

THE DEPENDENCE OF ELECTRICAL AND STRUCTURAL PROPERTIES WITH AGING OF SUPERCONDUCTOR CERAMICS

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ABSTRACT

This work presents the results of electrical resistance measurements as a function of temperature and x-ray diffractometry for 2223 superconductor pellets (critical temperature at around 110 K), after keeping them for 14 years under normal ambient conditions (25°C, 1atm and 50-70% humidity). The pellets were obtained after pressing a precursor powder previously prepared by a chemical process. The results indicate that the samples obtained from the chemical process are very stable, which represents extremely important results for technological applications.

1. INTRODUCTION

Since the discovery of high T_c superconductor material by Bednorz et al. [1], there has been constant research to considerably increase their critical temperature, and this objective has been reached with relatively success. However, for some of the obtained materials, though showing high critical temperature, their components are toxic, as Hg and Tl, or needing special storage conditions, as the YBCO case [2-4]. One of those materials not presenting the aforementioned characteristics is the BSCCO system, which in addition presents other superconducting phases with high T_c , as for instance the 2223 phase with $T_c = 110$ K [2-5]. Therefore, special effort has been carried out for this material along the years. Based on those facts, we studied this superconductor prepared by a chemical process, instead of the conventional solid state reactions, which is laborious and requires much time, notwithstanding leading to a non-homogeneous composition [4-7]. The behavior of some properties of the samples was checked up during the storage time under normal ambient conditions (25°C, 1atm and 50-70% humidity). Thereby, in this work we present for the first time, to our knowledge, important results in terms of technological applications, because before introducing any new material in the market it is fundamental that its stability and durability be tested and checked. Measurements of resistance versus temperature using four-probe dc and X-ray diffraction showed that it is a superconducting material close to 110 K and its electrical and structural properties were practically unaffected after 14 years under normal ambient conditions.

2. EXPERIMENTAL PROCEDURE

A chemical method was used to prepare the superconductor Bi-2223, whose steps are described as follows. Initially, we dissolved, separately, Bismuth (III) acetate $\text{Bi}(\text{C}_2\text{O}_2\text{H}_3)_3$, Calcium acetate $\text{Ca}(\text{C}_2\text{O}_2\text{H}_3)_2$, Copper (II) acetate monohydrate $\text{Cu}(\text{C}_2\text{O}_2\text{H}_3)_2 \cdot \text{H}_2\text{O}$, in a solution of glacial acetic acid 100% and Ammonium hydroxide, whose pH solution was kept at around 3. Lead nitrate $\text{Pb}(\text{NO}_3)_2$ and Strontium nitrate $\text{Sr}(\text{NO}_3)_2$ were also dissolved separately in a solution of ammonium hydroxide (0.003N) with $\text{pH} \approx 9$. All of the compounds that were used in these solutions presented at least 99.0% of purity. The compounds were used in convenient amounts, preparing the solution with the stoichiometric amounts, so that at the end of the process we would get a compound with a nominal composition 2223 - $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. The solution was kept in a magnetic stirrer under heating at 80°C to slowly evaporate it. After the material was dry, it was submitted to a calcination process between 600°C – 790°C for 8 - 24 hours using high alumina crucible, at room temperature and repeated many times. This process was always intercalated by grinding in an agate mortar in order to increase the composition homogeneity. Pellets of 20.0 mm of diameter and 1.0 mm of thickness were heat treated at 835°C/100 h with gas flux of 400:1 Ar/ O_2 using a 120°C/hour heating rate. The electrical resistance versus temperature measurements were carried out from room to liquid nitrogen temperature (300 K - 77 K), using the four-probe dc method. The electrodes were painted with conductor silver ink over a small sample taken from the pellets (3x10 mm²). This procedure enables to identify the presence of possible superconducting transitions and phase respective, when existing. This measures were carried out by an automatic system, using a programmable voltage/current source model 228A, a nanovoltmeter model 2182, a high performance DMM model 2000, all of them from Keithley Instruments Inc., dt 470 sd temperature sensor from Lake Shore Cryotronics, Inc. and so on [5-7]. Two different diffractometers were used, Rigaku model RU 200B and Shimadzu model XRD-6000, both using a $\text{CuK}_{\alpha 1}$ filter, for the first and last measurements, respectively

3. RESULTS AND DISCUSSION

Figure 1 shows the results of resistance versus temperature measurements from room to liquid nitrogen temperature of the pellets sintered at 835°C for 100 hours inside mixed

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atmosphere using a flowing gas with the following relation in 400:1 of Ar/O₂, effecting them in different occasions with a fourteen-year interval between each one. The first measure was done in 1995 and showed that at room temperature the sample demonstrated a resistance of 30 mΩ, while another measure took place after 14 years (2009) and showed as resistance of 42 mΩ. Both samples showed an ohmic behavior, i.e., the curve decreases linearly with the temperature until 120 K, when the superconducting transitions begin, thus the behavior is no longer ohmic.

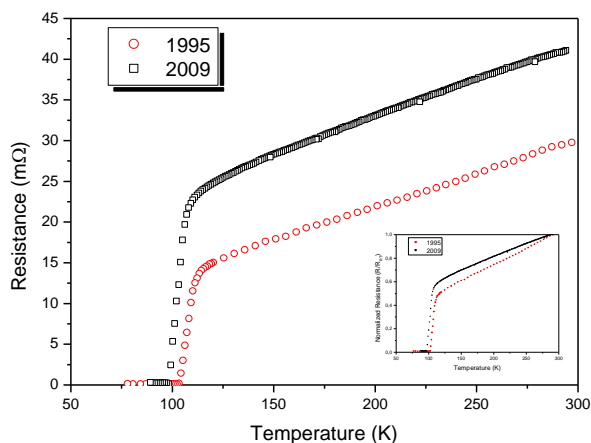


Figure 1 - Temperature dependence of resistance curves for the pellet sample sintered at 830°C for 100 hours in 400:1 of Ar/O₂ atmosphere effected in 1995 and 2009. The inset shows the normalized resistance versus temperature.

Based on these results, it can be observed that at the beginning of the transition, $T_{\text{onset}} = 114$ K, the resistance is around 17 mΩ for the first measure and 25 mΩ for the second one, such as $T_{\text{onset}} = 118$ K, implying a temperature difference of 4 K. There is a small temperature difference after the complete transition $T_c = 104$ K and $T_c = 99$ K between each measure, respectively. The difference between the resistances is due to the fact that the geometrical parameters of the electrodes were changed, that means they were remade since the old silver ink turned insulating and were then removed. However, the inset shows that there is no difference between the dependence of normalized resistance in function of temperature (room temperature - 300 K) or the differences are minimized.

On the other hand, such differences might be associated to the self-instability of phase 2223, the presence of segregation, such as Ca_2PbO_4 , which frequently forms along the synthesis process of the superconducting phase that together with ambient conditions (water vapor, carbon dioxide, others) could be favorable or the stable phase formation as 2212 / $T_c \sim 85$ K and 2201 / $T_c \sim 35$ K, causing the decrease of critical temperature, or the formation of nonsuperconducting phases [8-11]. Analyzing the x-ray diffractogram in Figure 2, it can be seen that no significant changes occurred in both measurements (first and last one), i.e., there are no new crystallographic or spurious phases. It is only possible to note the formation of just one new peak at

around $2\theta = 33.53^\circ$, which may be from phase Bi-2223 (see details in the inset). Crystallographic peaks that had not been identified before in the first measurements, as in $2\theta = 34.76^\circ$, 35.99° and in 48.78° , are present in the recent measurements. In terms of intensity, some changes were observed, however the intensity corresponded to the peak with highest intensity, i.e., at around $2\theta = 32.99^\circ$, it is in keeping with the same intensity of both old and recent measurements. The peak localized at around $2\theta = 34.63^\circ$ showed a significant increasing in the new measurement when compared to the previous measurements, however it was an unidentified peak. In general, the diffraction measurements showed that there are at least two identified superconducting phases, 2212 and 2223, and the latter is the predominant phase confirmed by the resistance as a function of the temperature measures.

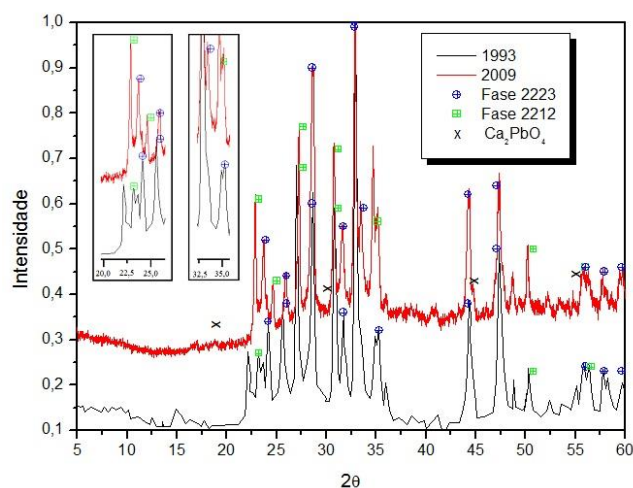


Figure 2 - X-ray diffractograms of the sample obtained in 1995 and 2009 with indexed crystallographic peaks and some details in the inset.

However, everything indicates that this sample did not have any significant modification in its structural and electrical properties. It is important to emphasize that some eventual differences between the diffractograms may be associated with the methodology used to perform the measurement, mainly because different equipments were used in this measurements, it is evident that this fact may cause minor differences in the calibration of each equipment.

4. CONCLUSION

Considering that high critical temperature superconducting materials degenerate quickly, for instance obtained by solid state reaction, despite being kept in special conditions, and knowing that in the chemical process the starting materials for calcination are produced by precipitating them together from solution. This has the advantage of mixing the constituents on atomic scale, which suggests a lower probability to obtain nonhomogeneous compounds. On the other hand it might be just the opposite in the solid state reaction, as the reactions in the last case need many steps

before reaching the equivalent level of the chemical process. Finally, we conclude that pellets obtained by chemical process of drying solution and phase 2223 of BPSCCO system with $T_c \cong 110$ K, normally an unstable phase, show insignificant variations (~5%) in their electrical characteristics and structural properties, even when they are kept under normal conditions. Therefore, we could suggest that the material obtained by this procedure can be used in technological applications because they are stable for a long time, at least fourteen years.

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REFERENCES

1. BEDNORZ, J.G.; MULLER, K.A., *Z. Phys. B* 64 (1986) 189.
2. HELLSTROM, E.E. *MRS Bull.* XVII (1992) 45.
3. LEE, D.; CONDORATE SR., R.A.; TAYLOR, J.A., *Physica C* 350 (2001) 1.
4. MAEDA, H.; TANAKA, Y.; FUKUTOMI, M.; ASANO, T., *Jpn. J. Appl. Phys.* 27 (1988) L209.
5. CARVALHO, C.L.; SANTOS, D.I.; RUBO, E.A.A.; AEGERTER, M.A. Proceedings of 11th Brazilian Congress of Engineering and Materials Science, Águas de São Pedro, Brazil, 1994, p. 689-691.
6. CARVALHO, C.L.; SANTOS, D.I.; RUBO, E.A.A.; AEGERTER, M.A. Proceedings of II Annual Meeting of Brazilian Society of Japanese Lineage Researcher, São Paulo, Brazil, 1994, p. 57-61.
7. SANTOS, D.I.; RUBO, E.A.A.; CARVALHO, C.L. – 10th Brazilian Congress of Engineering and Materials Science, Águas de Lindóia, Brazil, 1992, p. 376-379.
8. POOLE JR., C.P.; DATTA, T.; FARAH, H.A., *Copper Oxide Superconductors* - John Wiley & Sons, Inc. 1988.
9. MURALIDHAR, M.; SATYAVATHI, S.; HARI BABU, V.; PENA, O.; SERGENT, M., *Materials Science and Engineering B* 20 (1993) 312.
10. XIE, M.; ZHANG, L.W.; CHEN, T.G.; LI, X.T.; CAI, J., *Physica C* 206 (1993) 251.
11. GARNIER, V.; AMBROSINI, A.; DESGARDIN, G., *Journal of Materials Science: Materials in Electronics* 13 (2002) 353.