

Oxygen Stoichiometry and Surface Treatment Effect on Electromigration Stability of High- T_c $Tl_2Ba_2CuO_{6+x}$ Superconductor

V.V. Dyakin, V.S. Yefanov, M.A. Tanatar, A.I. Akimov, and A.P. Chernyakova

Electromigration stability of $Tl_2Ba_2CuO_{6+x}$ ceramics is shown to decrease significantly when the material is treated in water vapor atmosphere. The T_c decrease in these samples is accompanied by a resistance increase, while the Seebeck coefficient, S , remains unchanged. The authors conclude that the main effect comes from grain-boundary degradation under the water vapor treatment. For initial samples, electromigration stability strongly depends on the sample oxygen doping level and increases for materials with higher oxygen content. The effect is assumed to be due to the filling of interstitials in Tl-O layers by oxygen atoms.

Keywords

electromigration, high-temperature superconductors, stability

1. Introduction

OXIDE high- T_c superconductors are known to be metastable compounds and to degrade quickly under the influence of ambient factors—primarily water vapor and carbon dioxide, different chemical reagents, and thermal cycling (Ref 1, 2). Rajan et al. (Ref 3) have shown that the compounds may degrade under long-term high-density current flow as well, and the phenomenon of electromigration was shown to proceed even under superconducting current (Ref 4). Recently, Mitin et al. (Ref 5) have shown that an electromigration treatment at the liquid nitrogen temperature allows the T_c of the compound $Tl_2Ba_2CuO_{6+x}$ to be increased significantly.

It is known that at low temperatures ($T < 0.5T_m$, where T_m is the melting point of the material) the main mechanism for atom movement in metals is grain-boundary migration (Ref 6). Therefore, it is of interest to study the effect of grain-boundary treatments on the electromigration process in high- T_c oxide superconductors.

This article reports on electromigration studies in $Tl_2Ba_2CuO_{6+x}$ compound at room temperature. This compound was chosen because of (1) the very high sensitivity of its T_c and normal-state properties to oxygen stoichiometry (Ref 7, 8), (2) the possibility of obtaining oxygen-overdoped materials with bipolar conductivity and thus of studying possible electron wind effects, and (3) the lack of vacancies in the Tl-O layers, in contrast to $YBa_2Cu_3W_{7-x}$. The presence of the vacancies is known to promote accelerated ion movement in solids (Ref 9), so it can be assumed that their presence can support accelerated degradation of these materials.

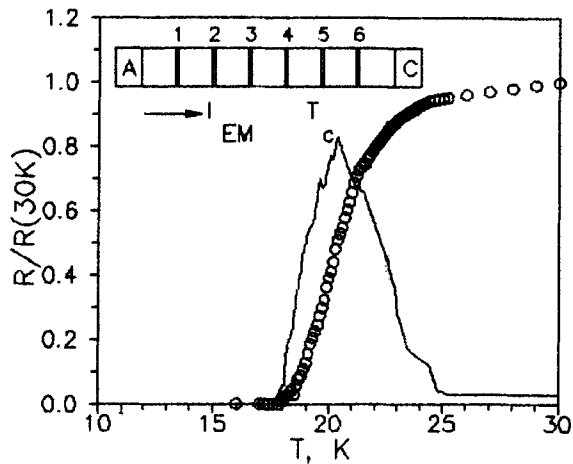
V.V. Dyakin, V.S. Yefanov, and M.A. Tanatar, Institute of Surface Chemistry, Ukrainian Academy of Sciences, 252650 Kiev, Ukraine; A.I. Akimov and A.P. Chernyakova, Institute of Solid State and Semiconductor Physics, Belorussian Academy of Sciences, 220726 Minsk, Belarus.

2. Experimental Method

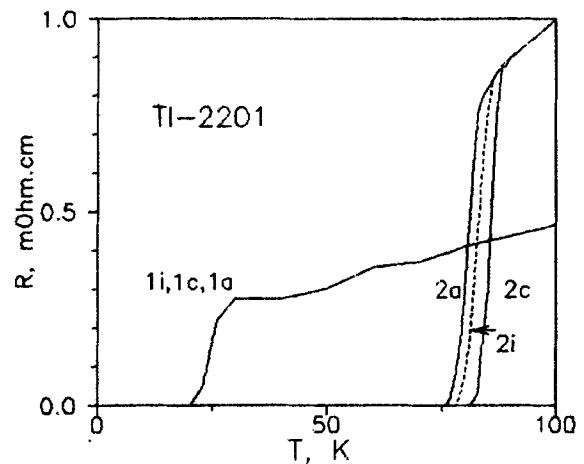
High-density ceramics obtained by a two-stage solid-state reaction were used in the studies. The samples were obtained by mixing $BaCO_3$ and CuO in a 2:1 molar ratio and sintering the mixture at 1123 K in air for 2 h. This precursor was ground, mixed with Tl_2O_3 in a 1.4:1 molar ratio, pressed into pellets 16 to 20 mm in diameter, and sintered at 1123 K for 8 h in an oxygen flow (Ref 10). Sample bars with dimensions of nearly 10 by 0.5 by 1 mm were saw cut from the pellets and then ground to the typical 10 by 0.3 by 0.1 mm dimensions used in the studies.

Eight ohmic indium contacts were alloyed by an ultrasonic soldering procedure along the sample length; contact resistances were typically below 0.1 Ω (see the inset in Fig. 1a). Resistance (R) measurements were performed by passing constant probe current (usually 1 mA) through the outer pair of contacts (A and C, Fig. 1a) and measuring the voltage drops between the pairs of inner contacts: 1 and 2, 2 and 3 ..., 5 and 6 (R_{12} , R_{23} ..., R_{56} , respectively). As is typical in resistance measurements, probe current direction was reversed and the values obtained were averaged. Resistance temperature dependences were measured by programmed cooling of a sample at typical rates of 1 K/min down to the liquid nitrogen temperature and 0.1 to 0.2 K/min down to the liquid helium temperature. The value of T_c was determined as a point of the maximal derivative dR/dT value (Fig. 1a). Reproducibility of the $R(T)$ curves for different parts of the samples shows that it can be estimated to be the same within ± 0.2 K throughout the sample length.

Four sample types were used in the studies. As-grown samples (1i) had superconducting transition temperatures, T_c , of 20 ± 0.5 K. To obtain higher T_c , some as-grown pellets were annealed at 620 to 670 K for 6 to 12 h in an argon ambient. The best samples obtained (labeled 2i) had T_c values of 82 ± 0.5 K (Fig. 1b). Resistivity, ρ , for both samples was in the range of 1 to $3 \times 10^{-3} \Omega \cdot \text{cm}$. Some of the 1i and 2i samples, after alloying contacts, were treated in saturated water vapor ambient at room temperature for 48 h. Before this treatment, a vessel with the sample was evacuated to remove residual carbon dioxide. After removal from the vessel, the sample was dried by heating at 373 K in vacuum for 15 min. The samples obtained (labeled H1i and H2i for 1i and 2i, respectively) had the same T_c as the initial



(a)



(b)

Fig. 1 (a) Typical resistance versus temperature curves for $Tl_2Ba_2CuO_{6+x}$ sample 1i (circles) and its derivative (solid curve), showing a technique of the T_c determination. Inset shows contact geometry used in the electromigration studies. (b) $R(T)$ curves for samples of $Tl_2Ba_2CuO_{6+x}$ (1) as grown and (2) heat treated in argon ambient at 670 K. The notations *i*, *c*, and *a* refer to initial samples and to the cathode and anode regions of current-treated samples, respectively.

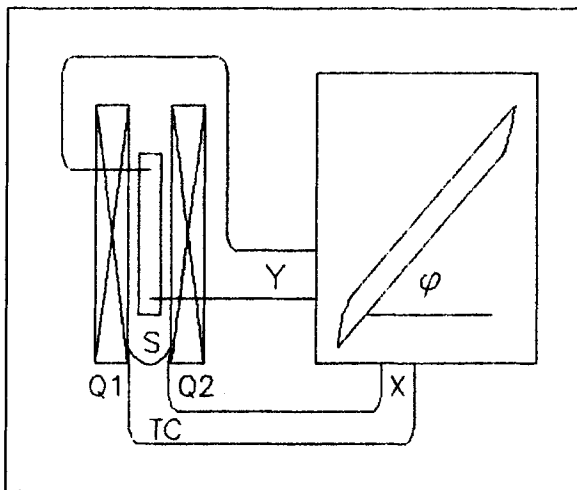


Fig. 2 Block diagram of the setup used for thermopower measurements. Q1 and Q2, quartz blocks; TC, copper-constantan differential thermocouple; X and Y, X and Y inputs of the plotter

samples, but their resistivity was higher (typically by 5 to 10%).

To study the effect of current flow on sample properties, a direct current of 0.2 to 2 A—called electromigration (EM) current hereafter—was passed through the sample in the direction from the anode (A) to the cathode (C) (Fig. 1a). The voltage drop at the inner contacts was controlled, and EM current was regulated in such a way that the sample temperature increase, determined from the resistance change, was always below 10 K. Periodically, EM current was switched off and $R(T)$ curves were measured on different parts of the sample. Resistances for

parts of the samples lying close to the A and C current leads (namely, 1 and 2, and 5 and 6, respectively) were found to change most significantly during current flow and are discussed hereafter as the anode (a) and cathode (c) regions of the samples, respectively.

Electron probe microanalysis (EPMA) of the samples was performed using a JCA-733 (JEOL Japan) analyzer at a probe voltage 15 kV. Metallic thallium and $YBa_2Cu_3O_{7-x}$ single crystals were used as standards for thallium and for barium and copper determination, respectively. The composition of the ceramics was measured by using a large electron beam spot (50 μ m in diameter) at three different points of the sample surface and averaging the results. The data were represented as relative changes of sample composition with respect to untreated sample 1i. The accuracy of this relative element determination was estimated to be $\pm 5\%$.

Seebeck effect, *S*, studies were performed using an alternating gradient technique (Ref 11) on the initial samples and on parts of the samples cut after the electromigration treatment from the sample bar—an anode region (a), lying between contacts 1 and 2, and a cathode region (c), lying between contacts 5 and 6. Temperature gradients were created by heating one of the quartz bars (Q1 and Q2, Fig. 2) and were transmitted to the sample (S) through a 100 μ m diam gold wire. The value of the temperature gradient was measured with a copper-constantan differential thermocouple (TC) with a sensitivity of α . The voltage signals from the sample and the thermocouple were supplied to an X-Y plotter, and the loop was drawn by alternating heating of the quartz bars. The Seebeck coefficient, *S*, was determined from the slope (angle ϕ , Fig. 2) of the linear part of the loop, according to:

$$S = \alpha \times \tan \phi - S_{\text{gold}} \quad (\text{Eq 1})$$

where t_g is tangent and the values of S_{gold} were taken from the literature (Ref 12). The apparatus was calibrated with a 99.99% pure lead sample. The relative accuracy of the S measurements was estimated to be $\pm 0.1 \mu\text{V/K}$.

3. Results and Discussion

The electrical current flow (current density j below 3 kA/cm^2) leads to significant changes in sample properties (Table 1). The most interesting effect is the increase in T_c up to 2.5

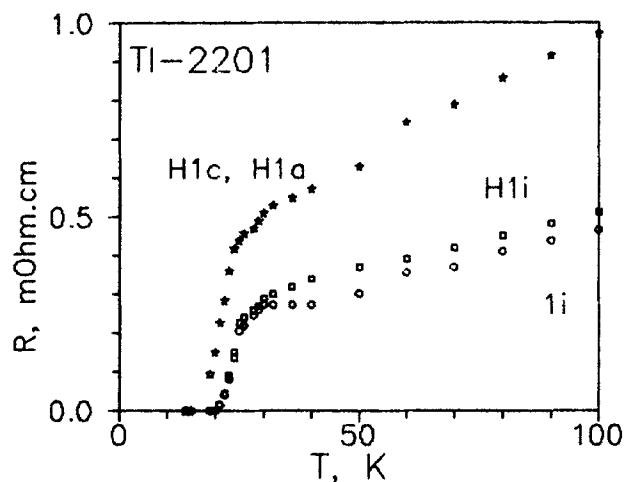


Fig. 3 Resistance versus temperature curves for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+x}$ sample 1: as grown (1i), after water vapor treatment (H1i), and after EM current treatment (H1c and H1a)

K at the cathode (R_{56} , 2c, Fig. 3) and its decrease by nearly the same amount near the anode (R_{12} , 2a, Fig. 3) after passing an electrical charge, Q , of $10 \times 10^6 \text{ C/cm}^2$ through the sample 2i, similar to the results of Mitin et al. (Ref 5). For the sample H2i, the resistivity increases homogeneously along the sample length at a rate of $10^{-10} \Omega \cdot \text{cm/cm}$, and T_c decreases by 2 to 2.5 K after passage of 10^6 C/cm^2 (Fig. 3, curves H2a, H2c) and by almost 6 K for $10 \times 10^6 \text{ C/cm}^2$. At the same time, changes in T_c for sample 1i after passage of $10 \times 10^6 \text{ C/cm}^2$ charge never exceeded 0.5 K; for the water-vapor-treated sample, H1i, a monotonous T_c decrease and resistivity increase were found. Reference samples of 1i, 2i, H1i, and H2i shows changes in neither resistivity nor T_c when stored for the time of electromigration treatment, allowing us to ignore degradation of the samples due to the ambient effect during storage.

To study the origin of T_c changes, the chemical composition along the length of the samples was studied by means of the EPMA technique (see Table 1). The results show that concentrations of the heavy atoms (thallium, barium, and copper) remain unchanged within experimental uncertainty for all four sample types. Because the oxygen content is rather difficult to determine with sufficiently high accuracy in this experiment, it was estimated qualitatively by using the room-temperature Seebeck coefficient, S . The S value in the cathode region increased from 2.7 to 3.5 $\mu\text{V/K}$. This increase is typical for the decreased oxygen doping level in the materials due to the lower oxygen content (Ref 8). In the anode region of the sample, S decreased to 2.3 $\mu\text{V/K}$, suggesting a higher oxygen doping level. For the other samples, the S value generally was unchanged.

The results obtained show that for the water-vapor-treated samples, the decrease in T_c and the increase in resistance are typical, although S remains unchanged. This behavior may be related to the degradation of the sample grain boundaries, not

Table 1 Parameters of the electrical current treatment and changes in the $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+x}$ sample properties and chemical composition

Sample type	N	$j, \text{kA/cm}^2$	$Q, \text{MC/cm}^2$	$\rho, \text{m}\Omega \cdot \text{cm}$	T_c, K	$S, \mu\text{V/K}$	Relative units		
							Tl	Ba	Cu
1i		1.2	20.2	-2.2	1.00	1.00	1.00
1c	1	1.2	1	1.2	20.2	-2.2	1.02	0.98	0.98
1c	2	1.2	10	1.1	20.2	-2.2	1.03	1.02	1.03
1c	3	2	10	1.1	20.4	-2.3	0.97	0.96	1.04
1a	1	1.2	1	1.2	20.2	-2.2	1.03	1.02	1.02
1a	2	1.2	10	1.1	20.2	-2.2	1.05	1.03	1.05
1a	3	2	10	1.1	20.1	-2.1	0.98	0.98	0.97
2i		2.5	83.5	+2.7	1.00	1.00	1.00
2c	1	1.5	1	2.5	84.5	+2.9	0.98	1.02	1.02
2c	2	1.5	3	2.6	85.2	+3.2	0.98	1.03	1.03
2c	3	1.5	10	2.6	86.0	+3.5	0.96	1.04	0.98
2a	1	1.5	1	2.5	83.0	+2.5	0.97	1.05	0.97
2a	2	1.5	3	2.5	82.5	+2.4	0.98	1.03	1.03
2a	3	1.5	10	2.4	82.0	+2.3	1.00	0.97	1.00
H1i		1.3	20.2	-2.2	1.03	0.98	1.03
H1c	1	1.4	1	1.5	19.0	-2.2	1.04	1.02	1.05
H1c	2	1.4	10	2.1	17.0	-2.2	0.98	0.98	0.97
H1a	1	1.4	1	1.7	18.7	-2.2	0.97	0.98	0.98
H1a	2	1.4	10	2.0	17.4	-2.2	1.02	1.04	0.97
H2i		2.7	83.4	+2.5	0.96	1.04	1.00
H2c	1	2.2	1	3.5	82.2	+2.5	0.97	0.98	1.02
H2c	2	2.2	10	5.1	78.0	+2.5	0.98	1.03	0.98
H2a	1	2.2	1	3.7	81.7	+2.5	0.95	1.03	1.03

the grains. Increased resistance of the samples after vapor treatment is strong evidence that some perturbations of the grains take place, probably promoting further sample degradation at the grain boundaries.

From the untreated samples we can conclude that, as a result of the EM current treatment, oxygen atoms migrate from the cathode toward the anode—in accordance with the oxygen anion negative charge, but contrary to the electron hole flow direction in the material. This may suggest that the electronic wind phenomenon is not of prime importance for such layered compounds, in contrast to organic conductors such as $\text{ET}_3\text{Ag}_x\text{I}_8$ (Ref 13). Strong dependence of the effect on the grain-boundary treatments allows us to conclude that an important role may be played by local overheating in the weak intergranular links and/or the creation of nucleation centers for new phase formation by the adsorbed water molecules. The same may be evidenced by the much larger effects observed in the $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+x}$ compound cooled to the liquid nitrogen temperature (Ref 5), because much higher current densities were used in these experiments.

Acknowledgment

The authors acknowledge the support of Ukrainian Scientific Council, Project “Veter.”

References

1. A. Ono, S. Takenouchi, and Y. Ishizawa, *Jpn. J. Appl. Phys.*, Vol 30, 1991, p L464-L467

2. K.D. Vernon-Parry, L.T. Romano, J.S. Lees, and C.R.M. Grovenor, *Physica*, Vol C170 (No. 1), 1990, p 388-394
3. K.C. Rajan, P. Parameswaran, J. Janaki, G.V.N. Rao, and T.S. Radhakrishna, *Bull. Electrochem.*, Vol 5 (No. 10), 1989, p 761-763
4. A.M. Prokhorov, Yu.M. Gufan, A.Ye. Krapivka, Ye.N. Lubnin, G.N. Mikhailova, Ye.G. Rudashevskii, A.S. Seferov, V.N. Sumarokov, V.A. Tarasenkov, and A.G. Chistov, *J. Exp. Theoret. Phys. Lett.*, Vol 51 (No. 2), 1990, p 132-134
5. A.V. Mitin, N.E. Alekseevski, and E.P. Khlybov, *Physica*, Vol C199 (No. 2), 1992, p 351-355
6. P.S. Ho and T. Kwok, *Rep. Prog. Phys.*, Vol 52 (No. 3), 1989, p 301-348
7. J.B. Parise, C.C. Torardi, M.A. Subramanian, J. Gopalakrishnan, A.W. Sleight, and E. Prince, *Physica*, Vol C159, 1989, p 239-244
8. M.A. Tanatar, V.V. Dyakin, V.S. Yefanov, A.I. Akimov, and A.P. Chernyakova, *Physica*, Vol C185-189 (Part 2), 1991, p 1247-1248
9. J.B. Boyce and B.A. Huberman, *Phys. Rep.*, Vol 51 (No. 4), 1979, p 189-200
10. A.I. Akimov, B.B. Boiko, V.I. Gatalskaya, S.E. Dem'yanov, A.L. Karpey, L.A. Kuruchkin, Yu.N. Leontovitch, L.P. Poluchankina, Ye.K. Stribuk, I.M. Starchenko, L.Z. Avdeev, O.V. Snigirev, S.V. Bogachev, M.M. Gaidukov, and A.M. Klushin, *Superconductivity Phys. Chem. Technol.*, Vol 2 (No. 1), 1989, p 41-48 (in Russian)
11. P.M. Chaikin and J.F. Kwak, *Rev. Sci. Instrum.*, Vol 46 (No. 2), 1975, p 218-223
12. R.P. Huebener, *Phys. Rev.*, Vol 135 (No. 5A), 1964, p A1281-A1284
13. V.A. Bondarenko, K.I. Pokhodnia, Yu.V. Sushko, and M.A. Tanatar, *Synthetic Met.*, Vol 41-43, 1991, p 2221-2224