JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 6, June 2007, p. 1767 - 1771

Synthesis of Bi(Pb)-2223 from two different precursors with the same stoichiometry

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Samples of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ (Bi(Pb)-2223) phase have been fabricated from two different oxide precursors with the same stoichiometry, synthesized by solid state reaction in the air at 815°C for 20 h. The first precursor was prepared by mixing Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO powders, while the second one through mixing Bi_2O_3 and PbO with $Sr_2Ca_2Cu_3O_x$ produced from $SrCO_3$, $CaCO_3$ and CuO powders. Pellets from the two precursors were prepared in the same conditions; heat treatment time was varied and intermediate grindings were applied. Although the maximum attained Bi(Pb)-2223 phase amount was about 50% and above 90% in the samples from the two precursors, respectively, the samples from the first precursor have generally shown better superconducting properties such as the critical temperature from resistivity measurements and intragrain critical current J_{cg} from magnetic susceptibility measurements. For our particular case the influence of the final heat treatment is relatively low and at the same time the precursor plays a major role in controlling growth processes and final superconducting properties. Lower room-temperature Seebeck coefficient of the thermoelectric power for the samples fabricated from the first precursor suggests that one mechanism through which this control is realized might be the modification of the oxygenation level in the samples produced from different precursors. It was also found that for the samples prepared from the two precursors, intermediate grinding after 110h or more of heat treatment enhances density, almost does not influence J_{cg} (or slightly improves it), decreases T_c, and does not influence significantly the amount of Bi(Pb)-2223 phase .

(Received November 14, 2006; accepted April 26, 2007)

Keywords: Bi(Pb)-2223, Precursors, Density, Transport parameters, Critical temperature, Intragrain critical current

1. Introduction

Twenty years passed since the discovery by Bednorz and Muller of high-T_c superconductors (HTS) [1]. Much effort has been done to investigate, apply and commercialize these materials and despite this sustained effort and their huge potential, very few applications of these materials are today on the market. One of the reasons is the high sensitivity of HTS to external factors making control of properties and their reproducibility very difficult.

Synthesis of ceramic HTS is usually via processing of precursor powders obtained by wet chemistry [2 1], cryochemical route [3 6], aerosol reaction [4 3], solid state reaction [1] and their combinations [5 9]. Intrinsic properties of the powders such as grain size and distribution, morphology and reactivity are important parameters influencing phase formation, growth, kinetics and properties. Phases in the precursors are the other key elements for the further processing evolution of the material. Even for the same starting cation stoichiometry, precursors are so different that in most cases it is not possible to compare optimization processes described in the literature, and not rare are cases when conclusions contradict each other. The result is that processing-properties dependencies are local, depending on each case. Hence, to compare two processing routes, and to extract reliable information of phase formation and properties optimization and control, experimental conditions should be identical.

Considering the problems from the previous paragraph, we have decided to synthesize samples by solid state reaction using two oxide precursor powder mixtures with the same stoichiometry. Preliminary results on these experiments are described in this article.

2. Experimental

Two precursor powders A and B with the same cation ratio Bi:Pb:Sr:Ca:Cu = 1.8:0.4:2:2:3 were prepared as follows:

Precursor A: the appropriate mixture of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO powders was mixed/grind manually, heated in the air at 815°C for 20 h and sieved through a 40 μm Cu-mesh.

Precursor B: A powder of $Sr_2Ca_2Cu_3O_x$ was obtained from a mixture of $SrCO_2$, $CaCO_3$ and CuO mixed/grind, palletized at 0.75GPa, heat treated in the air at 924°C for 85 h and sieved through a 40 μm Cu-mesh. Then, after regrinding, operations from the first step were repeated for two times, but the heat treatments were done at 947°C for 70 h and at 950°C for 75 h. Finally, as-prepared $Sr_2Ca_2Cu_3O_x$ powder was mixed with Bi_2O_3 and PbO.

If Bi and Pb oxides are added in one step followed by the heat treatment at 815°C for 20 h and applying the same procedures of grinding, pressing and sieving, the obtained precursor is named B1. On the other side, if the Bi and Pb oxides are added in two steps, i.e. half amount followed by the heat treatment and then another half followed by the

same heat treatment (815°C for 20 h) we obtain precursor B2.

From the precursors A, B1 and B2 superconducting samples were obtained. For some samples we have applied intermediate grinding (indicated with (+) in the Table 1) after 110 h or multiple of this time. Usually the heat treatment regime was the same: heating temperature was 848°C and samples were cooled by extracting them into room temperature atmosphere from our laboratory.

Table 1. Bi-2223 ceramic samples: notation and heat treatments. Note that sample 6A was heat treated at 852℃ for 85 h, furnace cooling was applied down to 650℃ and finally sample was extracted in the air.

Sample (from A)	Heat treatment time	Sample (from B1)	Heat treatment time	Sample (from B2)	Heat treatment time
1A	330 h	1B1	330 h		
2A	220 h + 110 h	2B1	220 h + 110 h		
3A	110 h + 110 h + 110 h	3B1	110 h + 110 h + 110 h		
4A	110 h	4B1	110 h		
5A	300 h	6B1	300 h	3B2	300 h
6A	85 h	5B1	450 h		
		7B1	500 h	4B2	500 h

Samples were investigated by density (standard Arhimede's method using ethanol as loading and weighting liquid), x-ray diffraction (XRD, $Cu_{K\alpha}$ - radiation), four probe electrical resistance, *ac* magnetic susceptibility vs. temperature down to 77 K (lock-in method), scanning electron microscopy (Philips SEM 515 and JEOL JSM-6400F equipped with microanalysis systems) and Seebeck effect at room temperature by the hot-finger method (using Pt-reference and a thermal gradient of 10 K) measurement. The *f* fraction of the high-temperature superconducting phase Bi(Pb)-2223 was estimated from XRD:
$f = (0010)_{2223}/(A(0010)_{2223}+A(008)_{2212})$, where $A(0010)_{2223}$ and $A(008)_{2212}$ represent the area of the (0010) and (008) peaks of the Bi(Pb)-2223 and Bi(Pb)-2212 phases, respectively (Table 2).

3. Results and discussion

Density of the samples is gathered in the Table 2. It is well known that during synthesis of Bi(Pb)-2223 samples, density increases and then decreases with processing time [6]. It is usually accepted that the increase of the Bi(Pb)-2223 amount, *f*, is directly accompanied by the decrease in density. In our case, for the sample obtained from the precursor A, a longer heat treatment time for the samples 6A, 4A, 5A, 1A is decreasing the density. Similar behavior can be observed for the samples 4B1, 6B1, 1B1 fabricated from the precursor B1. Although the samples from the precursors A and B1 are showing the same density tendency the fraction *f* of Bi(Pb)-2223 phase in the samples is very different: 35-48% for A-samples and 71-91% for B1-samples. It results that correlation between density and *f* is not direct and other parameters should be considered. For example, very long heat treatment times as for samples 7B1 and 4B2 seems to improve density. Also intermediate grinding, as for samples 2A, 3A and 2B1, 3B1 allows better packing leading to higher density. The reason for the discrepancy f-density might be related to the occurrence and properties of the liquid phase that is probably significantly influenced by the precursor. Other parameters such as oxygenation and phase assembly and so on should be also considered.

In Fig. 1, for the A-samples without intermediate grindings, resistive transitions are shifting from lower to higher temperature with the increase of heat treatment time (see samples 6A, 4A, 5A and 1A) while reduced resistance just above transition is decreasing. Samples 2A and 3A with intermediate grinding show lower critical temperatures and the result suggests that intermediate grinding and the moment when it is performed can significantly influence Bi(Pb)-2223 superconducting phase formation and its quality. For the precursor A intermediate grinding is not recommended, especially on the late stages of heat treatment (compare 2A and 3A). Results can be understood as follows: intermediate grinding might induce defects that might not recover by subsequent heat treatments and this is the case for the samples 2A and 3A. It is easy to understand that recovery processes will depend on the sample state at the time when grinding is done. Remarkable is that for the A-samples the tendency of the R-T curves is systematic, consistent and has high reproducibility. On the other side, B-samples show large scattering although the tendency is relatively similar, i.e. T_c increases with heating time from 4B1, 6B1 or 1B1 to 5B1 or 7B1. As about intermediate grinding the influence of this operation (samples 2B1 and 3B1) is likely positive if realized on the early stages of synthesis (sample 2B1), but the large observed scattering does not allow to draw a reliable conclusion. Next, if we compare A and B1 samples it is clear that better R-T transitions are obtained for the A-samples. This is exactly opposite to the results of XRD as already introduced in the previous paragraph: the A-samples are developing slowly and the amount of Bi(Pb)-2223 is low, but it is of higher quality, while B-samples are much faster in formation of the Bi(Pb)-2223 phase, but the quality of the best Bi(Pb)-2223 phase participating in the percolation of the current in the R-T measurements is lower. Discrepancy between phase amount f and R-T behavior suggest once more that samples from the two precursors A and B are experiencing very different growth processes and not only phase formation kinetics is affected. Growth processes are

overlapping and may have opposite influence finally imposing very different properties of the Bi(Pb)-2223 phase. Correlation *density-Tc-f* is a complex one and requires detailed understanding of the processes. At the same time, for the same solid state route from oxides one should pay much attention to the precursor as this is identified as one major element influencing subsequent processes and quality of the Bi(Pb)-2223 superconducting ceramic. Some thoughts related to this conclusion will be presented in the next paragraphs. From a practical point of view it is also clear that optimization and the degree of the samples quality control depend on precursor.

Table 2. Amount of the Bi-2223 phase, f, density, D, and peak temperature in χ''(T) curves, T_{pg}.

Sample (from A)	f(%)/D(g/cm^3)/ T_{pq}(K)	Sample (from B1)	f(%)/D(g/cm^3)/ T_{pq}(K)	Sample (from B2)	f(%)/D(g/cm^3)/ T_{pq}(K)
1A	48/4.61/105.8	1B1	91/4.5/98.9		
2A	40/5.66/107	2B1	93/5.18/103.1		
3A	50/5.73/106.7	3B1	97/5.71/103.8		
4A	45/5.76/104.3	4B1	71/5.77/100.8		
5A	45/4.37/104.3	6B1	91/4.79/101	3B2	93/-/97.7
6A	35/6.0/104.4	5B1	90/-/102.4		
		7B1	96/5.14/104.4	4B2	97/5.66/104.2

At temperatures above 77.3 K, the peak observed in the susceptibility curves χ"(T) (Fig. 2) is ascribed to losses in the grains. Losses in the intergranular regions cannot be observed in Fig. 2 because they occur at lower temperatures (below 77.3 K) as a consequence of the weak links behavior. The temperature T_{pg} of the intragrain maximum corresponds to the full penetration of the magnetic field into the grains and can be used as a relative measure of the intragrain critical current density. Values of T_{pg} are given in Table 2. Variation of T_{pg} with heat treatment time for each precursor is relatively low, with a slight tendency for enhancement for long times (see 6A, 4A, 5A and 1A or 4B1, 6B1, 1B1 and 7B1 or 3B2 and 4B2). Intermediate grindings are showing also a weak influence on T_{pg}, or, arguably, seems to produce a small enhancement of this parameter (see 2A, 3A for A-samples and 2B1, 3B1 for B samples) when heat treatment time is not longer than 330 h. The highest T_{pg} values for one processing condition (compare samples A, B1 and B2 from each row in Table 2) are always for the A-samples and this set shows also the lowest scattering that is consistent with the scattering behavior from the R-T measurements presented in the above paragraph.

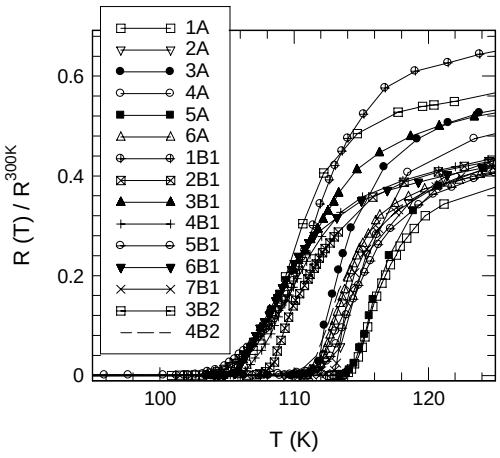

Fig. 1. Reduced resistance curves vs. temperature.

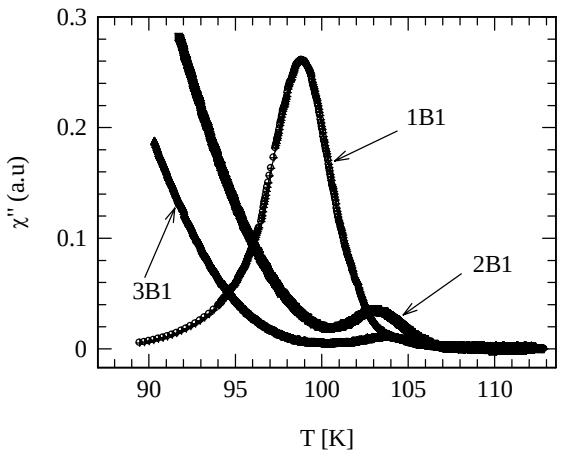

Fig. 2 χ''(T) curves for indicated samples.

As already mentioned the reason for the described behavior is in a large extent due to the precursor. The difference between B1 and B2 samples are not significant, while between A and B samples are. This suggests that starting phase assembly in the precursor is very important. A special notice requires Bi and Pb phases that are known to form liquid phases or phases related to this one such as $(Ca,Sr)_2PbO_4$ and Bi-rich phases, e.g. $Bi_2(Sr,Ca)_3O_6$ [7]. XRD patterns of the precursors are presented in the Fig. 3. The precursor powder A consist of Bi-2212 and Bi-2201 phases, a big quantity of $(Sr,Ca)CuO_2$ (1:1), some amount of CuO and traces of Ca_2PbO_4 (CP). The precursor powder B1 (similar to B2, not shown in Fig. 3) contains mainly Bi-2212 phase, very small quantity of $(Sr,Ca)CuO_2$ (1:1), a small amount of CuO and a small amount of CP. Another phase that seems to be present in the both precursors is $Bi_2(Sr,Ca)_3O_6$. The most significant difference between precursors is likely the amount of (1:1) phase. In the literature, this phase is considered to be one of the key phases to form Bi(Pb)-2223 through the reaction Bi-2212+(1:1)→Bi-2223, but an unanimous opinion among researchers has not been reached. In our case large amount of (1:1) in the precursor A is not favorable to attain a large

amount of Bi(Pb)-2223. A possible reason might be the presence in the precursor A of a large amount of an unknown phase (marked with '?'). This phase was not detected in the precursor B1. After the final heat treatment samples from set A contain Bi(Pb)-2223 as the major phase and residual phases are Bi-2201, CuO, CP, 21-Ca_2CuO_3 (2:1), $Sr_{0.9}Ca_{0.1}CuO_2$ (1:1), and $Sr_9Ca_5Cu_{24}O_{41+z}$ (14:24). Samples from set B show a large amount of Bi(Pb)-2223 and traces of impurity phases.

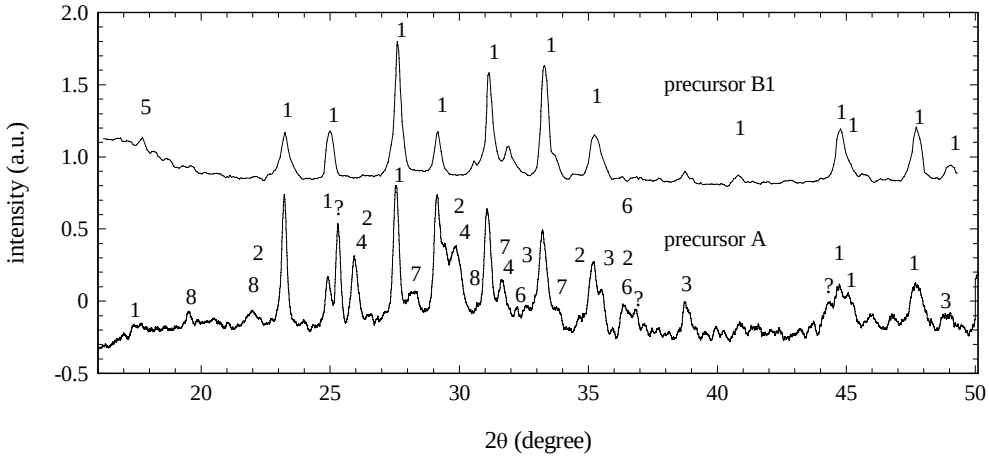

Fig. 3. XRD patterns of the precursors. Phases and Powder Diffraction Files according to which phases were identified are:1- Bi-2212 (40-0378, 41-0317), 2 – Bi-2201 (45-0315), 3 - CuO (41-0254), 4 $Sr_{0.9}Ca_{0.1}CuO_2$ (denoted 1:1, 48-1505), 5-Ca_2PbO_4 (denoted CP, 36-629, 24-207), 6 - Ca_2CuO_3 (denoted 2:1, 34-282), 7- $Sr_9Ca_5Cu_{24}O_{41+z}$ (denoted 14:24, 48-1501) and 8- $Bi_2(Sr,Ca)_3O_6$ [7].

EDS measurements confirm the presence of Bi-2223 and Bi-2212 phases in the samples A. In the same samples, individual polyhedral grains of phase (14:24) were also found. For B-samples, all investigated grains were ascribed to Bi-2223 phase. However A and B samples contain regions rich in Bi, Pb and Cu.

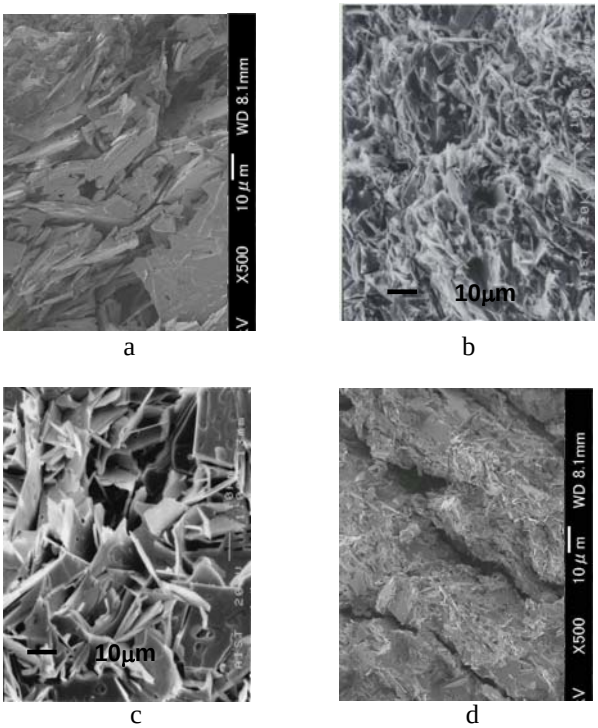

Fig. 4 SEM images of the samples: (a)- 5A, (b)-3A, (c)-6B1 and (d)-3B1.

SEM images for samples 5A, 3A and 5B1, 3B1 are presented in Fig. 4. Samples without intermediate grinding (5A and 5B1) are composed of larger grains than for the samples with intermediate grinding (3A and 3B1, grain size less than 10 μm). Morphology of the samples without grinding is different: sample 5A shows large blocks (up to 100 μm), while sample 5B1 is mostly composed of large individual plate-like grains (about 20 μm). Sample 3A with intermediate grinding is free of cracks while 3B1 is not. Cracks formation (and their healing, if any) can probably be related to the higher rate of Bi(Pb)-2223 phase formation reaction in the B-samples and, hence, with the different initial phase assembly of the precursors and their subsequent evolution.

The level of oxygenation in the samples might be different when starting with different precursors. Indeed Seebeck coefficient in the ceramic A-samples is in the range of 0-1.5 μV/K that is lower than for the B-samples, i.e. 2.3-5.4 μV/K. It was reported by many authors that atmospheres with different oxygen concentration result in different amount and properties of the superconducting phase for a fixed heat treatment. Non-superconducting phases are also influenced. In addition, samples oxygenation is also influenced by the intermediate grinding through the resulting different packing and induced defects. There is a tight relationship between precursor, growth processes and processing and final properties. Further detailed work is necessary to understand it for our routes employing different oxide precursors generating such unusually different results. Another issue is that the level of residual C in the precursor and hence in the samples might be different with implications on phase formation and properties. It was

reported that a relatively high amount of C suppresses phase formation of the Bi-2223 phase and decreases critical current density [8].

4. Conclusions

Samples of Bi(Pb)-2223 superconductor were prepared from two precursors with the same cation stoichiometry and by solid state route. Samples have shown significantly different properties with the most striking result being the fact that samples from one precursor allowed formation of maximum 50% Bi-2223 of relatively high quality from the T_c and J_{cg} points of view, while the other one led to samples (processed in the same conditions) with more than 90% Bi(Pb)-2223, but of lower quality. Such large differences are usually encountered when precursors are synthesized by very different methods, e.g. soft chemistry, cryochemistry, aerosol, combustion when compared with conventional solid state route. Current data does not allow explanation of our results in detail, but they point on the importance of the precursor's status for the phase formation and final properties of the superconductor. More experiments are necessary.

From a practical point of view it is concluded that each precursor regardless synthesis method requires careful and individual optimization approach.

Acknowledgements

The authors would like to express their gratitude to I.. Bradea for transport measurements. The Ministry of Education and Research of Romania supported this work within the framework of the CERES program.

References

[1] J. G. Bednorz, K. A. Muller, Zeitschrift Phys B **64**, 189 (1986).
[2] Y. K. Sun and W. Y. Lee, Physica C **212**, 37 (1993)
[3] K. H. Song, H. K. Liu, S. X. Dou, C. C. Sorrel, J. Am. Ceram. Soc. **73**, 149 (1992)
[4] T. L. Wang, S. W. Lyons, T. T. Kodas, Physica C **200**, 31 (1992)
[5] P. Krishnaraj, M. Lelovic, N. G. Eror, U. Balanchandran, Physica C **215**, 305 (1993)
[6] T. Hatano, K. Aota, S. Ikeda, K. Nakamura, K Ogawa, Jpn. J. Appl. Phys. **27**(Part 2), L2055 (1988).
[7] J.-.C Grivel, R. Flukiger, Physica C **235-240,** 505 (1994).
[8] A. Jeremie, G. Grasso, R. Flukiger, Physica C **225**, 53 (1995).

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