LBL-29075
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Journal of Materials Research

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March 1990

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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LBL #29075

ACOUSTIC EMISSION STUDY OF MICROCRACKING IN 123-TYPE CERAMIC SUPERCONDUCTORS

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Submitted to: Journal of Materials Research

March 14, 1990

This work was supported by the Electric Power Research Institute and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the United States Department of Energy, under contract No. DE-AC03-76SF00098.

ABSTRACT

Acoustic emission from sintered ceramic $YBa_2Cu_3O_{7-x}$ (YBCO) superconductor pellets provides a direct measure of microcracking behavior during processing. By detection and statistical analysis of acoustic events, the effects of cooling rates, processing atmosphere, average grain size, additives and grain alignment on microcracking in YBCO have been studied. The onset temperature and duration of acoustic emission during cooling correlate well with the oxygen partial pressure in the furnace. Rapid changes in oxygen partial pressure at constant temperature produce acoustic emission that is characteristic of microcracking. A reported critical grain size for microcracking in sintered polycrystalline YBCO of about 1 μm has been confirmed. Two superconducting compounds, $YSrBaCu_3O_{7-x}$ and $LaBaCaCu_3O_{7-x}$, with the 123 structure but with smaller crystallographic anisotropy were also examined. Recommendations are made for minimizing microcracking during processing of superconducting ceramics.

I. INTRODUCTION

Large-scale practical applications of oxide superconductors require bulk materials with greatly improved current-carrying capacities. Critical current densities for sintered $YBa_2Cu_3O_{7-x}$ (YBCO) ceramics appear to be limited by intergranular resistances and percolation path density.[1-4] The anisotropic expansion and contraction of YBCO grains during thermal processing, oxygenation, and cryo-cooling result in intra- and intergranular stresses that are largely relieved by microcracking.[5-7] While considerable effort has been devoted to investigation of grain boundary phases, grain orientation alignment and densification processes, limited attention has been paid to the role of microcracking in limiting the critical current density in bulk YBCO samples. Acoustic emission impulses produced during initiation and growth of cracks are qualitative and quantitative measures of the degradation in connectivity developing in a sintered ceramic form.[8,9] Acoustic events produced by sintered ceramic superconductor pellets during processing under a wide range of conditions have been detected and subjected to statistical analysis with the goal of improving the current-carrying capacity of the polycrystalline materials.

The psuedo-perovskite crystal structure of the 123-type oxide superconductors is characterized by pairs of copper-oxygen sheets with full oxygen occupancy alternating with copper-oxygen planes with partial oxygen occupancy. The crystallographic dimensions vary considerably with oxygen content, which is a sensitive function of both temperature and oxygen partial pressure. At ordinary pressures, YBCO is semiconducting and tetragonal (with stoichiometry $YBa_2Cu_3O_{\approx 6.5}$ and $c/a = 3.041$) above about 600 °C. The material

is therefore in the tetragonal form during sintering, which takes place between 850 °C and the melting point (which also depends on oxygen partial pressure). The ceramic takes up oxygen, if available, as it cools, producing the superconducting, orthorhombic structure ($YBa_2Cu_3O_{\approx 7.0}$, a/b = 1.017, c/b = 3.048) due to preferential occupancy of oxygen sites in one crystallographic direction (i.e. along the b-axis). The thermodynamics and kinetics of this phenomenon have been the subject of a vast number of studies using a variety of techniques.[10-15] The rate of oxygen uptake is affected not only by temperature and pressure but also by grain size, porosity and the presence or absence of second phases (e.g. $BaCO_3$, Ag). The resulting dimensional changes (-1% in a, +0.5% in b, -0.5% in c, -1% in volume) create inter- and intragranular stresses in grains whose strain relief has been confined by the sintering and densification processes. In addition, the coefficients of thermal expansion in the b and c direction differ by a factor of four.[10] Very rapid oxygenation may also produce macroscopic tensile stress within the outer layer of a sintered form or individual grain as it contracts around the oxygen-deficient interior.

The acoustic emission technique is a powerful, direct, semiquantitative method for investigating the cracking behavior of brittle materials.[8,9] It has successfully been applied to studies of microcracking in ceramics induced by electrochemical transformation[16,17] and by thermal expansion anisotropy.[18] The acoustic emission associated with ceramic microcracking is a burst phenomenon, i.e., the individual events are of short duration (less than one millisecond). The resulting shock wave is detected by a piezoelectric transducer, which converts the vibrational motion into an electrical signal. The location of the initial event relative to the sensor, the geometry and

makeup of the sample and waveguide (if any), and the frequency response characteristics of the sensor all contribute to the intensity and shape of the output waveform.[19] An absolute determination of the nature and size of the initiating event is therefore not possible. By collecting data from a large number of events from samples of similar dimensions and composition under varying conditions, however, a statistical comparison of the onset parameters and extent of cracking may be made.

II. EXPERIMENTAL

A. Materials Synthesis

$YBa_2Cu_3O_{7-x}$ was prepared by the standard oxide route.[20] $YBaSrCu_3O_{7-x}$ was prepared by the method of Veal et al.[21] $LaBaCaCu_3O_{7-x}$ was prepared by the method of Peng et al.[22] The purity of the compounds was checked by x-ray diffraction at each stage of preparation and processing. YBCO powder was ball milled in acetone to an average particle size of about 10 μm. $YBaSrCu_3O_{7-x}$ and $LaBaCaCu_3O_{7-x}$ were hand ground to an average particle size of about 25 μm. Silver-YBCO composites containing 10% silver by weight were prepared by mixing Ag_2O (which decomposes to metallic silver below 450 °C[23]) with ball milled YBCO powder.

B. Spray Dried YBCO

Submicron YBCO powder was prepared by a combination of spray drying and flash pyrolysis. An aqueous stoichiometric solution of yttrium, barium and copper nitrates was spray dried using a Yamato Pulvis GB22 "Minispray" dryer to give an intimately mixed powder of anhydrous nitrates. The powder was placed in a silver boat and flash pyrolyzed in air at 750 °C for three

minutes. The nearly amorphous powder was then heated in flowing oxygen at 850 °C for two hours to give phase-pure YBCO with an average particle size of about 1 μm.

C. Grain Boundary modification

Experiments were carried out in an effort to improve the mechanical and electrical properties of polycrystalline YBCO by introducing various reagents at the grain surfaces before sintering. The purpose was to modify the structure, composition, and/or number of boundary phases by localized reactions. The compounds investigated included the chloride, bromide, fluoride, and nitrate of copper dissolved in acetonitrile; silver nitrate, sodium and potassium chlorides in isopropanol; and barium nitrate in water. YBCO pellets were bisque-fired in air at 600 °C for 1 h to leave them porous but sufficiently strong to survive treatment with the solutions. The pellets were soaked in saturated solutions of the salts for 15 min and dried in air at 90 °C. Sintering was carried out in oxygen at 950 °C.

D. Acoustic Emission

The superconductor specimens were held in a specially constructed jig (Fig. 1) made of fused silica. A light spring maintained contact between the ceramic pellet and an acoustic waveguide, also of fused silica. Gold foil protected the jig and waveguide from chemical attack by the superconductor at elevated temperatures. The atmosphere within the jig was controlled by passing gases through it at slightly above ambient pressure. The temperature was monitored by a chromel-alumel thermocouple positioned near the sample. Acoustic emissions originating in the sample were detected by a piezoelectric

sensor attached to the end of the waveguide by epoxy cement. The data were collected and analyzed using an Acoustic Emission Technologies System 5000 operating with a 125 kHz to 2 MHz bandpass filter and a detector threshold of 0.06 V. Background noise was minimized by isolation of the jig from the furnace walls with external teflon supports at each end. The noise level observed during repeated blank runs was always below 5% of the signal level from actual samples.

Two types of statistical data were accumulated during constant rate cooling: "events" vs. time and "ringdown counts" vs. time. An "event" begins when the sensor output voltage exceeds the assigned threshold voltage. The output voltage oscillates, reaching its peak voltage in a few microseconds, then decaying until it no longer exceeds the threshold voltage, at which time the event has ended. The number of times the threshold voltage is crossed in the positive (increasing) direction during the event is the "ringdown count" for that event. Since larger events result in a greater number of ringdown counts, the ringdown count total is a relative measure of the magnitude of the microcracking from which the signals originate.

With the exception of the hot-forged pellets, all samples were sintered in the acoustic emission jig. Pellets 9.2 mm in diameter weighing 1.0 g each were pressed uniaxially at 100 MPa, then isostatically at 1300 MPa, resulting in green densities of about 70% of theoretical. The YBCO pellets were heated in flowing oxygen to 950 °C at a rate of 300 °C/h, held at 950 °C for four hours, and then cooled at constant rates in the appropriate atmosphere. The pellets of $YBaSrCu_3O_{7-x}$ and $LaBaCaCu_3O_{7-x}$ were sintered at 975 °C in oxygen, then cooled at 50 °C/h as for YBCO. Below 200 °C, cooling rates of 50 °C/h or greater were not possible. Very little acoustic emission was, however,

observed for any sample in this temperature regime, and its contribution to the total emission count is negligible.

E. Critical Currents

Critical current measurements were carried out at 77 K on bar-shaped samples cut from pellets. Silver electrode pads were evaporated in a four point pattern onto carefully cleaned surfaces, after which the bars were annealed at 500 °C for 1 h and cooled slowly in oxygen. Current and voltage leads were attached using In-10%Ag solder. V-I curves were obtained using a computer-controlled direct current source operating with a duty cycle of 20% (to minimize resistive heating of the contacts) and a voltage criterion of 1 μV/cm. Considerable dependance of critical current density on sample cross sectional area was observed. Comparisons were therefore made on specimens with 1 mm x 1mm cross sectional dimensions.

III. RESULTS

A. Oxygen Partial Pressure during Cooling

YBCO pellets, sintered in oxygen, were cooled at a rate of 50 °C/h in atmospheres of different oxygen content. The results for pure oxygen are shown in Fig. 2(a). Each point represents the accumulated ringdown count total for events occuring in a three minute period during which the temperature dropped 2.5 °C. The onset of intense acoustic emission corresponds with the tetragonal-to-orthorhomic phase transition, which occurs above 650 °C for an oxygen partial pressure of 1 atm.[10] The emission peaks sharply around 600 °C then falls off rather rapidly, becoming negligible below 300 °C. The acoustic emission curve for a pellet sintered in oxygen

but cooled in an atmosphere of dry, CO_2-free air [Fig. 2(b)] exhibits a slightly lower onset temperature and emission over a broader temperature range. The total ringdown count for cooling from 950° to 200 °C (Table I) is approximately the same for the two samples cooled in oxygen-containing atmospheres. In dry argon (O_2 concentration < 1 ppm), however, the transition and its accompanying emission pattern are largely absent [Fig. 2(c)]. The pellets were examined by scanning electron microscopy (SEM). Intergranular and transgranular microcracks (Fig. 3) were readily visible in the oxygenated pellets, while they were nearly absent in the argon-cooled sample.

B. Changes in Oxygen Partial Pressure

To investigate the effects of sudden changes in oxygen partial pressure, YBCO pellets were sintered in oxygen, then cooled to various temperatures and held at constant temperature while the oxygen content of the ambient atmosphere was rapidly changed. At 600 °C, the acoustic emission responses (Fig. 4) to sudden switching from 1 atm of oxygen to 1 atm of argon and from argon to oxygen are immediate and intense. The behavior in each case is remarkably reproducible. Whereas the response to deoxygenation takes place at a slowly decaying rate over a period of several minutes, with some minor emissions even after 20 minutes, the response to the introduction of oxygen into deoxygenated YBCO is very sharp, with a few minor "aftershocks" followed by nearly total quiescence. The relative integrated intensities for oxygenation- vs. deoxygenation-induced microcracking depend strongly on temperature (Fig. 5). SEM examination of fracture surfaces of pellets subjected to repeated oxygen-argon cycling (Fig. 6) revealed a large

accumulation of debris in the pores, presumably due to exfoliation of the rapidly contracting surface.

Increasing the oxygen partial pressure gradually from zero to 1 atm over a period of a few hours while holding a sample at 500 °C so as to minimize dynamic effects and allow stress relaxation through plastic deformation was not effective in reducing the total microcracking response. An alternative method of gradually passing through the phase transition is to cool very slowly at constant oxygen pressure. A YBCO pellet was sintered for 6 h at 950 °C in oxygen and then cooled at 5 °C/h in oxygen. Due to instrumental limitations upon the time span of data accumulation, acoustic emission data were collected from 750 °C to 250 °C (Fig. 7). Each point represents the accumulated ringdown count for a twenty minute period. While the onset temperature is unchanged from that observed in rapidly cooled samples, the peak of activity is shifted to about 300 °C. The noisy appearance of the curve is actually due to the occurrence of a number of large emission spikes during slow cooling, indicating sudden release of built-up stress. The overall ringdown count total (Table I) for the slowly cooled sample was about one-third that of a more rapidly cooled one. Slow cooling appears, therefore, to be an effective means of reducing microcracking in YBCO.

C. Silver Addition

The chemical and mechanical compatibility of silver with the ceramic superconductors have made it a popular additive for increasing the density and normal-state conductivity of sintered YBCO.[24-26] It has also been suggested that the high solubility of oxygen in silver increases the efficiency of oxygenation of YBCO pellets containing silver. Silver-YBCO

composites have been shown to have increased fracture toughness, ductility, and machinability.[27] The acoustic emission from a 10% silver YBCO composite pellet is shown in Fig. 8. The onset of intense microcracking was shifted to lower temperature by about 50°. The peak cracking rate and the total ringdown count were about one-third those of similarly-processed samples not containing silver.

D. Grain Size

The critical grain size for suppression of microcracking in YBCO has been calculated variously as 0.5 μm,[28] 1.0 μm,[5] and 3.4 μm.[29] The results of phenomenological studies of twinning and microcracking in YBCO[5,29] indicated a critical grain size of 1 to 2 μm. The acoustic emission output of a pellet of the submicron spray-dried powder, cooled in oxygen at 50 °C/h, (Fig. 9) was very low, comparable to that of an argon-cooled (unoxygenated) sample.

E. Grain Alignment

Grain alignment (texturing) has been shown to result in improved critical current densities in YBCO[30,31]. Since intergrain stress is minimized by alignment, it should also be advantageous for reducing microcracking in polycrystalline YBCO ceramics. Acoustic emission experiments were carried out on two samples, supplied by GTE Laboratories, which had been textured by hot forging.[32] In critical current measurements carried out at beforehand at GTEL, J_c for sample HF-25 was 1800 A/cm^2 at 77K in zero applied field, while J_c for sample HF-33 was 3000 A/cm^2 under the same conditions. To avoid microstructural alteration, the samples were heated at 25 °C/h to 750 °C, held for four hours, and cooled in oxygen at 50 °C/h. Both samples showed

reduced acoustic emission relative to untextured pellets (Fig. 10 and Table I). The onset temperature was lowered to about 600 °C. The emission curves are characterized by spikes similar to those seen in the very slow cooling experiments.

E. Alternate Compositions

Two other superconducting compounds of the YBCO structure type were investigated. $LaBaCaCu_3O_{7-x}$ is tetragonal in the superconducting state (T_c = 78K), with lattice parameters a = 0.3870 nm and c = 1.1610 nm, c/a = 3.000.[33] While little is known about the reaction processes during sintering and oxygenation of this material, the near absence of crystallographic anisotropy might be expected to result in relatively crack-free processing. The emission pattern during cooling in oxygen at 50 °C/h (Fig. 11) shows low activity down to about 570 °C, when a series of very strong signals were recorded. This was followed by a broad band of acoustic emission centered around 400 °C. The overall ringdown count total was similar to that of oxygen-cooled YBCO. A scanning electron micrograph (Fig. 12) of a fracture surface of the pellet shows large cracks surrounding a pore. The ceramic had, however, sintered to very high density, in contrast to the behavior of YBCO. No secondary phases were observed here or in the x-ray diffraction pattern.

Substitution of half of the barium in YBCO by strontium produces $YBaSrCu_3O_{7-x}$, with T_c = 82K and considerably less anisotropy, with lattice parameters a = 0.3822 nm, b = 0.3839nm, c = 1.1531nm, b/a = 1.004, c/a = 3.017.[21] Like $LaBaCaCu_3O_{7-x}$, $YBaSrCu_3O_{7-x}$ sintered to high density and good phase purity, but with more and larger macroscopic cracks. The acoustic

emission ringdown count total for cooling in oxygen was more than twice that for YBCO. The presence of two distinct emission peaks (Fig. 13) suggests the possibility of another phase transition in addition to simple oxygenation.

F. Critical Currents

Critical current measurements (Table II) were carried out on samples cut from 25 mm diameter pellets processed in the same way as the acoustic emission samples. The most consistent results were obtained on unmodified YBCO that had been calcined and ground repeatedly, sintered at 940 °C in oxygen, cooled to 750 °C in oxygen, then cooled to room temperature in argon. These deoxygenated pellets were more likely to survive the cutting and sanding required to prepare them for the J_c tests. They were annealed in oxygen for an additional 10 h at 400 °C after the silver contact treatment described above in order to assure complete oxygenation. Samples which had been subjected to many cycles of oxygenation and deoxygenation crumbled when attempts were made to cut them. J_c values for all samples tested ranged from near zero to 1000 A/cm^2. The highest values were obtained with samples of small cross sectional area. Explanations for this widely observed phenomenon[34] include natural selection of samples with continuous conduction paths (uninterrupted by cracks or secondary phase regions), confinement of current flow to the sample surfaces, and self-field effects. Beyond the preference for machining in the tetragonal form, no clear systematic dependence of J_c on the parameters studied here could be extracted from the scatter of data.

G. Grain Boundary Modification

The low current-carrying capacities of sintered ceramic superconductors have largely been blamed upon intergranular resistances arising variously from the presence of normal second phases at grain boundaries,[35-37] normal regions within the superconductor structure at grain edges,[38-40] and lattice misalignment of grains.[4,41] Our attempts to modify the grain boundary properties of sintered polycrystalline YBCO through treatment of bisque-fired pellets with solutions of metal salts followed by sintering in oxygen have so far met with failure. With the sole exception of potassium chloride, massive degradation of the physical integrity of the pellets and chemical decomposition of the superconducting phase occurred during sintering. In the case of potassium chloride, dissolution and recrystallization of YBCO occured within the pores where the KCl had been deposited. There was, however, no improvement in the measured critical current of a pellet so treated.

IV. DISCUSSION

Microcracking in YBCO ceramics is clearly related to the uptake of oxygen during cooling from the high temperatures required for sintering of these complex and reactive materials. The phase transformation which accompanies introduction of oxygen into the high-temperature tetragonal structure creates considerable intergrain stress in specimens with randomly-oriented grains. When the transformation is rapid, particulary with large-grained material, contraction of the grain surface results in surface flaking and intragranular cracking. This may also occur on a macroscopic scale, especially in high-density samples with closed porosity, as the entire outer layer of the ceramic is placed in tension. The increased anisotropy of thermal contraction of the orthorhombic phase relative to the tetragonal form may

also contribute to microfracture during cooling.

Acoustic emission data collected during cooling and oxygenation of YBCO are well correlated with the onset and extent of microcracking observed in the samples by SEM. It appears that very slow cooling through the tetragonal to orthorhombic transition may reduce the amount of microfracture, particularly that which arises from intragranular stress. Reducing the grain size to about 1 μm or less is an even more effective means of suppressing microfracture. The spray-dried samples in this study also sintered faster and to slightly greater density than those prepared by the conventional calcining and grinding method. Unfortunately, the measured critical current densities for spray dried samples were not found to be superior. Perhaps the increased number of grain boundaries and/or the presence of second phases due to the single-step calcination is responsible.

This was also true for the silver composites. Although they were considerably more rugged and more readily polished, some difficulty was experienced in forming good current contacts to the silver-doped samples. While silver in sufficiently high concentration (10% or more) does lower the normal state conductivity, it does little to improve the superconducting critical current. In addition, above 920 °C in air or above 850 °C in argon, silver appears to accelerate the decomposition of YBCO to Y_2BaCuO_5 and barium and copper oxides, probably by dissolving and transporting copper.

The textured samples prepared by hot forging showed reduced microcracking and very much improved critical currents. The acoustic emission from these samples appeared in large bursts, suggesting release of strain over a relatively large area. Since the grain size in these samples is 50 to 100 μm due to grain growth during hot forging, it may be that these large events are

due to intragrain stresses caused by too rapid oxygenation. The bulk density of the hot forged samples is greater than 95%. Thus there may have been surface cracking due to the absence of interconnected porosity and the accompanying slow rate of oxidation in the interior of the samples. Very slow cooling may alleviate this problem.

Markedly different acoustic emission responses were observed to rapid insertion versus removal of oxygen at constant temperature. These results nicely parallel those of Tu et al.,[11] who monitored the normal state resistivity of YBCO under similar conditions. They found a very sharp decrease in resistivity during oxygen uptake and a gradual increase during deoxygenation. They interpreted their data in terms of a low and oxidation-state dependent activation energy for oxygen insertion, and a relatively high and constant activation energy for oxygen removal. The dilatometry data of O'Bryan and Gallagher [10] for rapid oxidation and reduction of YBCO at 500 °C show nearly identical behavior. The significantly lower level of microcracking during deoxygenation is consistent with the suggestion[11] that the rate of oxygen removal is controlled by a surface reaction sufficiently slow that the ceramic remains nearly homogeneous with respect to oxygen stoichiometry, and is therefore not stressed macroscopically.

V. CONCLUSIONS

It is clear that microcracking must be held to a minimum if YBCO ceramic superconductors are to be used in high current applications. Grain alignment is the most effective means of both reducing microcracking and increasing critical currents. Slow cooling and avoidance of rapid changes in oxygen partial pressure are also effective, especially in large-grained materials.

While the addition of silver does increase the mechanical strength and normal state conductivity of randomly oriented sintered ceramic YBCO, it does not improve the critical current. Silver may even have a deleterious effect if high processing temperatures must be maintained for a long time. The use of a superconducting material with a less anisotropic structure and/or lower sensitivity to oxygen concentration is an attractive solution to the microcracking problem. Successful application of these materials awaits development of detailed knowledge of the reactions and phase transitions which occur during processing of alternative compositions.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Naomi Naito of GTE Laboratories for supplying the hot forged YBCO samples used in this study.

This work was supported by the Electric Power Research Institute and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the United States Department of Energy, under contract No. DE-AC03-76SF00098.

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TABLE I. Total acoustic emission ringdown count during cooling.

Sample	Avg. Part. Size	Cooling Rate	Atmosphere	Total Ringdown Count
YBCO	10 μm	50 °C/h	oxygen	275 K
YBCO	10 μm	50 °C/h	dry air	242 K
YBCO	10 μm	50 °C/h	argon	34 K
YBCO	10 μm	5 °C/h	oxygen	87 K
YBCO, 10% Ag	20 μm	50 °C/h	oxygen	92 K
YBCO[a]	1 μm	50 °C/h	oxygen	28 K
YBCO[b]	50-100 μm	50 °C/h	oxygen	51 K
YBCO[c]	50-100 μm	50 °C/h	oxygen	86 K
LBCCO[d]	> 100 μm	50 °C/h	oxygen	233 K
YBSCO[e]	> 100 μm	50 °C/h	oxygen	626 K

[a]Spray-dried.

[b]Hot forged, No. HF-25.

[c]Hot Forged, No. HF-33

[d]$LaBaCaCu_3O_{7-x}$

[e]$YBaSrCu_3O_{7-x}$

TABLE II. Critical current densities in YBCO.[a]

Sample Description	J_c (A/cm^2)
Ball milled, argon cooled, 50 °C/h	0[b]
Ball milled, air cooled, 50 °C/h	233 347
Ball milled, oxygen cooled, 50 °C/h	213 446 607 377
Ball milled, oxygen cooled, 5 °C/h	412
10% Silver, oxygen cooled, 50 °C/h	140
Spray-dried, oxygen cooled, 50 °C/h	350
KCl-treated, oxygen cooled, 50 °C/h	310 360

[a]sample dimensions 1.0 x 1.0 x 25 mm^3.

[b]not superconducting.

FIGURE CAPTIONS

FIG. 1. Acoustic emission apparatus.

FIG. 2. Acoustic emission from YBCO during cooling at 50 °C/h in: (a) oxygen, (b) dry, CO_2-free air, (c) argon.

FIG. 3. Scanning electron micrograph of transgranular cracks in pore surface of oxygenated YBCO.

FIG. 4. Acoustic emission responses of YBCO to rapid changes in oxygen partial pressure at 600 °C.

FIG. 5. Ratio of acoustic emission intensities vs. absolute temperature. I(Ox) and I(Ar) are integrated intensities for oxygenation and deoxygenation, respectively.

FIG. 6. Scanning electron micrographs of fracture surfaces of YBCO pellets: (a) subjected to repeated oxygenation/deoxygenation cycling, (b) cooled in argon.

FIG. 7. Acoustic emission from YBCO during cooling at 5 °C/h in oxygen.

FIG. 8. Acoustic emission from YBCO-10% Ag composite during cooling at 50 °C/h in oxygen.

FIG. 9. Acoustic emission from submicron (spray-dried) YBCO during cooling at 50 °C/h in oxygen.

FIG. 10. Acoustic emission from hot forged YBCO during cooling at 50 °C/h in oxygen: (a) sample HF-33, (b) sample HF-25.

FIG. 11. Acoustic emission from $LaBaCaCu_3O_{7-x}$ during cooling at 50 °C/h in oxygen.

FIG. 12. Scanning electron micrograph of fracture surface of sintered $LaBaCaCu_3O_{7-x}$, showing high density, cracks around pore.

FIG. 13. Acoustic emission from $YBaSrCu_3O_{7-x}$ during cooling at 50 °C/h in oxygen.

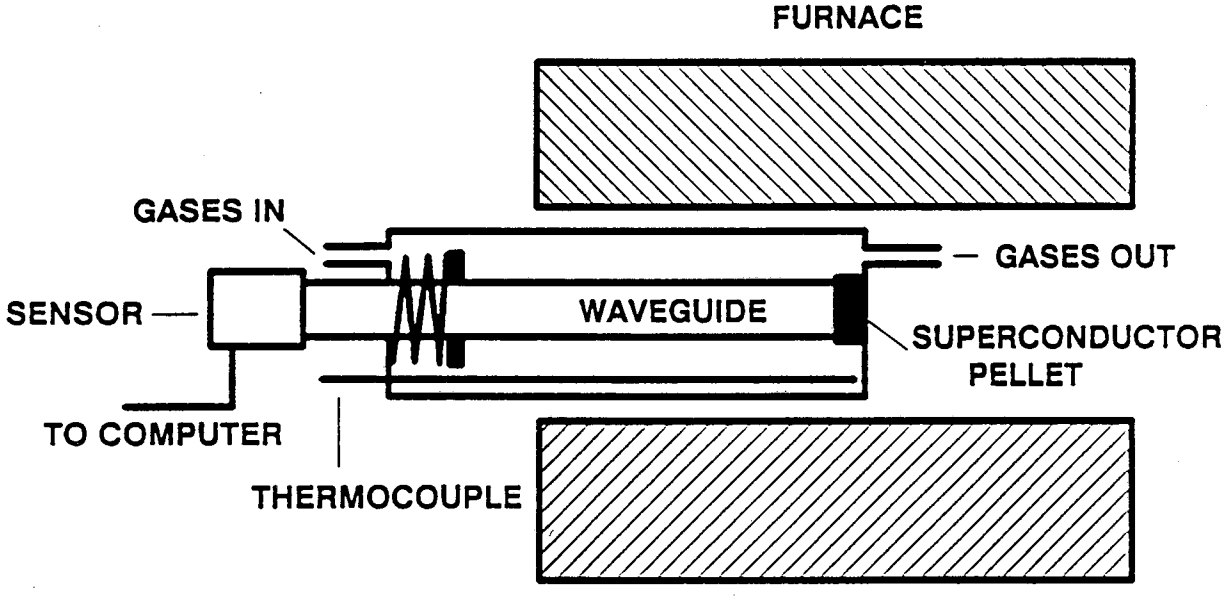
FURNACE
GASES IN
GASES OUT
SENSOR
WAVEGUIDE
SUPERCONDUCTOR
PELLET
TO COMPUTER
THERMOCOUPLE

Figure 1

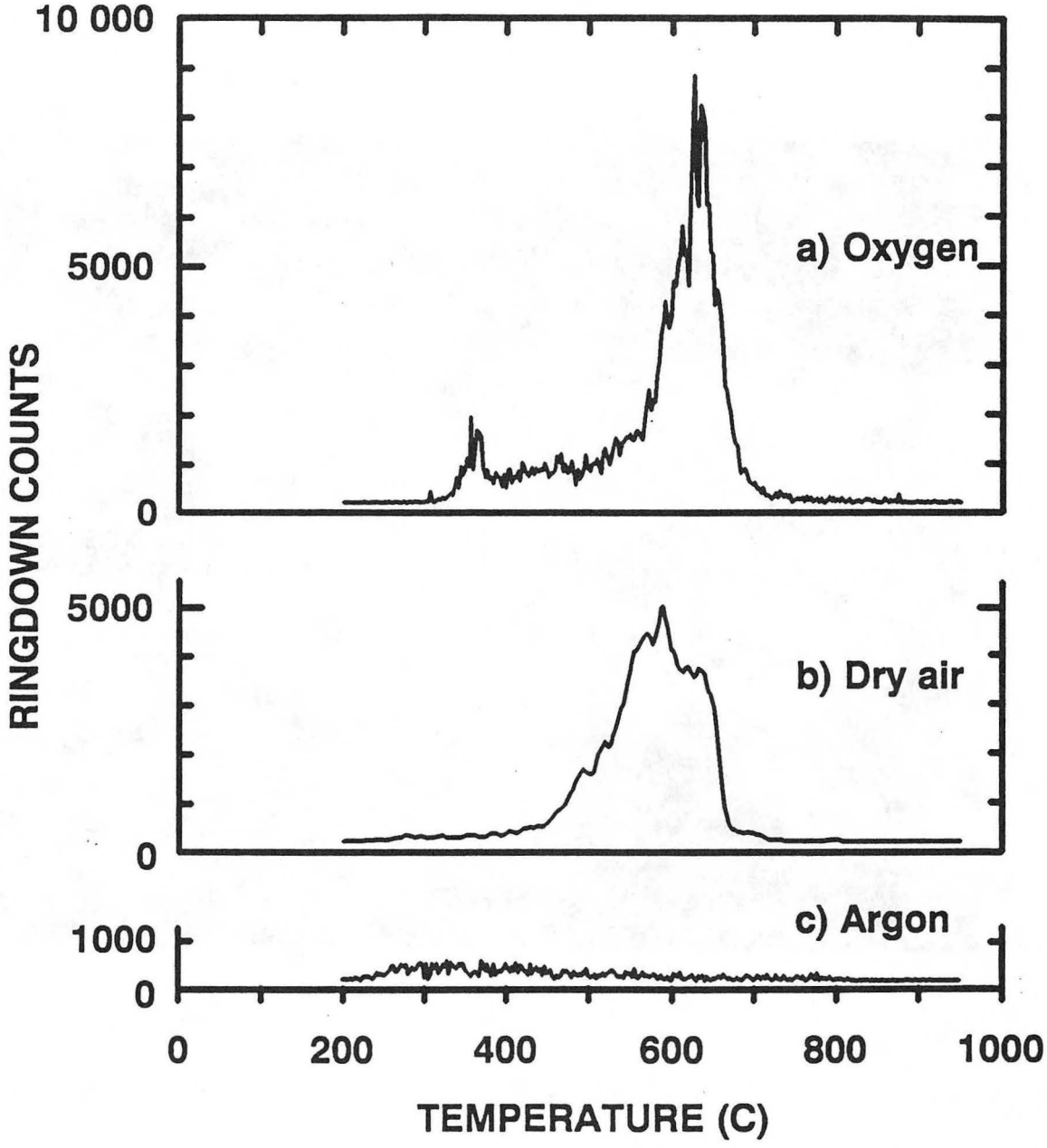
10 000
5000
0
a) Oxygen
5000
0
b) Dry air
1000
0
c) Argon
RINGDOWN COUNTS
0
200
400
600
800
1000
TEMPERATURE (C)

Figure 2

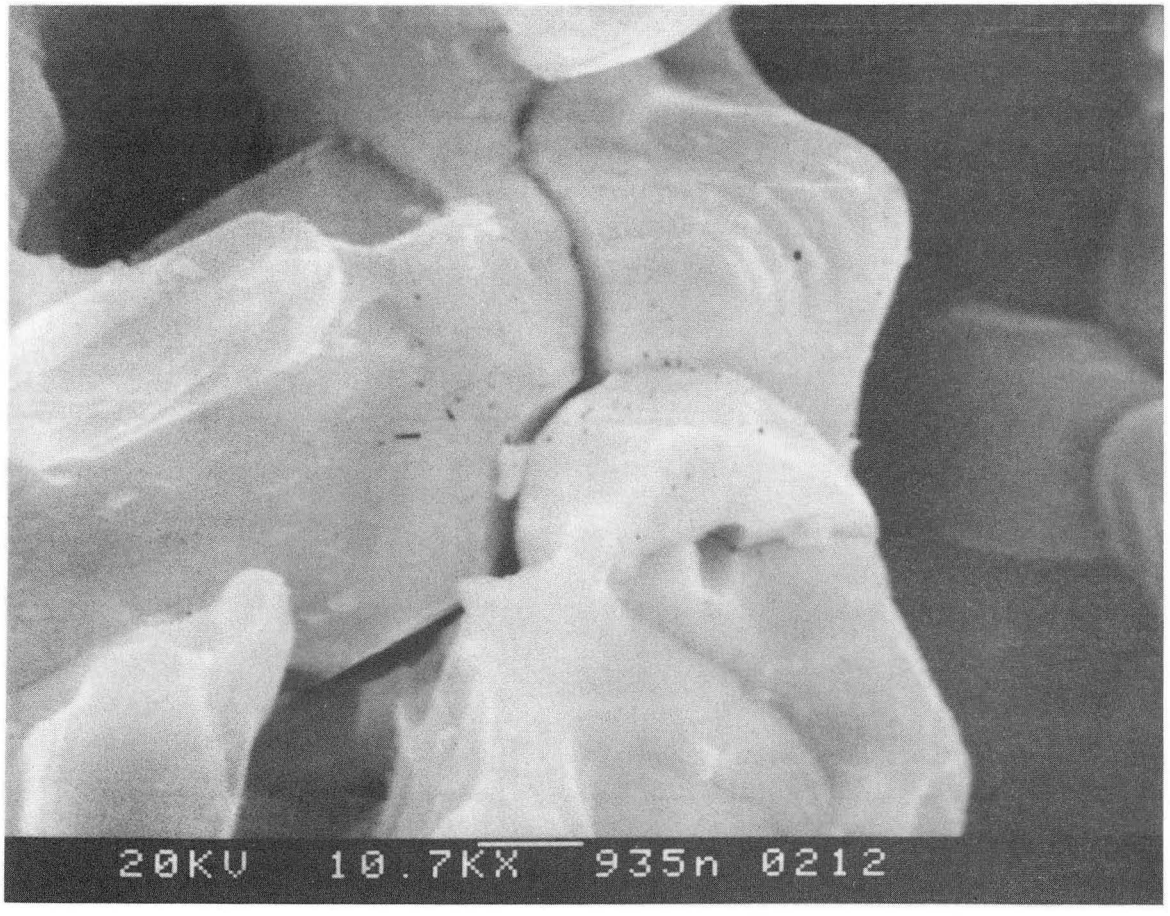

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Figure 3

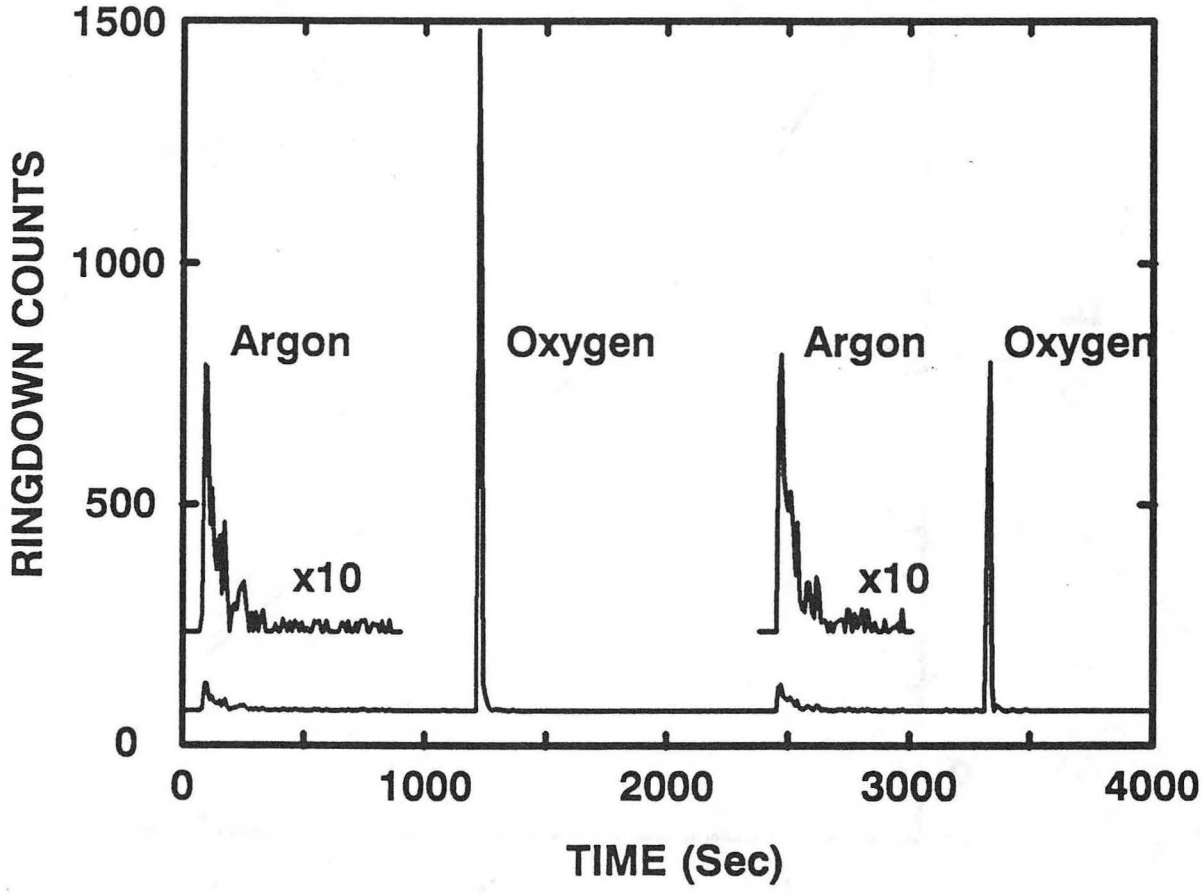
1500
1000
500
0
RINGDOWN COUNTS
Argon
Oxygen
Argon
Oxygen
x10
x10
0
1000
2000
3000
4000
TIME (Sec)

Figure 4

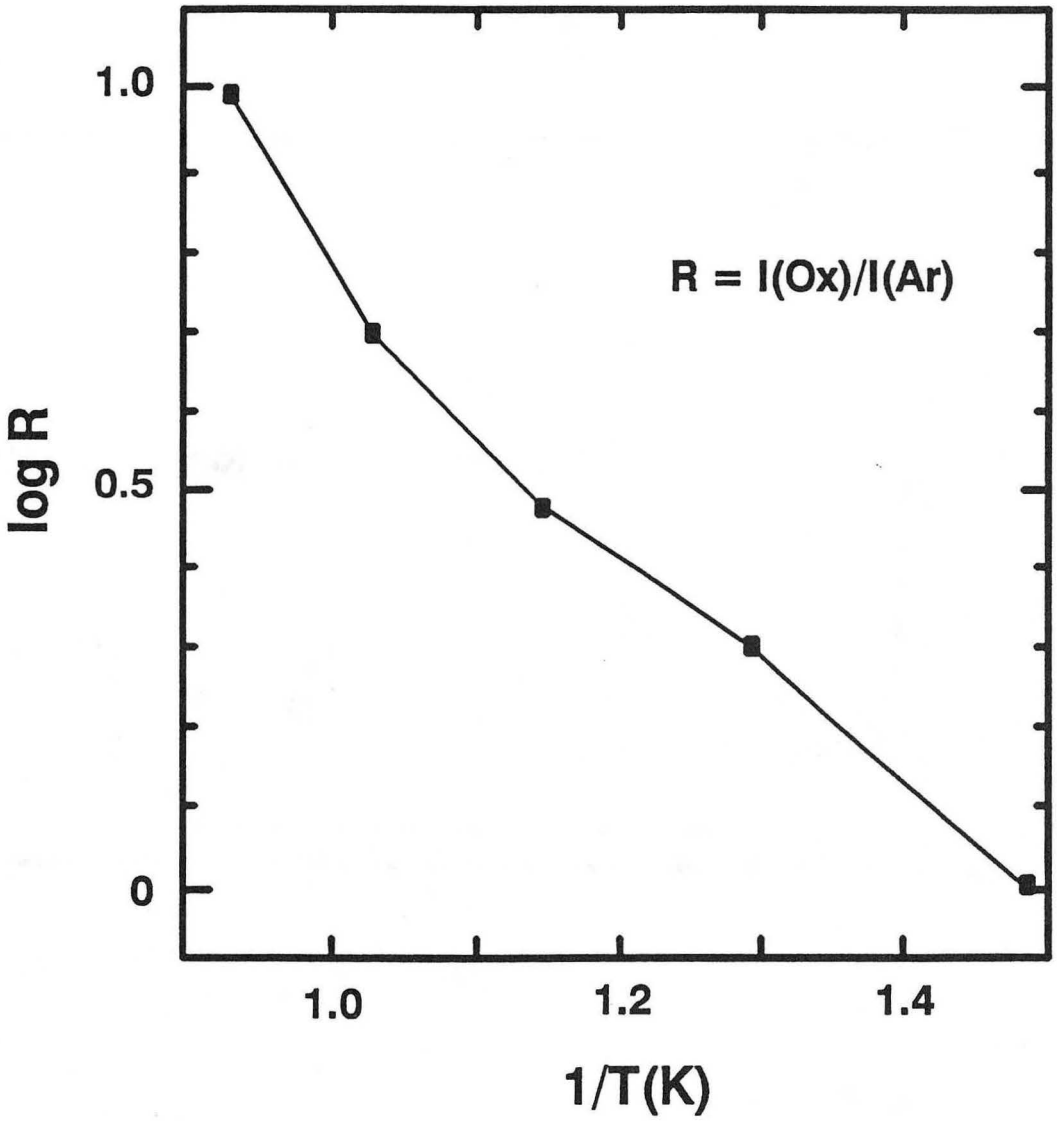

Figure 5

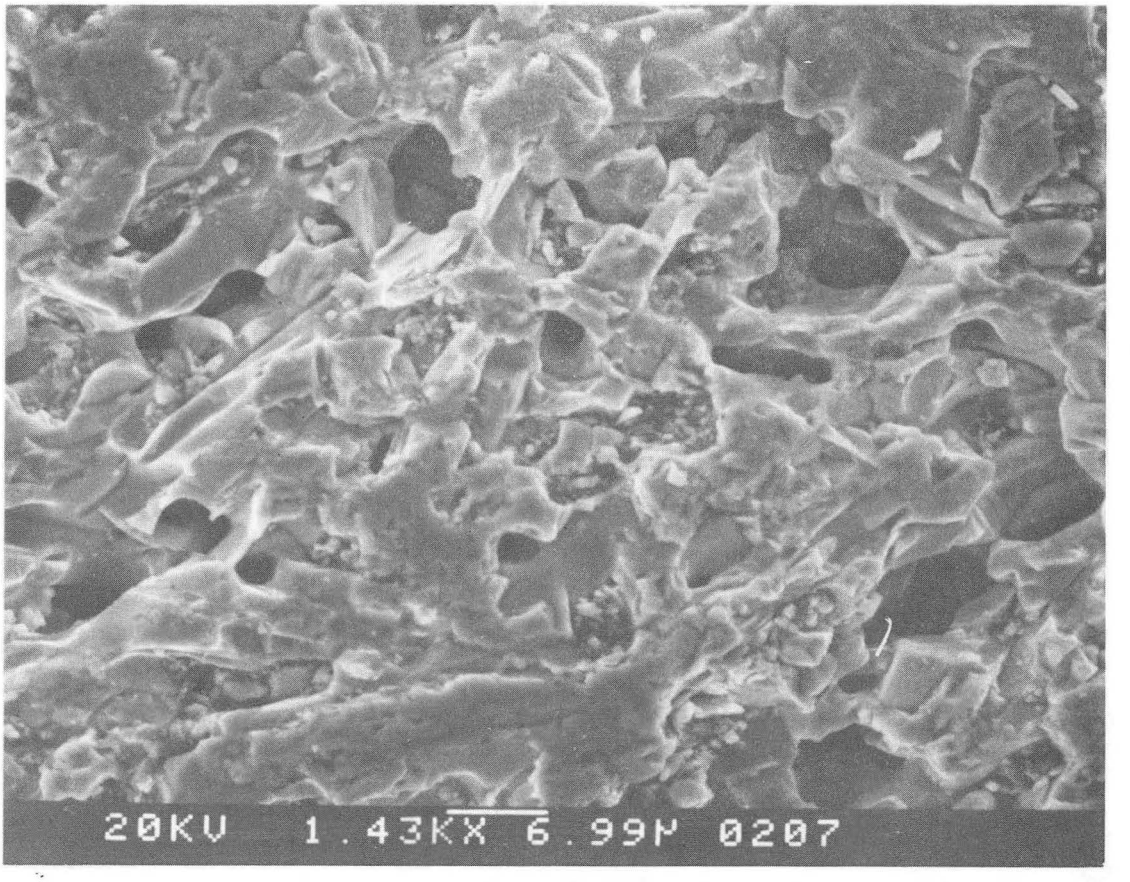

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Figure 6 (a)

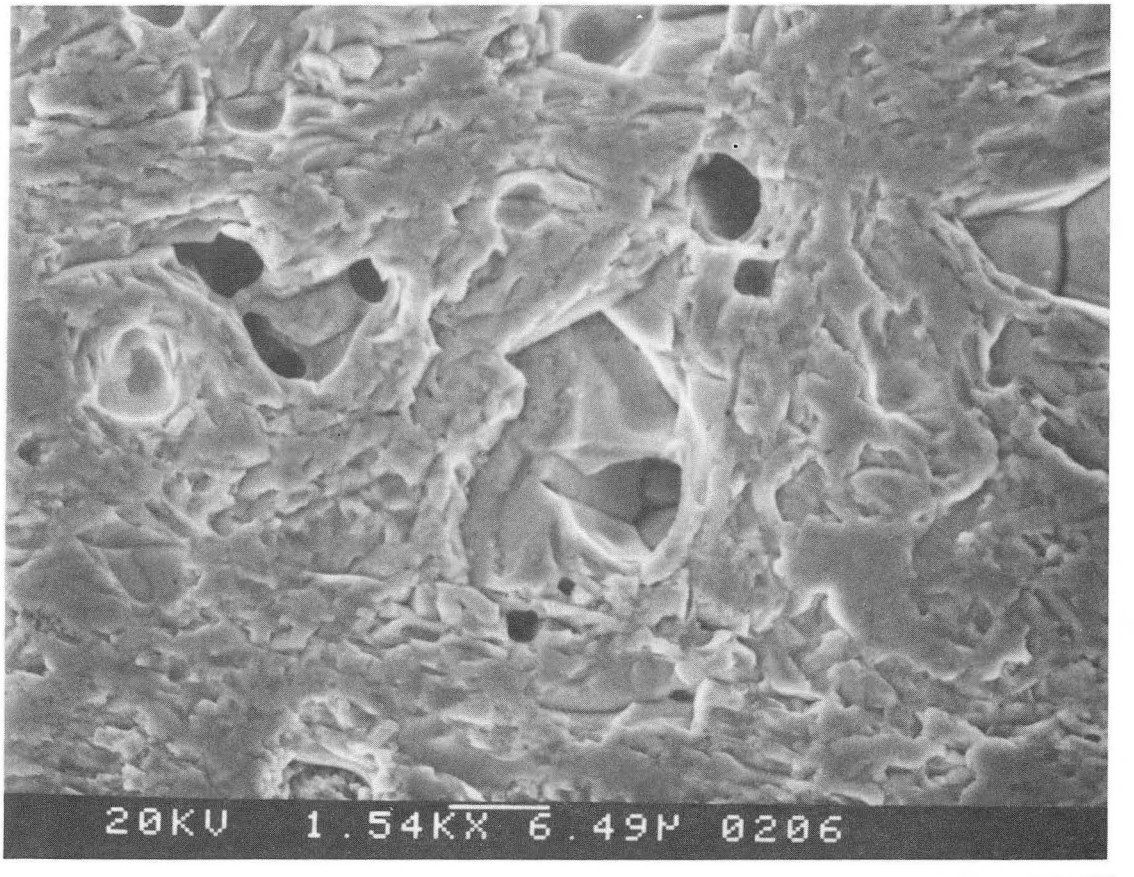

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Figure 6 (b)

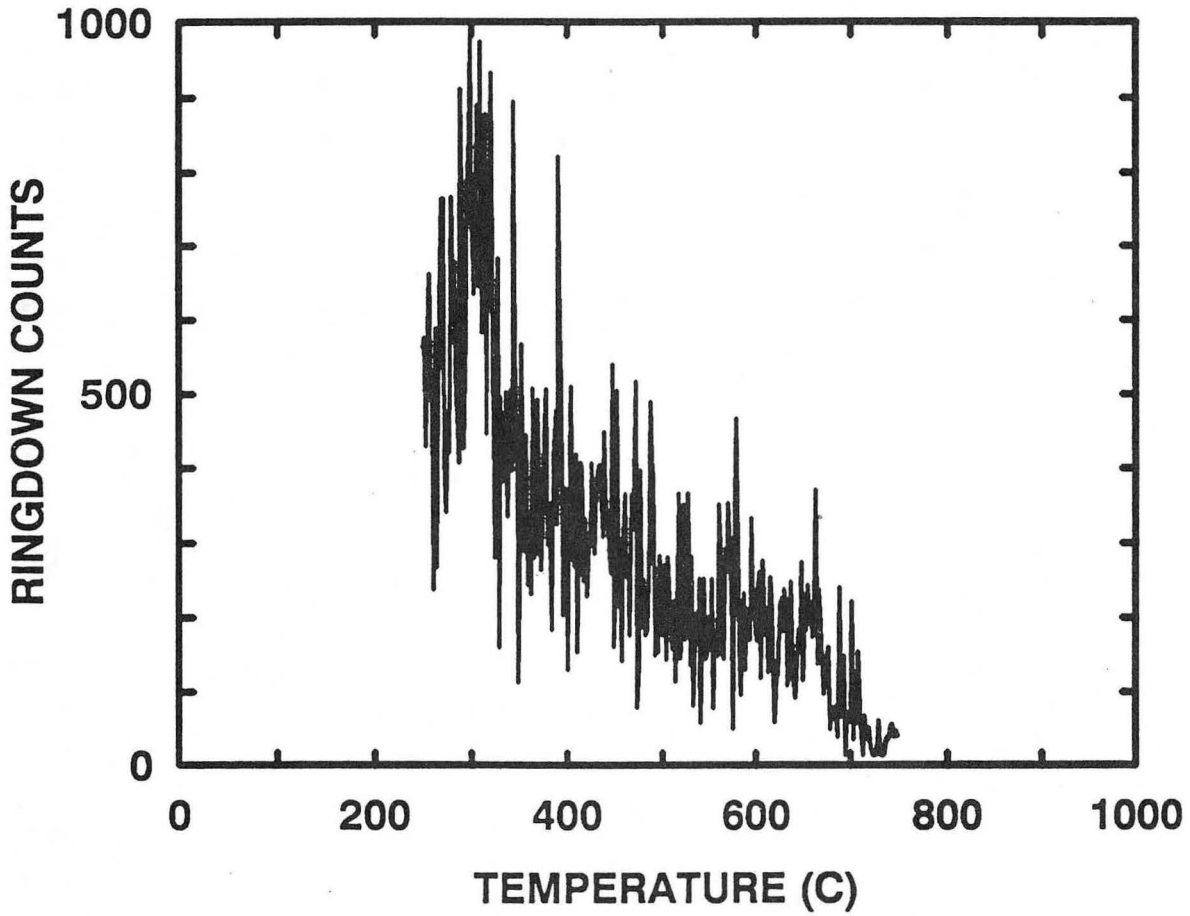
1000
500
0
RINGDOWN COUNTS
0
200
400
600
800
1000
TEMPERATURE (C)

Figure 7

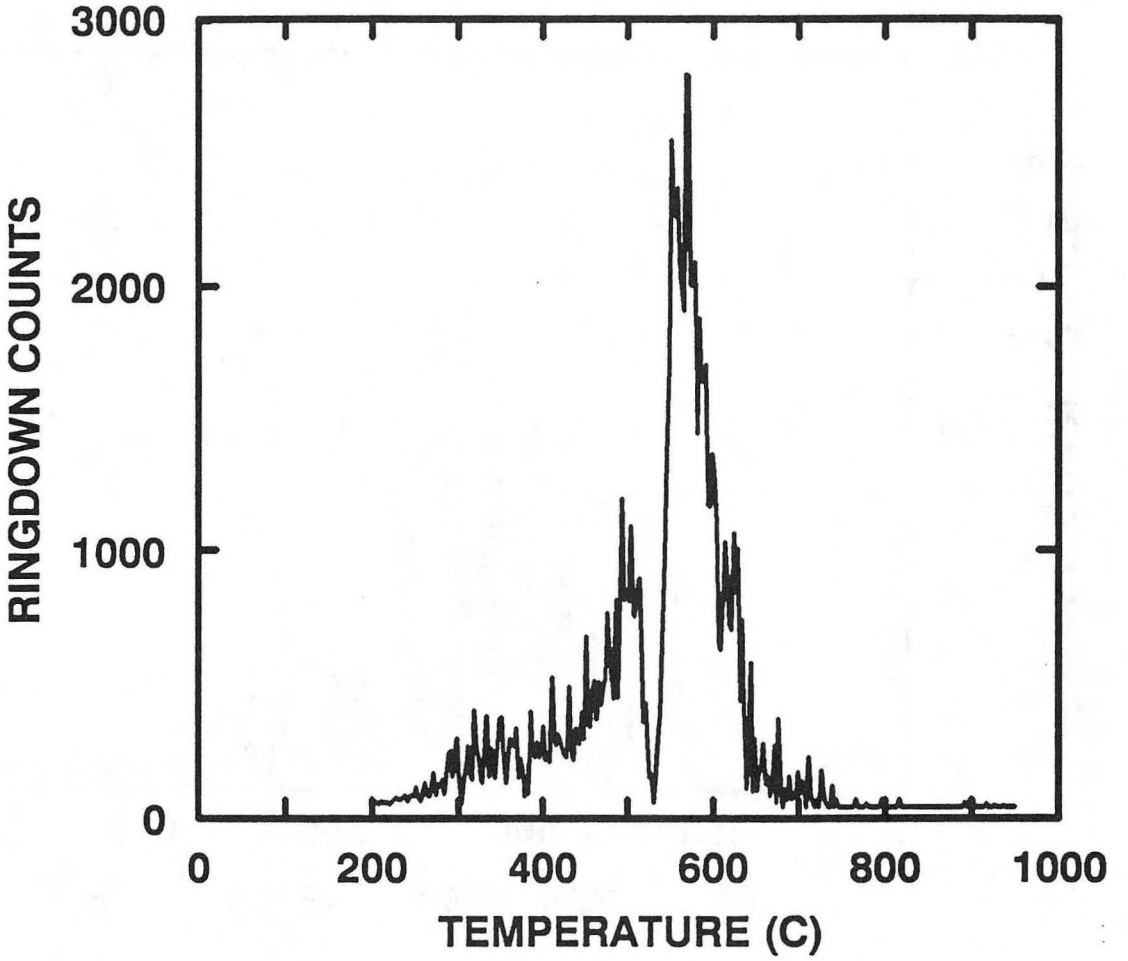
3000
2000
1000
0
RINGDOWN COUNTS
0
200
400
600
800
1000
TEMPERATURE (C)

Figure 8

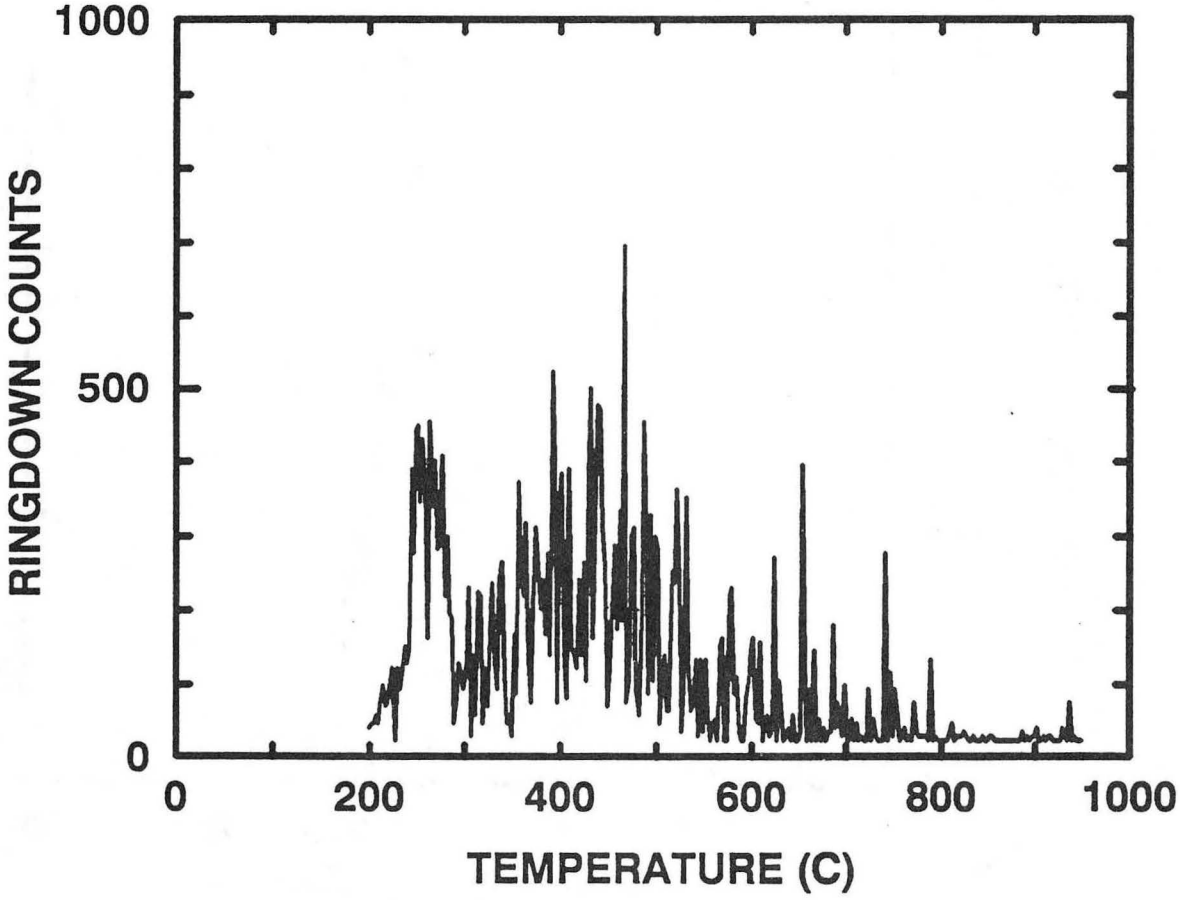
1000
500
0
RINGDOWN COUNTS
0
200
400
600
800
1000
TEMPERATURE (C)

Figure 9

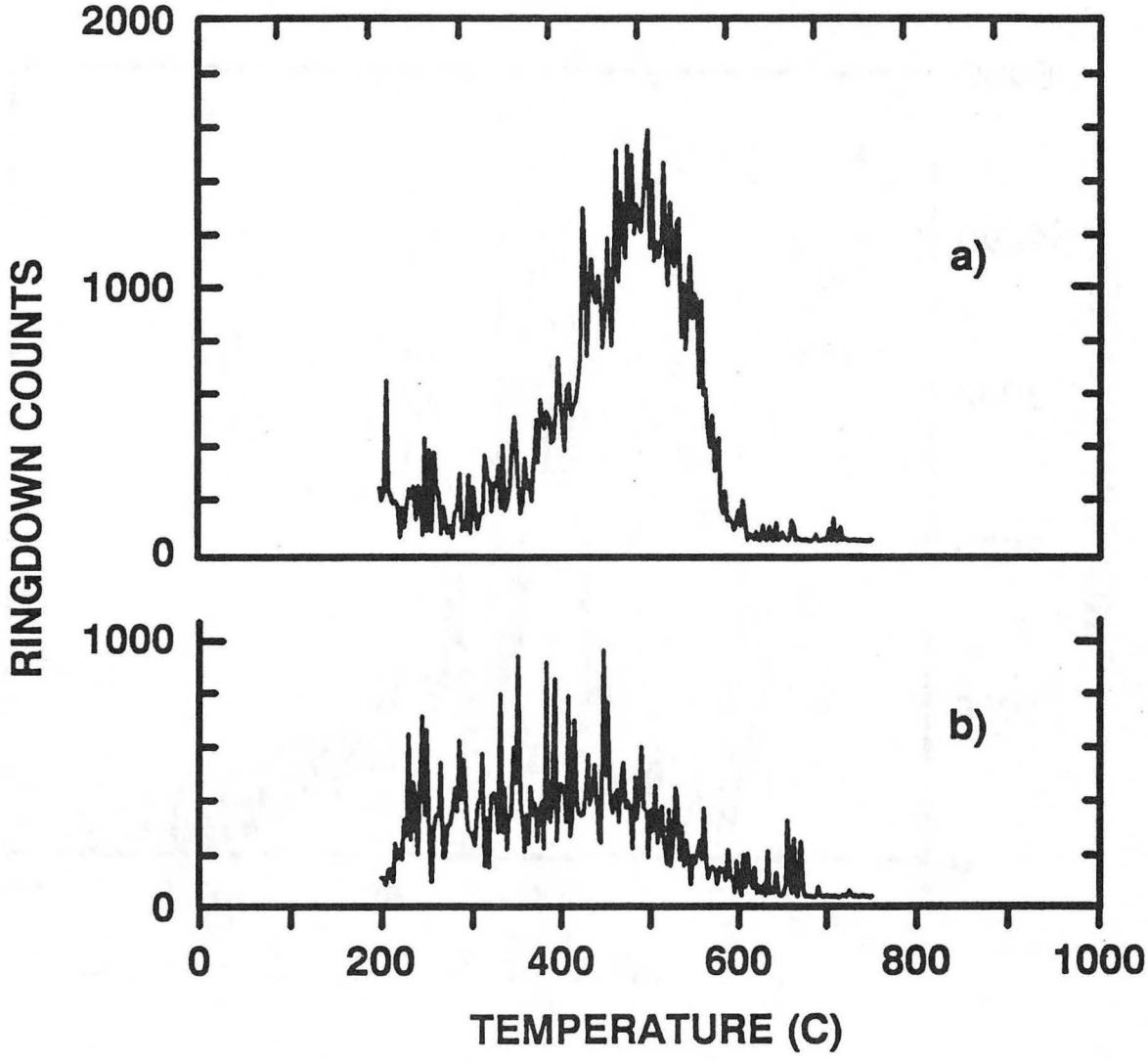
2000
1000
0
1000
0
RINGDOWN COUNTS
a)
b)
0
200
400
600
800
1000
TEMPERATURE (C)

Figure 10

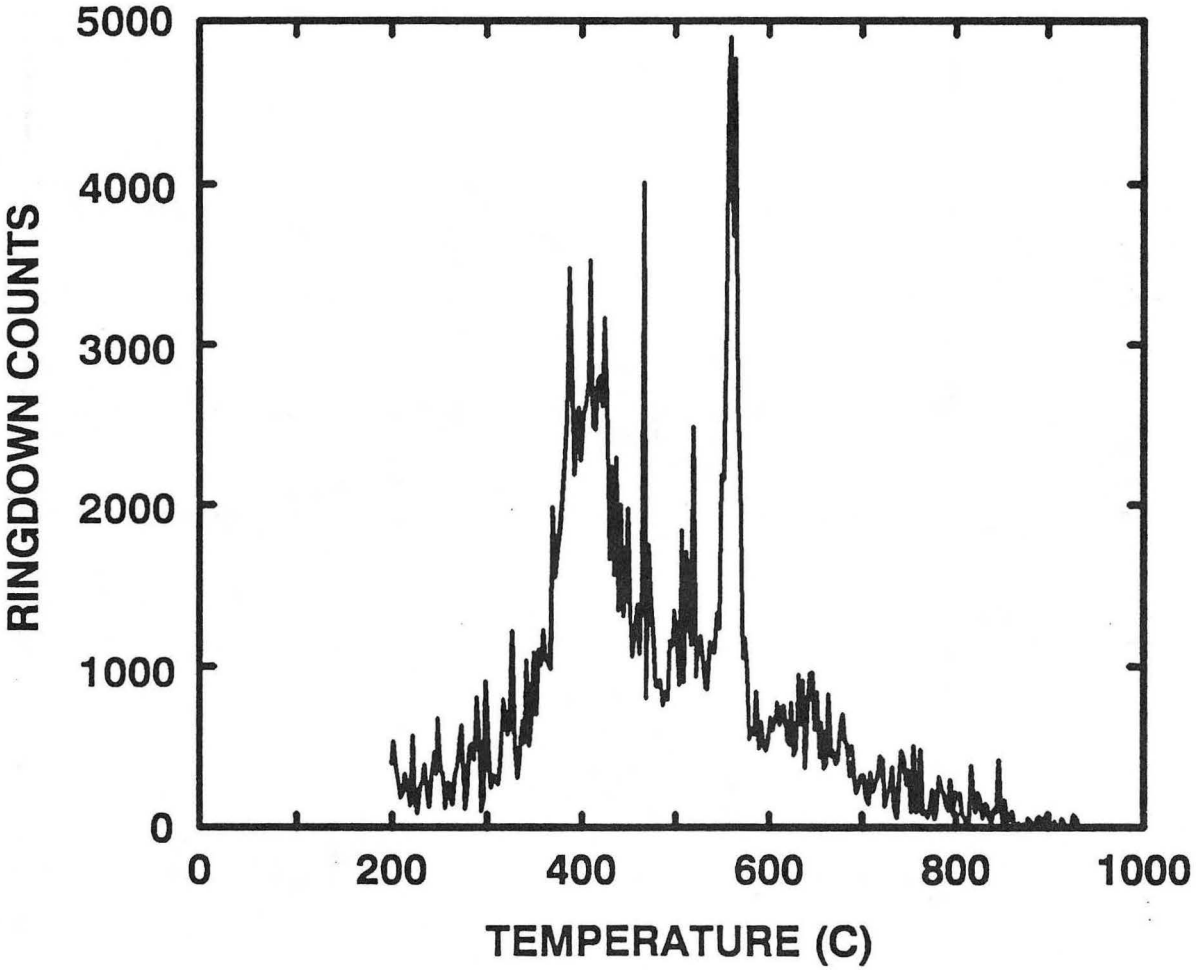
5000
4000
3000
2000
1000
0
RINGDOWN COUNTS
0
200
400
600
800
1000
TEMPERATURE (C)

Figure 11

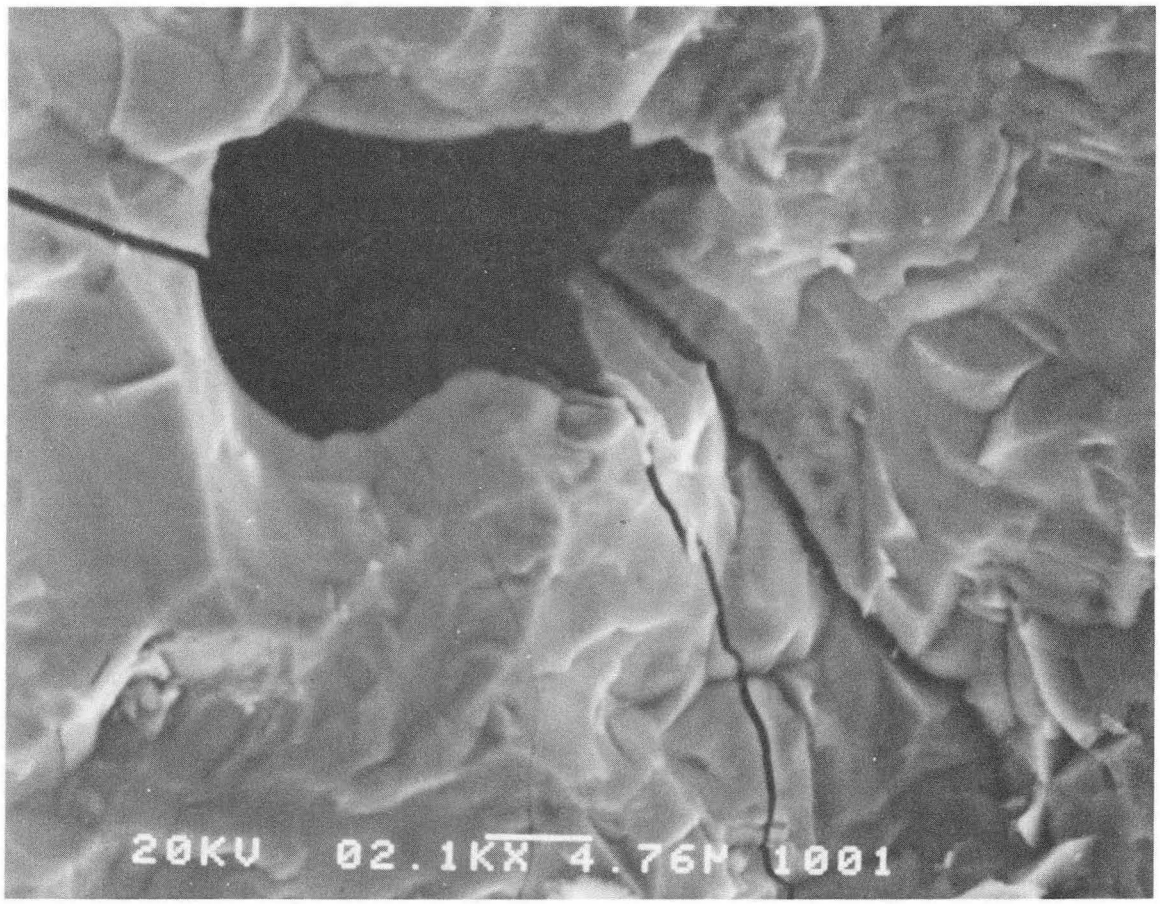

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Figure 12

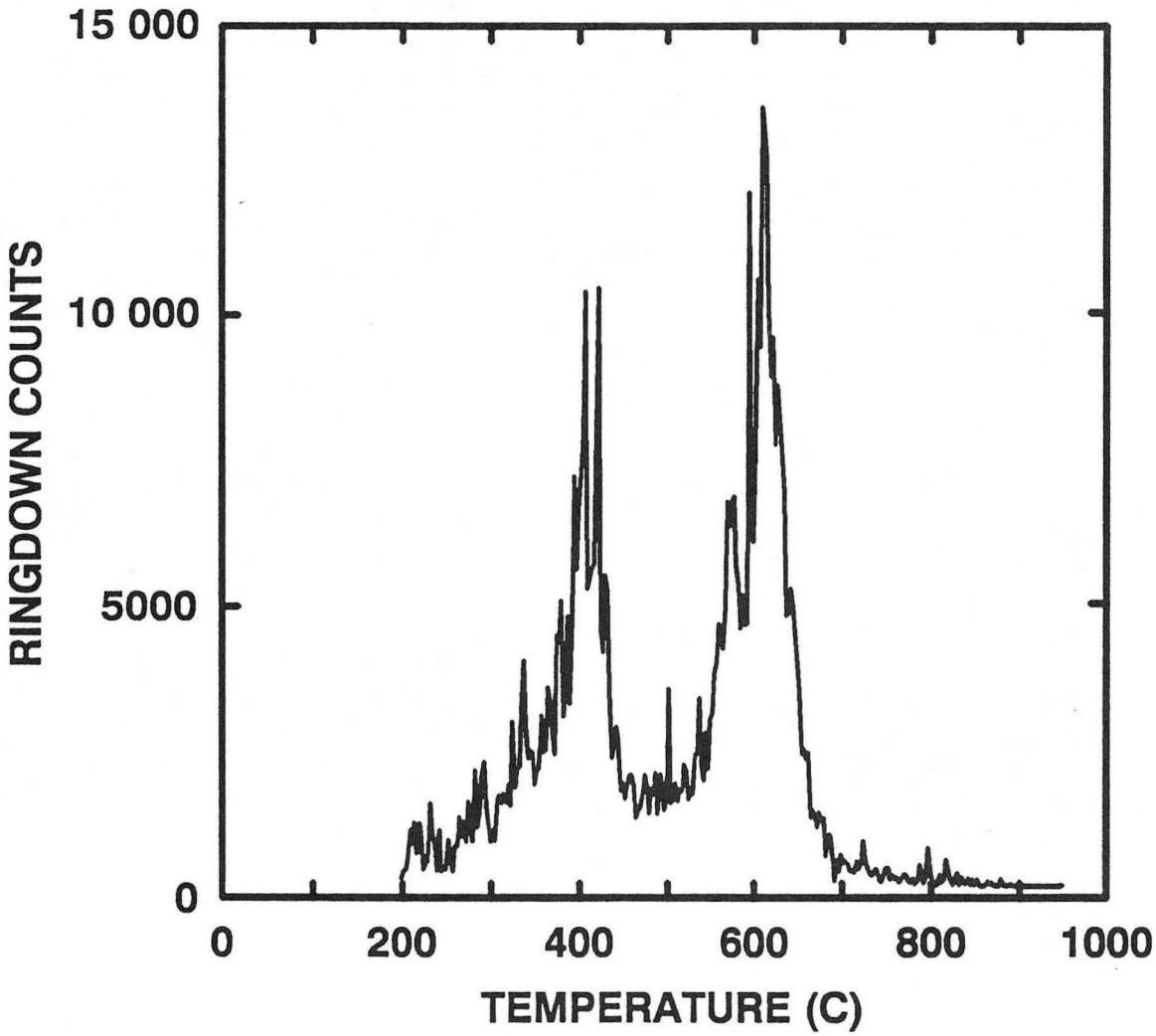
15 000
10 000
5000
0
RINGDOWN COUNTS
0
200
400
600
800
1000
TEMPERATURE (C)

Figure 13

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