OXYGEN ION CONDUCTIVITY IN DYNAMICALLY COMPACTED YBa$_2$Cu$_3$O$_{7-x}$

N.J. Kiwiet*†, J. Schoonman*, A.C. van der Steen‡,
H.H. Kodde‡, M.A. Schrader‡

*Laboratory for Inorganic Chemistry, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, the Netherlands
‡Institute of Applied Chemistry, TNO, Zeist, the Netherlands
‡Prins Maurits Laboratory, TNO, Rijswijk, the Netherlands

ABSTRACT

Powders of YBa$_2$Cu$_3$O$_{7-x}$ are densified with high pressure dynamic compaction to 93% TMD. The microstructure and electrical properties of the compacted material are investigated by SEM and impedance spectroscopy. The bulk oxygen ion conductivity is studied using a solid state electrochemical cell (O$_2$)/Pt / YSZ / YBa$_2$Cu$_3$O$_{7-x}$ / YSZ / Pt(O$_2$), as a function of temperature (400 - 800°C), over the frequency range of 1 to 65,000 Hz.

INTRODUCTION

At temperatures above 300 °C YBa$_2$Cu$_3$O$_{7-x}$ is both an electronic as well as an ionic conductor. The conductivity of YBa$_2$Cu$_3$O$_{7-x}$ is a function of the types of defects present, the oxygen ordering in the crystal lattice, as well as the porosity, grain size, and grain boundaries. Most commonly YBa$_2$Cu$_3$O$_{7-x}$ has been prepared by conventional methods of pressing and sintering. In this work preliminary results on the characteristics of dynamically compacted YBa$_2$Cu$_3$O$_{7-x}$ are

Superconductivity 683
In dynamic compaction an explosion generates a high pressure shock wave which passes through the sample. With a single step densities very close to the theoretical maximum density (TMD) are achieved. For ceramics dynamic compaction can cause fracturing and plastic deformation of the crystals. The frozen microstructure of the post shock sample can add unique properties to the material. An excellent review of the recent achievements in shock induced material synthesis can be found in reference 1. Recently there has been an interest in utilizing dynamic compaction to prepare compressed monolithic forms of the new high temperature superconductors (2,3). The purpose of this work was to investigate the effect of dynamic compaction upon the electronic and ionic conductivity of YBa$_2$Cu$_3$O$_{7-x}$.

**EXPERIMENTAL**

The YBa$_2$Cu$_3$O$_{7-x}$ powder was synthesized by calcining a mixture of Y$_2$O$_3$, BaCO$_3$, and CuO at 950°C for 22 hours, this process was repeated three times. The cylindrical technique was used to compact the powder. Before dynamic compaction the YBa$_2$Cu$_3$O$_{7-x}$ powder was statically pressed in a steel cylindrical tube (i.d. = 10 mm, o.d. = 12 mm, L = 120 mm) to 70 % TMD (4.480 g/cm$^3$). A second PVC cylinder (i.d. = 42 mm, o.d. = 50 mm, L = 175 mm) containing the explosive was placed around the sample cylinder. The explosive was Trigonite, which is a mixture of ammonium nitrate, aluminum and TNT. Trigonite has a detonation velocity of about 3.6 km/s resulting in a shock pressure of tens of GPa. After detonation the inner diameter of the tube was reduced to 8.68 mm indicating a density of 92.8 % TMD (5.940 g/cm$^3$). Similar values for the density were confirmed through pycnometric measurements.

A dry diamond saw was used to cut 1-3 mm slices of the dynamically compacted sample. Before measurements the pellets were resurfaced by lightly grinding with 600 grit SiC paper. For the low temperature resistivity measurements 4 gold point contacts were sputtered onto the sample.

A solid state cell: (O$_2$)Pt / YSZ /YBa$_2$Cu$_3$O$_{7-x}$/ YSZ / Pt(O$_2$) was used for the high temperature conductivity measurements (where YSZ is 8 mol% yttria stabilized zirconia purchased from GIMEX). The YSZ pellets were 12 mm in diameter and 0.5 mm thick. Both sides of the YSZ pellets were polished.
to a mirror finish with 6 micron diamond paste. A thin layer of platinum was sputtered on one side of each YSZ pellet. The platinum layer was made porous through high current aging.

A computer controlled Solartron 1250 Frequency Response Analyzer in combination with a 1286 Electrochemical Interface was used for impedance spectroscopy. Measurements were taken using a 20 mV AC signal over the temperature range of 400 to 800 °C and the frequency range of 1 to 65,000 Hz.

RESULTS

XRD: The x-ray diffraction patterns taken before and after dynamic compaction are shown in Figure 1. The pattern for the starting material confirmed the presence of the 1-2-3 composition possessing the orthorhombic phase. The cell parameters corresponded with literature values for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, where $x = 0.1$ (4). The oxygen content was also confirmed with high temperature controlled oxygen loss experiments measured under vacuum (5). After dynamic compaction there was no shift observed in the cell parameters (measured relative to a $\text{Al}_2\text{O}_3$ standard). Oxygen loss experiments, however, indicated a slight decrease in the oxygen content to a value of 6.8 (5).

The largest change observed in the x-ray patterns was in the relative peak heights of the $<103>$, $<110>$, and the $<013>$ reflections (2$\theta$ = 32°). From the literature it is known that for orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, where $x = 0$ the $<103>$ and $<110>$ reflections overlap in the x-ray spectra yielding a 2:1 peak ratio relative to the $<013>$ reflection. For tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ when $x=1$ the $<103>$ and the $<013>$ overlap yielding a 2:1 peak ratio relative to the $<110>$ (4). Although in both x-ray patterns the peaks are poorly resolved it is clear that after dynamic compaction the relative peak heights change. A similar distortion is observed at 2$\theta$ = 58°. The x-ray patterns suggest a loss of orthorhombicity. Most likely through dynamic compaction the oxygen becomes disordered resulting in a slight distortion of the orthorhombic unit cell.

Morphology: Scanning electron micrographs were taken before and after dynamic compaction. From the SEM's the particle size of the starting material was estimated to vary between 1 - 10 microns. After shock wave treatment the sample is nearly ideally compacted. The grain structure has disappeared and hardly any cavities are observed. Macroscopically only a few small cracks were observed. These cracks extended radially from the center of the cylinder. Experiments are currently in progress with different

Superconductivity 685
explosives to minimize radial cracking.

**Electronic Conductivity:** The low temperature resistivity behavior is shown in Figure 2. It is clear that shock treatment converts the expected superconducting behavior to semiconducting behavior. A slight lowering of the resistance occurred at 94 K. Upon heating and cooling there was very little hysteresis observed in these measurements. A dip in the resistance curve always appeared in the 90 - 94 K range. Although the dynamically compacted \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) did not display a superconducting transition it was observed to have diamagnetic properties. The observation of the Meissner effect as well as the dip in the resistance curve at 94 K confirm the presence of superconducting \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \). The semiconducting behavior observed in the resistivity measurements is indicative that there is no superconducting path present. The loss of transport superconductivity is most probably related to the loss of orthorhombicity.

** Ionic Conductivity:** The ionic transport was studied using the solid state electrochemical cell: \((\text{O}_2)\text{Pt} / \text{YSZ} / \text{YBa}_2\text{Cu}_3\text{O}_{7-x} / \text{YSZ} / \text{Pt(O}_2)\). Here the ionically reversible \( \text{Pt(O}_2) / \text{YSZ} \) electrodes serve to block electronic carriers allowing for the ionic transport in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) to be independently measured. A typical example of the impedance spectrum for this cell is shown in Figure 3. The best fit of the impedance data was obtained with the equivalent circuit shown in Figure 4. Here \( R_2 \) represents the bulk resistance of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \), \( Q \) is the capacitive element associated with the \( \text{YSZ} / \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) interface, and \( R_1 \) the resistance of that interface. The YSZ electrodes used in these experiments had a negligible influence on the impedance data. From \( R_2 \) the resistance corresponding to the ionic motion in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) is obtained. An Arrhenius plot of \( \log (\sigma_1) \) vs \( 1/T \) is shown in Figure 5. For comparison the data obtained through similar measurements on a pressed and sintered pellet of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) are also shown. From the x-ray data and resistivity measurements it is clear that the structure of the dynamically compacted sample is different from statically pressed \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \). Thus, a simple comparison between the two samples cannot be made.

If the difference in conductivity between the two samples was simply due to a difference in porosity (i.e. surface area)
one would expect a higher conductivity with decreasing porosity (6). Although the dynamically compacted sample has a lower porosity the measured conductivity is an order of magnitude less than the statically pressed sample. Thus the difference between the two samples cannot be attributed to differences in surface area.

The activation energy for oxygen ion conductivity is only slightly greater in the dynamically compressed sample. Considering the limits of experimental error (±10%) not much weight is given to this observation. Although the activation energy is similar the conductivity is an order of magnitude less for the dynamically compacted sample, indicating a much lower concentration of mobile charge carriers. Possibly upon dynamic compaction a portion of the oxygen ions become trapped resulting in a much lower conductivity.

CONCLUSIONS

It has been observed that shock treatment of YBa$_2$CuO$_{7-x}$ results in a slight distortion of the orthorhombic unit cell. This structural change converts the expected superconducting behavior to semiconducting behavior. Although a superconducting transition is not observed the sample does display diamagnetic properties. The ionic conductivity of the shock treated sample was found to be an order of magnitude less than that of a statically pressed and sintered sample. It is suggested that dynamic compaction distorts the oxygen ordering in YBa$_2$CuO$_{7-x}$ resulting in changes in both the electronic and ionic conductivity of the sample.

Acknowledgment: We thank D.K. Dijkken for preparing the YBa$_2$CuO$_{7-x}$ powder and performing the high temperature oxygen loss experiments. Appreciation is also given to J. S. Swinnea for helpful comments on the x-ray data.

REFERENCES


Figure 1: X-ray data of: a) starting material, b) dynamically compacted sample.
Figure 2: Low temperature resistivity measurements for the dynamically compacted sample.

Figure 3: Impedance spectrum for the cell: \( (O_2)_{Pt} / YSZ / YBa_2Cu_3O_{7-x} / YSZ / Pt(O_2) \) taken at 890 K in \( O_2 \).
Figure 4: Equivalent circuit used to fit impedance data.

Figure 5: Arrhenius plot of the ionic conductivity of YBa$_2$Cu$_3$O$_{7-x}$: sintered sample (TMD = 89 %), dynamically compacted sample (TMD = 93 %).