

Anomalous thermoelectric power of overdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ superconductor

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All the samples possess single-phase character and their superconducting transition temperatures ($T_c^{R=0}$) are 85, 90, and 72 K, respectively for Bi2212-MQ, Bi2212-N₂, and Bi2212-O₂. Though the Bi2212-MQ and Bi2212-N₂ samples are in near optimum doping regime, the Bi2212-O₂ is an overdoped sample. $T_c^{S=0}$ values obtained through $S(T)$ data are also in line with those determined from the temperature dependence of resistance ($T_c^{R=0}$) and dc magnetization (T_c^{dia}). Interestingly, $S(T)$ behavior of the optimally doped Bi2212-MQ and Bi2212-N₂ samples is seen to be positive in whole temperature range, the same is found negative for the overdoped Bi2212-O₂ sample above $T_c^{S=0}$. This anomalous $S(T)$ behavior is seen in the light of the recent band structure calculations and the ensuing split Fermi surface as determined by angle-resolved photoelectron spectroscopy. © 2009 American Institute of Physics. [doi:10.1063/1.3248265]

I. INTRODUCTION

Though the discovery of high T_c superconductivity (HTSc) in perovskite cuprates¹ is among one of the greatest scientific achievements, the theoretical understanding of the phenomenon is still elusive. The observance of the high superconducting transition temperatures of up to 132 K (Ref. 2) and the anomalous normal state physical properties of the HTSc are quite intriguing.^{3–5} Principally not only the pairing mechanism for very high T_c has been undecided, precise normal state electrical or thermal conduction processes are also far from being clear.^{3–7} Thermoelectric power $S(T)$ behavior in this regard is one of the important physical property. Unlike the resistivity $R(T)$, the $S(T)$ precisely mimics the exact electronic conduction process in terms of the dominating charge carriers.^{8,9} For example in NaCoO₂ the electrical conduction is though through highly metallic Co–O layers, the $S(T)$ is controlled from phonon drag Na–O, giving rise to high conductivity along with the higher S value.¹⁰ In case of HTSc cuprates, several articles exist in the literature on their $S(T)$ and apparently no consensus have yet been arrived at.^{4,11–14} Though the $R(T)$ behavior mostly match in various reports the $S(T)$ does not.^{11–15} This is precisely because of the split Fermi surface and ensuing two-band structure in most of HTSc.^{12,16–18} Further, the distribution of oxygen in highly inhomogeneous HTSc samples hampers the real output. This is particularly true in case of Bi-based cuprates.¹⁹ In case of Bi-based systems though negative $S(T)$ is reported in some reports for the overdoped Bi2201 samples,¹³ the same is also reported positive in Bi2212.²⁰ This could primarily be attributed to inhomogeneous oxygen distribution within the grains of polycrystalline samples.^{19–21} In present

article we address this problem, and present the $S(T)$ results on oxygen-homogenized Bi2212 samples from optimum to overdoping regime.

II. EXPERIMENTAL DETAILS

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi2212) samples were synthesized through solid-state reaction route, as described elsewhere.²² The samples thus produced are named as Bi2212-MQ. From among Bi2212-MQ set, one of the samples is further annealed in flow of N₂ gas at 600 °C for 24 h and cooled slowly to room temperature in same atmosphere. This sample is named as Bi2212-N₂. Another sample from Bi2212-MQ set is annealed in O₂ gas flow at 800 °C for 36 h and cooled slowly to room temperature in same atmosphere. This sample is named as Bi2212-O₂. XRD patterns of the samples are recorded by using Cu $K\alpha$ radiation (Rigaku miniFlex-II, $\lambda=1.54$ Å). $R(T)$ measurements were performed for all the mentioned samples in the temperature range of 20–300 K on a close cycle refrigerator, using four-probe method. Temperature dependence of dc magnetization of the Bi2212-MQ and Bi2212-O₂ samples was carried out on a superconducting quantum interference device magnetometer (Quantum Design) both in zero field-cooled (ZFC) and field-cooled (FC) configurations. The thermogravimetric (TG) analysis is carried out on a Mettler Toledo system. The thermoelectric power $S(T)$ measurements were carried out on an automated precision measurement system,²¹ and the repeatability of the experiment is checked. This was done precisely because years before we got *ve* $S(T)$ for the overdoped Bi-2212 samples.²⁰

III. RESULTS AND DISCUSSION

The room temperature XRD patterns of Bi2212-MQ, Bi2212-N₂, and Bi2212-O₂ samples are depicted in Fig. 1(a). All the samples exhibit phase purity with tetragonal struc-

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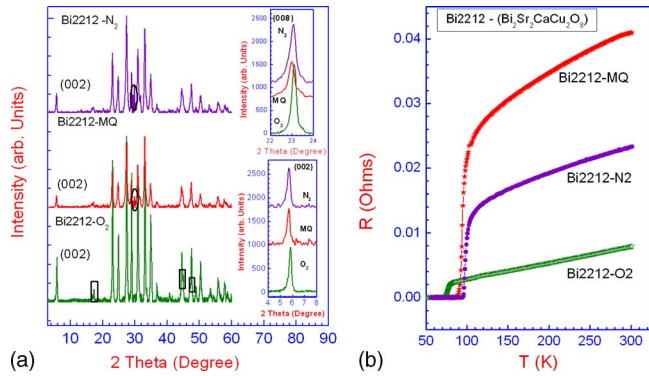


FIG. 1. (Color online) (a) X-ray diffractograms of the various Bi2212 samples, the inset shows the extended low angle characteristic (002) peak. (b) Temperature dependence of resistance $R(T)$ of the Bi2212-MQ, Bi2212-N₂, and Bi2212-O₂ samples.

ture. The characteristic low angle {002} peak is seen distinctly at $2\theta \sim 5.8^\circ$. Any intermixing of Bi2212 phase (002 at $2\theta \sim 5.8^\circ$) with that of Bi2201 (002 at $2\theta \sim 7.6^\circ$) or Bi2223 (002 at $2\theta \sim 4.6^\circ$) is also ruled out. The lattice parameters a and c of Bi2212-MQ and Bi2212-O₂ samples calculated with Rietveld refinement are 3.8238 ± 0.0004 , 30.8744 ± 0.0037 and 3.8177 ± 0.0048 , 30.7645 ± 0.0036 Å, respectively. The observed decrease in lattice parameters for Bi2212-O₂ sample vis-à-vis the Bi2212-MQ sample is clear indication of the increased oxygen content for the same sample.^{23,24} The decrease in c parameter for Bi2212-O₂ sample is also clear from its characteristic low angle (002) and (008) peak shift toward higher angle [see inset Fig. 1(a)]. In fact the lattice parameters are calculated from all observed diffractions peaks with a computer program, and as such the alone low angle (002) peak gives off values of the c parameter. The extended (002) peak is shown in inset of Fig. 1. This is to stress upon the fact that with long hour O₂ annealing the phase transformation from Bi-2212 to 2201 or 2223 has not taken place in the presently studied samples. The shift in both (002) and (008) peaks toward higher 2θ value for Bi2212-O₂ sample is clear indication of its decreased c parameter and hence increased oxygen content. The variation in lattice parameters is in general agreement with previous reports.^{23,24} Further the careful look of the XRD patterns in Fig. 1(a) shows that in case of Bi2212-MQ and Bi2212-N₂ some extra peaks are seen (marked with circles), which are highly reduced in case of Bi2212-O₂ sample. The extra peaks cannot be due to unreacted material because all the samples are from the same master batch (930 °C partial melt +860 °C 20 h annealing+quenching to room temperature) but are different in their oxygen loading. We believe these extra lines (marked with circles) arise from the inhomogeneous distribution of oxygen and thus ordering of oxygen-poor and rich material pockets in these samples. On the other hand the Bi2212-O₂ sample is mostly devoid of the extra XRD lines (circle marked regions) and rather shows the splitting of Bi–O originated selected planes (rectangle marked regions) on its XRD pattern in Fig. 1(a). In Bi-based superconducting systems the excess oxygen goes to Bi–O layers and dopes mobile holes to the Cu–O₂ superconducting planes.²⁵ The splitting marked by rectangle in

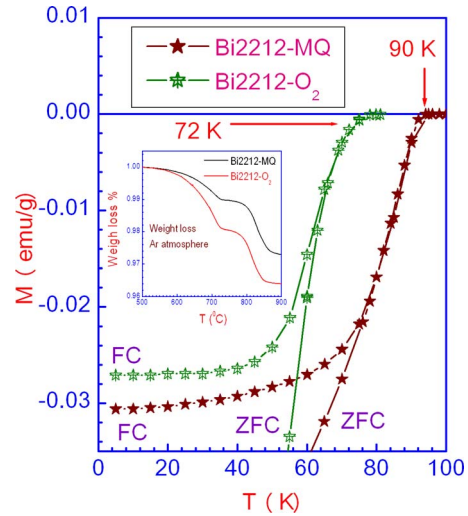


FIG. 2. (Color online) Temperature dependence of dc magnetization of the Bi2212-MQ and Bi2212-O₂ samples in ZFC and FC configurations, inset shows the TG plots in Ar with heating rate of 4 °C/min for both the samples.

XRD patterns are good indicators of excess oxygen in the system, which resides in the Bi–O plane and affects the in plane Bi–O stretching Raman active modes.²⁶ The decrease in Bi–O planes splitting are good indicators of the fact that the presently studied Bi2212-O₂ sample is most probably homogeneously oxygenated. Although as mentioned earlier, it is difficult to prove the homogenous distribution of oxygen in polycrystalline samples, on the other hand the discussion presented above strongly indicate that the presently studied Bi2212-O₂ sample is well oxygenated.

The resistance versus temperature plots $R(T)$ for Bi2212-MQ, Bi2212-N₂, and Bi2212-O₂ samples are given in Fig. 1(b). The normal state conductivity of Bi2212-O₂ sample has improved tremendously in comparison to both Bi2212-MQ and Bi2212-N₂ samples, indicating a higher density of mobile carriers in Bi2212-O₂ sample in comparison to Bi2212-MQ and Bi2212-N₂ samples. Interestingly, the superconductivity transition temperature (T_c) is least around 72 K for the Bi2212-O₂ in comparison to 85 and 90 K, respectively, for Bi2212-MQ and Bi2212-O₂ samples. This shows that Bi2212-O₂ annealed sample is overdoped, i.e., having better normal state conductivity with lower T_c in comparison to Bi2212-MQ and Bi2212-N₂ samples. dc magnetization measurements of the Bi2212-MQ and Bi2212-N₂ samples in both ZFC and FC situations in an applied field of 10 Oe are shown in Fig. 2. Both ZFC and FC become negative (diamagnetic) at T_c^{dia} of around 90 and 72 K respectively for Bi2212-MQ and Bi2212-O₂ samples. The superconducting transition temperature values being determined from magnetization (T_c^{dia}) and resistivity ($T_c^{R=0}$) are in good agreement with each other, see Figs. 1(b) and 2. The decrease in T_c of Bi2212-O₂ sample is known to be from overdoping of carriers in the same.^{23–26} To demonstrate the fact that Bi2212-O₂ sample really possesses more oxygen than as compared to Bi2212-MQ, the TG plots of these two samples are given in inset of Fig. 2. The experiment is carried out in flow of Ar gas with heating of 4 °C/min. It is seen that the weight is

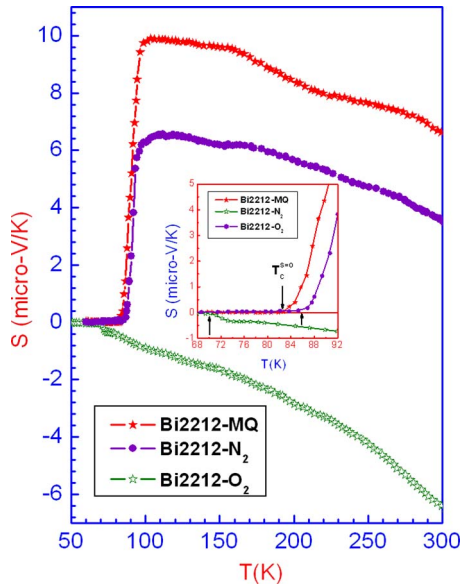


FIG. 3. (Color online) Temperature dependence of thermopower $S(T)$ of the Bi2212-MQ, Bi2212-N₂, and Bi2212-O₂ samples.

nearly unaltered until around 550 °C and later decreases between 600 and 850 °C by around 2.5% and 3.5% respectively for Bi2212-MQ and Bi-2212-O₂ samples. Certainly the Bi2212-O₂ sample has more oxygen than the Bi2212-MQ. As far as exact content of oxygen is concerned, the decomposition details of Bi2212 superconductor in various gas environments and heating schedules are underway and will be reported later.²⁷ Another viable method used for oxygen content determination of HTSc compounds is the iodometric titration. However, the same is not directly applicable in case of Bi, Tl, and Hg-based compounds due to fluctuating valence of Bi, Tl, and Hg.²⁸

The thermoelectric power $S(T)$ behavior of the studied Bi2212-MQ, Bi2212-N₂, and Bi2212-O₂ samples is given in main panel in Fig. 3. All the three samples exhibit superconductivity with $T_c^{S=0}$ at nearly the same $T_c^{R=0}$ temperatures. As far as the observation of superconductivity is concerned both the $R(T)$ and $S(T)$ measurements corroborate each other [Figs. 1(b) and 3]. However, there is one striking difference i.e., the normal state $S(T)$ is though positive for Bi2212-MQ, Bi2212-N₂, the same is negative for Bi2212-O₂ sample. This behavior is anomalous in a single band scenario. However, such an outcome is speculated in the recent ARPES results for the $S(T)$ of overdoped Bi-based cuprates in particular and others in general.¹⁶ On the other hand in case of overdoped YBCO (YBa₂Cu₃O₇) the observation of positive $S(T)$ is discussed in terms of two band (Cu–O chain and plane) contributions. For Bi and Tl-based cuprates the two band model was applied considering the Bi–O to be electron (e) type layer and the Cu–O₂ planes as the hole (p)-type.^{29,30} The idea originated from the band structure calculations,^{31,32} indicating that Bi–O bands above the Fermi level dip down to form pockets resulting in conduction. These models were applied and could explain some of the $S(T)$ data for Bi (Refs. 20 and 30) and Tl (Ref. 29) based cuprates. However with

this model, interestingly if Bi–O/Tl–O e-type layer dominates, the $S(T)$ may become $-ve$, and could stem out in Hall (n_H) measurements as well. This type of fitting of data i.e., $-ve S(T)$ and $n_H(T)$ based on classical two band model (e-type Bi/Tl–O and p-type Cu–O₂) has not yet been realized. Another draw back is that the classical two-band model could not explain the resistivity ($R-T$) data. Though the intriguing normal state physical properties of HTSc are yet a challenge to scientific community, the $S(T)$ can be well explained on the basis of van Hove singularity in particular for Bi-based cuprates.¹⁶ Further the same corroborates the ARPES findings in general.

Very recently Kaminski *et al.*¹⁸ reported detailed ARPES studies and concluded that for heavily overdoped Bi2212 system, the antibonding sheets become electronlike. It is shown that for number of holes per Cu–O plane in excess of 0.22, a crossover from hole to electron conduction takes place. In case of (Bi,Pb)₂(Sr,La)₂CuO₆, simultaneous ARPES and $S(T)$ were performed by Kondo *et al.*¹³ and the thermopower data were fitted from positive to negative spectrum for underdoped to overdoped samples. The recent ARPES studies^{13,18} have clearly predicted the negative $S(T)$ behavior for the heavily overdoped samples as has been observed in the present studies for the longer hours O₂ annealed overdoped Bi2212 samples. The primary cause for such a behavior was predicted quite some time back by McIntosh and Kaiser¹⁶ in terms of a van Hove singularity in the electronic density of states of HTSc cuprate superconductors.

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