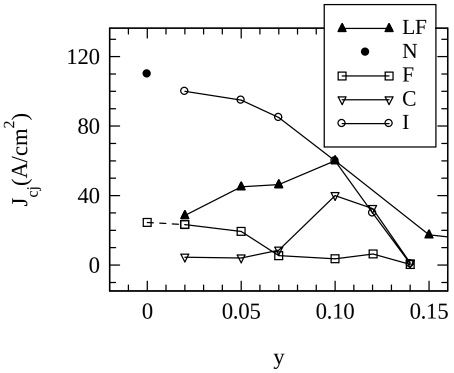

Fig. 4. Intergrain critical current density J_{cj} vs. y of flux-type M-addition for I, C, F, N and LF samples.

In our article [5] we have investigated two solid state reaction routes for a given starting composition ($Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_x$) and raw materials: the route in which a precursor $Sr_2Ca_2Cu_3O_z$ is used resulted in high amount of Bi2223 phase of relatively low quality, while the route without precursor led to formation of low amount of Bi2223 of high quality.

The next step was to add Ba for a starting composition $Bi_{1.8}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_x$. We used the $Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_z$-precursor route. In this situation the amount of Bi2223 significantly increased, phase was obtained faster with a higher reproducibility and, more important, the high quality of the Bi2223 phase was preserved. Results will be presented in detail elsewhere.

On the other hand, addition of LiF or LiCl into a partially reacted powder with starting composition $Bi_{1.7}Pb_{0.4}Sr_{1.5}Ca_{2.5}Cu_{3.6}O_x$ and of LiI at an earlier stage (i.e. into the initial mixture of individual oxides and carbonates with the same cation stoichiometry) produced samples with improved characteristics maximizing some of them [4, 6]. For example in Fig 2b $T_{p1}(y)$ for the samples $(Bi_{1.7}Pb_{0.4}Sr_{1.5}Ca_{2.5}Cu_{3.6}O_x)_{1-y}(LiF)_y$ (denoted LF) is positioned at higher temperatures than T_p for the best Ba-added sample ($Bi_{1.8}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_y$ denoted N) obtained by us up to now. The same samples are showing a similar dependence for $T_c(y)$ in Fig. 3. But, in the Fig. 4 and 5 situation is reversed and N-sample is superior to LF-samples. Moreover, N-sample and, in fact, all samples with Ba are not showing two intra-granular peaks suggesting that Ba-addition is leading to more homogeneous samples than M-type addition. Although our comparative analysis is not perfect since compositions and technological routes are not perfectly the same the next idea and question is what will happen if both Ba and M additions are introduced in the superconductor. Ideal situation would be to obtain homogeneous samples (only one peak in T_p) with high amount of Bi2223 phase as for the N-sample (with Ba and M-free) and of high quality at the level of the maximum $T_{P1}(y)$, $T_c(y)$, $J_{cj}(y)$ as for the LF samples (Ba-free and M-added).

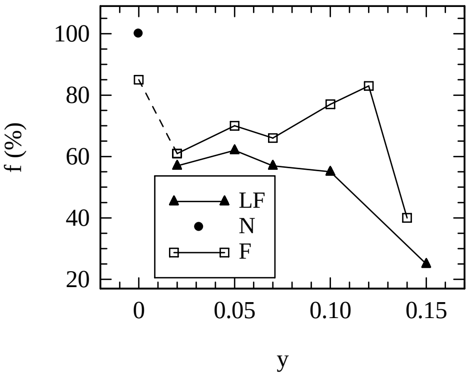

Fig. 5. $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi2223) phase concentration vs. y of flux-type M-addition for N, F and LF samples.

Results for $(Bi_{1.8}Pb_{0.4}Sr_{1.8}Ba_{0.2}Ca_2Cu_3O_x)_{1-y}M_y$ samples prepared in this work are presented in Figs. 2-5. As already mentioned in the section 2, Experimental, $\chi''(T)$ is showing for all the samples two intragranular peaks as for the LF (or more general as for $(Bi_{1.7}Pb_{0.4}Sr_{1.5}Ca_{2.5}Cu_{3.6}O_x)_{1-y}M_y$ samples without Ba). Few samples are showing occurrence of just P1 peak while P2 cannot be visualized within the sensitivity of our measuring method (Fig. 2b). Such samples were found for samples I, F and C with y=0.07 and 0.10, y=0.12 and 0.14 and y=0.12, respectively. This positive result is shadowed by the fact that all $T_p(y)$ curves for P1 and P2 are located at lower values than for the best samples added with Ba (N-sample) or with M (LF-samples). Maximum critical temperature T_c (Fig. 3) and critical current density of the intergrain region J_{ci} (Fig. 4) are also inferior for Ba and M-added samples I, C and F. Exception seems to be for the I-samples showing a higher J_{ci} for y=0.02-0.07 than the LF samples (Fig. 4). However, J_{ci} is lower than for the sample N.

Generally the Bi2223 phase concentration, f, in the I, F and C samples are usually better than for the $(Bi_{1.7}Pb_{0.4}Sr_{1.5}Ca_{2.5}Cu_{3.6}O_x)_{1-y}M_y$ samples, but are inferior to N-sample (Fig. 5).

Another observation is that the general tendency of the superconducting characteristics (Figs. 2-4) vs. y is somehow similar to those observed for the $(Bi_{1.7}Pb_{0.4}Sr_{1.5}Ca_{2.5}Cu_{3.6}O_x)_{1-y}M_y$ samples without Ba: $T_{p1}(y)$ (Fig. 2b) and $T_c(y)$ (Fig. 3) are showing a convex shape with a maximum, while $T_{p2}(y)$ (Fig. 2b) and $J_{cj}(y)$ (Fig. 4) are decreasing or are relatively constant. Slightly convex with a maximum or just decreasing are the tendencies for the f(y) curves (Fig. 5). Noteworthy, in the case of $T_c(y)$ curves (Fig. 3); the location of the maximum likely shifts to lower *y* and the variation with *y* is smaller for I, F and C samples comparative to LF samples. The quality ranking among I, F and C samples is approximately preserved as for $(Bi_{1.7}Pb_{0.4}Sr_{1.5}Ca_{2.5}Cu_{3.6}O_x)_{1-y}M_y$) samples. For example, among the samples with different type of M-addition the best $T_{p1}(y)$ is for samples with LiF, i.e for samples F (Fig. 2b) and LF [4].

In summary our results indicate that double addition of Ba and M for our samples is leading to intermediate or lower results than for LF or N samples. Addition of M compounds has a very strong influence, but a clear explanation of the results cannot be expressed and more investigations are necessary. Data from Fig. 2 may suggest that there is a selective differential mechanism generating grains with different properties (P2 and/or P1 in $\chi''(T)$ curves) A key role is played by the M-addition.. At the same time some details within this mechanism can be controlled by the second addition, in our case Ba. From this point of view further research on double or multiple additions should continue. How should be the additions to achieve a good control remains an open question. In our case we used M compounds recognized to act as flux. They are also showing substitution properties (e.g. Li substitute for Cu). According to our results flux properties have a stronger influence on the final superconducting properties of the material than the insertion ones [4]. For Ba addition situation is different, and growth and insertion effects are comparable although to separate and investigate the effects present data are not enough and, hence, to draw a final conclusion is not possible. This image would not be complete without considering the technology optimization process. For a given technological route optimization process should take into consideration specific details of each sample (addition type, size, shape, distribution, concentration, when and how it is introduced in the sample, relationship with the matrix material, details of the matrix, processing conditions and so on) at local and overall level. Appropriate optimization of each sample is thought to lead to samples with controlled and maximized overall characteristics possibly better than for the best samples from this article or literature. Systematic, complex optimization studies on addition-technology-properties relationship and search for new suitable additions are highly required.

4. Conclusions

We have introduced at different concentrations flux-type additions such as LiF, LiCl or LiI into BSCCO bulk samples in which Sr is partially substituted for Ba. Grains of Bi2223 of different quality are observed from susceptibility measurements. This separation is similar to the samples without Ba and added with the same flux compounds. This separation was not observed for the samples with Ba and without flux-type additions. Similarities and differences between the samples added with Ba and flux compounds on the one hand, and the samples added with flux compounds or only with Ba on the other hand, suggest that the strongest influence is given by the flux compounds, but some aspects can be controlled through Ba addition. Samples with Ba and flux compounds have shown lower or intermediate characteristics when compared with those for samples separately added with Ba or flux compounds.

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