Low ac field response of Bi-based superconductors with addition of Antimony oxide

I.R. Metskhvarishvili[1], G.N. Dgebuadze[1], B.G. Bendeliani[1], T.E. Lobzhanidze[2], M.R. Metskhvarishvili[3], G.N. Mumladze[1]

[1]Department of Cryogenic Technique and Technologies, Ilia Vekua Sukhumi Institute of Physics and Technology, Mindeli str. 7, 0186 Tbilisi, Georgia
[2]Department of Chemistry, Faculty of Exact and Natural Sciences, Ivane Javakhishvili Tbilisi State University, Chavchavadze Ave. 3, 0179 Tbilisi, Georgia
[3]Department of Physics, Georgian Technical University, Kostava str. 77, 0175 Tbilisi, Georgia
E-mail: metskhv@yahoo.com

Abstract. We report the effects of the addition of Sb_2O_3 on the superconducting properties of Bi-2223 system. Samples with composition $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3Sb_xO_y$ (x=0,0-0.8 wt.%) are prepared by the solid-state reaction method. Ac susceptibility and high harmonic response of polycrystalline superconductors are measured in weak *ac* and *dc* magnetic fields. Critical state models are used to explain the nonlinear magnetic response and it is found that the low field odd harmonic response is qualitatively explained reasonably well within the Kim-Anderson regime. We observed that, the low level Antimony doping enhances the transport critical current densities J_c.

1. Introduction

The Bismuth based superconductors with substitution or addition of various dopants is an interesting topic for study. Antimony belongs to the fifth group elements and is metalloid. Substitution by antimony or by other fifth group elements improves the superconducting parameters of the high-temperature superconductors.

The effect of the partial substitution of Bi simultaneously by Pb and Sb on the superconductive properties of the Bi-2223 system has been investigated in many works. It has been shown that the optimal sintering temperature is about of 845°C, which yields the highest density value and the highest volume fraction of Bi-2223 phase [1]. It was observed that antimony makes the system more reactive, enhances the kinetics of the reaction and promotes the high-T_c phase [2]. Siddiqi and Akhtar [3] observed that low-concentration of Sb (2%) promotes the formation of high temperature phase (2223). It was found out that Sb has no effect on increasing the transition temperature of this system. The maximum superconducting transition temperature observed in the $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ system was T_c = 108 K, which was completely independent from the doping of Sb. Iqbal and Mehmood [5] made substitution of Sr by Sb and

---

1   metskhv@yahoo.com

concluded that the maximal value of the volume percentage of high temperature (2223) phase was 69.44% for the sample having Sb content of x=0.06. Hongbao [6] studied the partial substitution of Bi by Sb $Bi_{2-x}Sb_xSr_2Ca_2Cu_3O_y$ (x=0.05, 0.1, 0.15, 0.2). All of these samples have superconducting transition temperature of about at 120 K. Unlike the above-mentioned works, the aims of our studies are investigations of the effect of Sb_2O_3 addition on superconductive properties of Bi-2223 system.

2. Experimental

The Sb-doped samples $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3Sb_xO_y$ were prepared by the conventional solid-state reaction method. The concentrations of Sb were in the range of x=0.000, x=0.002, x=0.004, x=0.006 and x=0.008 identified as 0, 0.2, 0.4, 0.6 and 0.8 wt.%. The powders of Bi_2O_3 (99.9% Aaldrich), PbO (99.9% Sigma-Aldrich), $SrCO_3$ (99.9% Aaldrich), $CaCO_3$ (99.9% Oxford ChemServe), CuO (98% Sigma-Aldrich) and Sb_2O_3 (99% Aldrich) were weighed in necessary atomic ratios. These oxides were thoroughly mixed and ground by using a mortar and pestle and charged in alumina crucibles. The mixtures were first calcined in air by using of the temperature programmed muffle furnace (KSL-1100X-S, MTI-corporation, temperature accuracy $\pm1^oC$).The first heat treatment schedule was: 120^oC for 4 h, 200^oC for 2 h, 400^oC for 2 h, 600^oC for 2 h, 800^oC for 2 h and then was quenched to room temperature. The powder was reground and calcined in air at $800^\circ C$ for 30 h. The resulting powders were ground and pressed into the pellets of 10 mm diameters and 2 mm thickness by a hydraulic press (Holzmann-maschinen, Type: WP10H) with about 900 MPa. These pellets were sintered in air at 850 for 100 h. The samples were allowed to cool at natural furnace cooling. The prepared patterns were characterized by X-ray diffraction (XRD, Dron-3M) with CuK*a* radiation.

We have studied the real part of *ac* susceptibility χ' and the magnitude of the amplitudes of the high harmonics. In our experiment we discuss the case when collinear constant and variable fields $H(t) = H + h cos\omega t$ are applied to the sample. In this case, the induction $B(t)$ could be expanded into Fourier series as $B(t) = \frac{a_0}{2} + \sum_n(a_n cosn\omega t + b_n sinn\omega t)$. In case $h \ll H$, the expression for a_n and b_n coefficients [7], which are determined in our experiment are:

$$a_0 = 2\mu_{eff}H, \quad a_1 = \frac{\mu_{eff}h^2}{4\pi j_c(H)d}, a_{2k+1} = 0, \quad k \geq 1; \qquad (1)$$

$$b_{2k+1} = -\frac{\mu_{eff}h^2}{8\pi^2 j_c(H)d}\frac{1}{(k^2-1/4)(k+3/2)}; \quad a_2 = \frac{\mu_{eff}h^3}{32\pi d}\frac{d}{dH}\left\{\frac{1}{j_c(H)}\right\}, \quad a_{2k} = 0, \quad k > 2;$$

$$b_{2k} = -\frac{\mu_{eff}h^3}{16\pi^2 d}\frac{d}{dH}\left\{\frac{1}{j_c(H)}\right\}\frac{k}{(k^2-1/4)(k^2-3/2)}$$

Here, μ_{eff} is the effective permeability of the ceramic material, which takes into account the fact that the field does not penetrate into the granules, h is a variable field, d is a thickness of the sample, H is a constant field and j_c is the critical current density. Errors in high harmonics measurement could be as high as ~ 2% when the measuring signal is lower than 0.2 μV. However, the error does not exceed 0.5% for higher amplitudes [8].

The phase method was used to study the real parts of the linear susceptibility [9].The errors in the determination of χ' at higher frequencies than 1 kHz does not exceed 1%.

3. Result and discussion

The X-ray diffraction patterns for all samples are plotted in Figure 1. As one can see, the samples consist of a mixture of Bi-2223 and Bi-2212 phases as the major constituents. From the XRD results one will notice that the low Sb concentration samples (0.2 wt.% and 0.4 wt.%) was dominated by high-T_c 2223 phase. However, in higher doping (0.6 wt.% and 0.8 wt.%) concentration, the low T_c-phase 2212 is dominant.
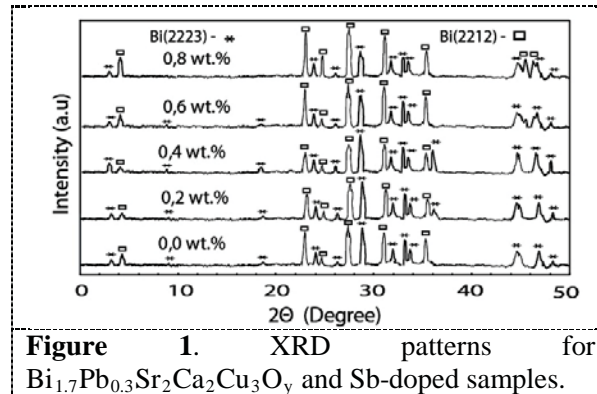
Figure 1. XRD patterns for $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ and Sb-doped samples.

Figure 2 shows the temperature dependences of the real $(-4\pi\chi')$ part of *ac* susceptibility for un-doped and doped samples, measured in zero magnetic fields (*H*=0) at *h*=1 Oe, *f*=20 kHz. The diamagnetic onset temperature of the superconducting transition for 0.0 wt.% sample is about $T\approx110$ K and T_c monotonically decreases with increasing Sb content. As we see un-doped (0.0 wt.%) and low doped (0.2 wt.%) samples clearly show a two step decrease with *T*, which reflects the flux shielding from and between the grains. The high doped samples (0.4-0.8 wt.%) do not show two steps and full screening of applied *ac* magnetic fields for samples, whose Sb_2O_3 doping is in the range 0.4 wt.%, is observed at *T*~92 K.

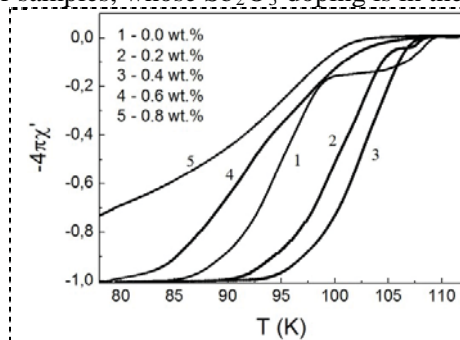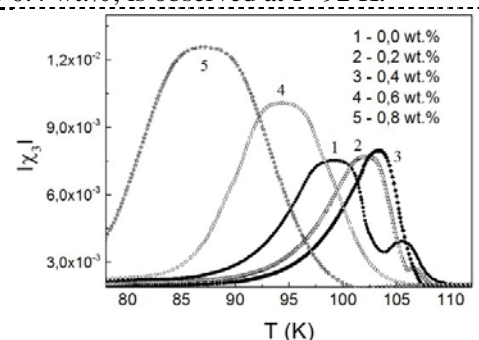**Figure 2.** Temperature dependences of the real χ' parts of ac susceptibility.

Figure 3. Temperature dependences of the amplitude of the third harmonics.

Measurements of temperature dependence of the magnitude of the third harmonics at *h*=1 Oe, *f* = 20 kHz, *H* = 0 are presented in figure 3. Like $-4\pi\chi'(T)$ dependence for un-doped and 0.2 wt.% doped samples, the $\chi_3(T)$ presents a two-peaks plot. The high-temperature peak could be caused by the penetration of the field into the crystallites and be associated with intragranular critical current density, j_{cg}, while the low-temperature maximum is due to the penetration only into the Josephson medium formed by weak links between the crystallites. The latter is associated with intergranular critical current density j_{cJ}.

According to (1), amplitudes of each harmonics are inversely proportional to the critical current density $b_n \approx 1/j_c$. Thus, $j_c(H)$ function could be determined by studying the dependencies of these harmonics on the magnitude of the constant field *H* at a fixed amplitude of *h* [7]. From Figure 4 it follows that for un-doped and doped samples b_3 is very sensitive to the low external *dc* fields and is linearly increasing. The observed behavior of the third harmonic could be explained by Kim-Anderson critical state modal dependences of critical current density on the magnetic induction [10-12] $J_c(B) = J_0/(1 + B/B_0)$. Additionally, it should be noted that we have carried out such experiments in a large temperature range and $b_3(H)$ is not changed for all three samples.

Figure 5 presents dependence of the transport critical current densities on temperature j_{cJ} value calculated from $\chi_3(T)$ measurements using equation (1). As we see j_c value for the un-doped sample is 85 A/cm^2 and the largest value of critical currents observed in sample 0.4 wt.% is equal to 115 A/cm^2.
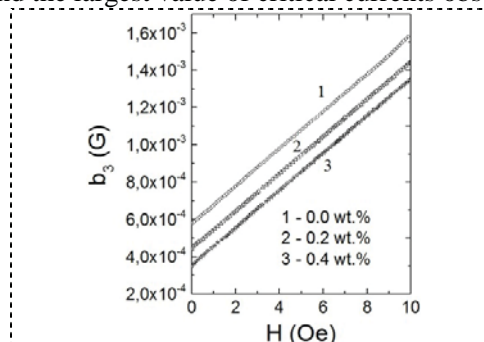

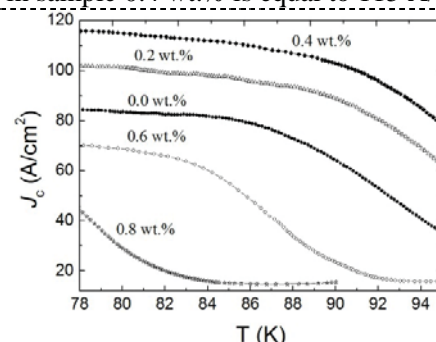| **Figure 4.** Dependence of the third harmonic on *dc* fields, *h*=1 Oe, *T*=78 K | **Figure 5.** Dependence of the critical current densities on temperature. |

4. Conclusion

The effect of Sb$_2$O$_3$ doping on Bi-2223 system has been studied by the low fields *ac* susceptibility and the third harmonic response. Temperature dependences of χ' show a two step process, for un-doped and small doped (0.2 wt.%) samples. It is important to note that the high doped samples (0.4-0.8 wt.%) do not show two steps. The absence of two-step behavior could be explained in terms of smaller grain size in the high doping samples, so that grains are fully penetrated at a lower field value. We found that in the low level doped samples, Antimony enhances the value of the transport critical current densities from 85 A/cm^2 (0.0 wt.%) to 115 A/cm^2 (0.4 wt.%). Critical state models are used to explain the nonlinear magnetic response in un-doped and doped samples, with a generalized field dependence of critical current J_c: $J_c(B) = J_0/(1 + B/B_0)$.

5. Acknowledgements

References

[1]   Kocabas K, Bilgili O andY asar N 2009 J. Supercond. Nov. Magn. **22** 643
[2]   Fruth V, Popa M, Ianculescu M A, Stir M, Preda S and Aldica G 2004 J. Eur. Ceram. Soc. **24** 1827
[3]   Siddiqi S A and Akhtar B 2003 Mod. Phys. Lett. B **17** 199
[4]   Heiras J, Krauss W and Politis C 1990 Int. J. Mod. Phys. B **04** 131
[5]   Iqbal M J and Mehmood R 2006 Mater. Sci. Eng. B **135** 166
[6]   Hongbao L, Xiaonong Z, Yaozu C et al 1988 Physica C **156** 804
[7]   Ginzburg S L, Khavronin V P, Logvinova G Yu et al. 1991 Physica C **174** 109
[8]   Metskhvarishvili I R 2009 J. Low Temp. Phys. **155** 153
[9]   Metskhvarishvili I R et al 2013 J. Low Temp. Phys. **170** 68
[10]   Kim Y B, Hempstead C F and Strnad A R 1962 Phys. Rev. Lett. **9** 306
[11]   Anderson P W 1962 Phys. Rev. Lett. **9** 309
[12]   Kim Y B, Hempstead C F and Strnad A R 1963 Phys. Rev. **131** 2486