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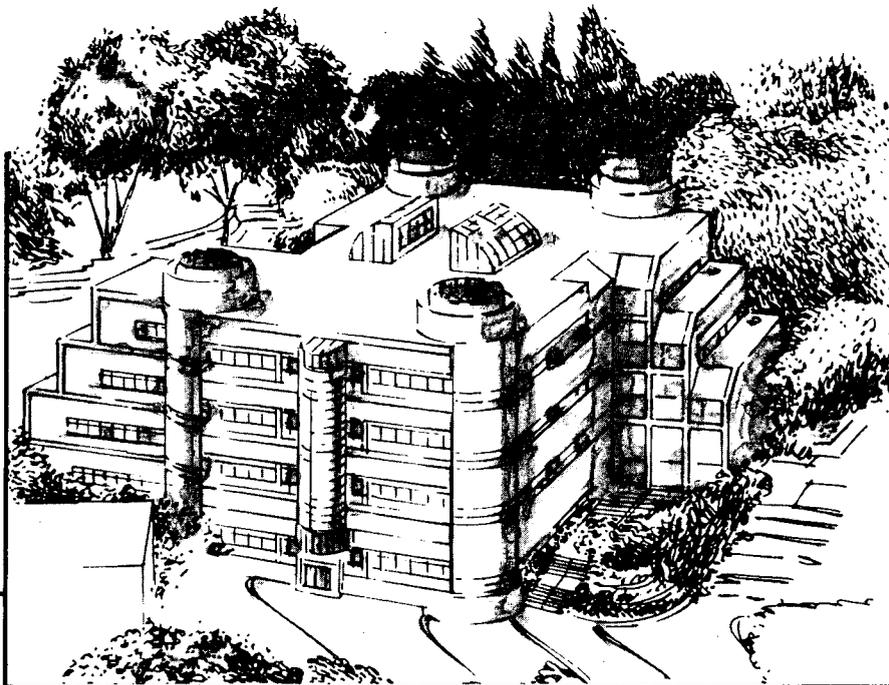
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**Oxidation Kinetics  
in Superconductors**

T.J. Richardson and

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**Materials and Chemical Sciences Division**  
**Lawrence Berkeley Laboratory • University of California**  
ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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OXIDATION KINETICS AND MICROCRACKING IN SUPERCONDUCTING

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  CERAMICS

Thomas J. Richardson and Lutgard C. De Jonghe

Center for Advanced Materials

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory

One Cyclotron Road

Berkeley, CA 94720

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## Abstract

The anisotropic expansion and contraction of crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) during thermal processing, oxygenation and cryo-cooling result in intra- and intergranular stresses that are largely relieved by microcracking. Acoustic emission signals produced during microcracking are qualitative and quantitative measures of the degradation in strength and electrical connectivity in a sintered ceramic. A method is described for detecting and evaluating acoustic emission generated within YBCO samples during processing. The intensity, onset temperature and duration of cracking during post-sintering cooldown depend upon the oxygen partial pressure. Sudden changes in oxygen pressure also induce cracking. The influence on cracking of sample porosity is also discussed.

## Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) undergoes a phase transition from a tetragonal, non-superconducting, oxygen-poor phase to an orthorhombic, superconducting, oxygen-rich phase during cooling through a transition temperature which is dependent upon the oxygen partial pressure. The transition occurs over a rather narrow range of oxygen stoichiometry and is accompanied by a strongly anisotropic lattice distortion (1,2). The uptake of oxygen is rapid at temperatures above  $400^\circ\text{C}$  (3), resulting in rapid dimensional changes as the transition takes place (4). In sintered polycrystalline samples the induced strain causes inter- and intra-grain cracking, visible in optical and electron micrographs. These cracks reduce the strength of the ceramic, its current-carrying capacity, and its resistance to environmental attack. Here we report preliminary results of an acoustic emission study of microcracking in YBCO.

## Experimental Details

The acoustic emission apparatus (shown schematically in Figure 1) consists of a sample holder enclosed in a tube equipped with gas flow controls. A piezoelectric sensor coupled to the sample by means of an acoustic waveguide converts the acoustic signals to voltages which are digitized and processed by the Acoustic Emission Technologies System 5000. The flow tube, sample holder, and waveguide are made of fused silica. A light spring maintains contact between waveguide and sample.

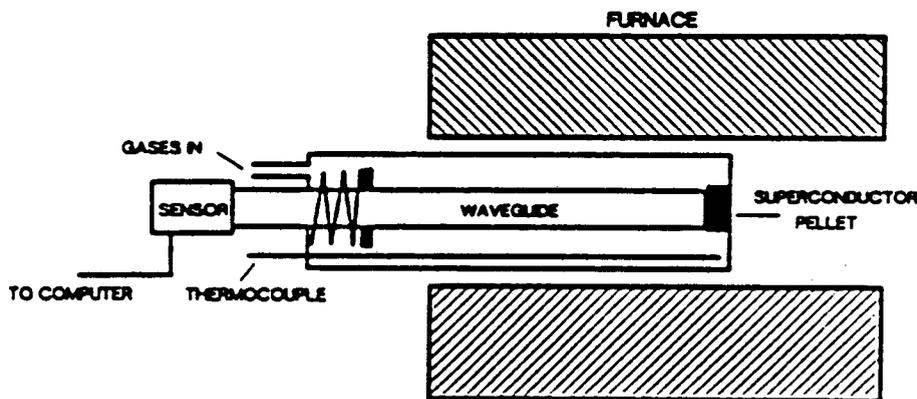


Figure 1 - Acoustic emission apparatus.

Uniaxially pressed powder compacts of YBCO with a relative green density of 67% were mounted in the apparatus, sintered at  $940^\circ\text{C}$  to a final density of 80-85% and cooled under carefully controlled conditions of temperature and oxygen partial pressure.

## Results

Sintering and cooling ( $50^\circ/\text{hour}$ ) in an atmosphere of pure argon resulted in a low and fairly constant level of emissions during the cooldown phase (Figure 2, upper trace). In air or in pure oxygen, however, a great deal of acoustic activity was observed during cooling (Figure 2, middle and lower traces). In air, intense cracking begins at about  $500^\circ\text{C}$ , peaks around  $400^\circ\text{C}$ , and continues down to about  $300^\circ\text{C}$ . In oxygen, the onset of cracking takes place at about  $600^\circ\text{C}$ , and the

temperature range of high cracking intensity is narrower.

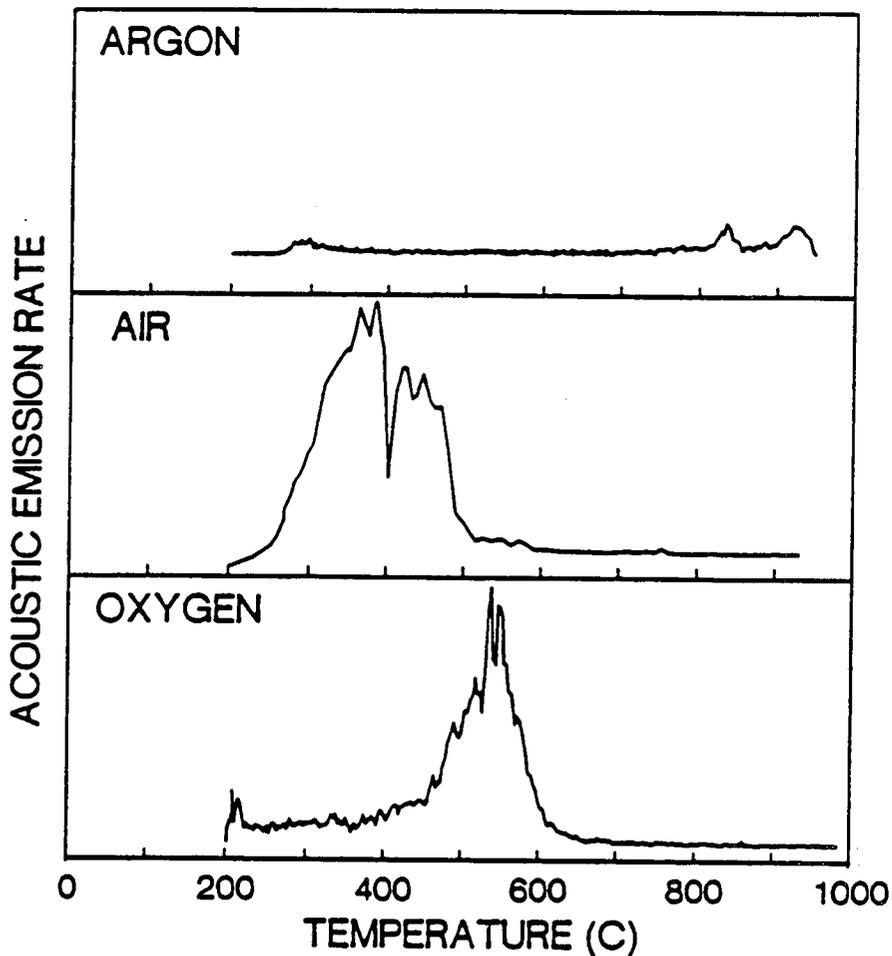


Figure 2 - Acoustic emission during cooling.

Further experiments, in which the  $O_2$  pressure was changed rapidly at constant temperature, show that cracking<sup>2</sup> also results from removal of oxygen from the ceramic, albeit at a lower intensity than for oxygen introduction. Typical data for a sample held at 600°C while the ambient gas was rapidly changed from oxygen to argon and back to oxygen are shown in Figure 3. The relative AE intensity for increasing vs. decreasing oxygen content is temperature dependent as are the absolute intensities. These observations are consistent with the known oxygen uptake/discharge kinetics of YBCO (3,4).

Cold isostatic pressing of the ceramic powder to a relative density of 76% followed by sintering and cooling in oxygen resulted in a final density of 90-92%. The intensity of cracking during cooling of these samples was not significantly different from that observed for porous samples. The more dense pellets reacted more slowly to rapid changes in  $O_2$  partial pressure at constant temperature, giving broader peaks for both oxygenation and deoxygenation. The integrated intensities of the cracking responses were, however, not reduced.

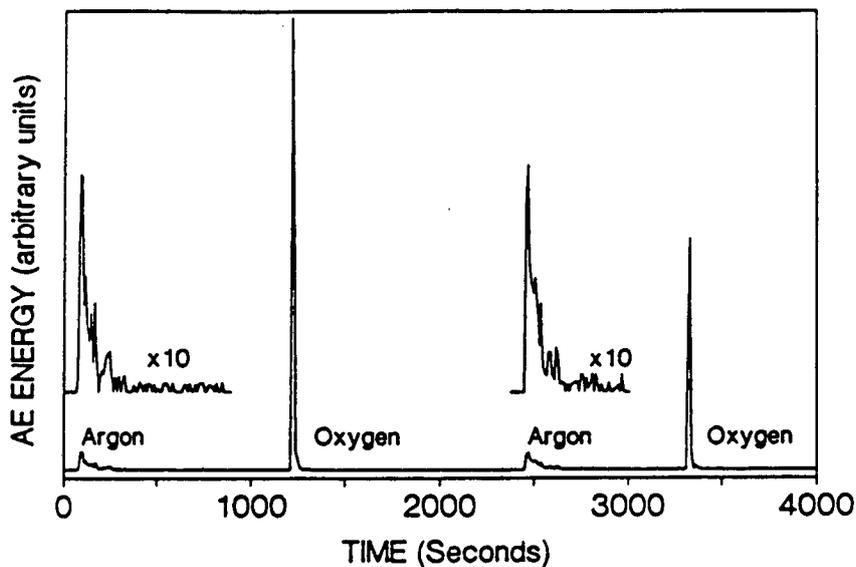


Figure 3 - AE due to rapid changes in oxygen partial pressure at 600°C.

### Discussion

By detecting and processing acoustic signals generated within the ceramic material during heat treatment and manipulation of oxygen partial pressures, a direct correlation has been found between oxygenation and microcracking. While it is not possible in experiments conducted at ambient pressure to completely separate cracking due to oxygenation stress and cracking due to anisotropic thermal contraction, the strong dependence of cracking behavior on oxygen partial pressure demonstrates the importance of oxygen uptake in the production of microcracking.

In order to minimize microcracking during ceramic superconductor processing, it is essential to avoid unnecessary changes in temperature or oxygen partial pressure. While the relationship between microstructure and cracking is not yet well-defined, it may be that a critical grain size exists, below which microcracking is greatly reduced.

Acoustic emission detection offers a unique means of determining the causes and extent of microcracking during ceramic processing. A comprehensive study of the effects of variations in processing parameters and composition on cracking in sintered YBCO and of the effects of cracking on critical current density is under way with the goal of reducing or eliminating cracking and mitigating its deleterious consequences.

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LAWRENCE BERKELEY LABORATORY  
CENTER FOR ADVANCED MATERIALS  
1 CYCLOTRON ROAD  
BERKELEY, CALIFORNIA 94720