MICROWAVE PROCESSING OF $Bi_2Sr_2CaCu_2O_{8+\delta}$

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Abstract:

Microwave processing of a high temperature superconducting (HTS) material was explored as an alternative route to conventional heat treatment processes. $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) was reacted by microwave processing. Extensive XRD and microstructural investigations were carried out on pellet samples processed for various durations. Samples showed noticeable amounts of Bi2212 in exterior regions, particularly after thirty minutes of processing time.

Introduction:

The $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase of bismuth strontium calcium copper oxide (Bi2212) is a high-temperature superconducting ceramic with a critical temperature between 75 and 95 K *(1)*. To obtain Bi2212, a stoichiometric mix of powders is packed into tubes and mechanically deformed into tapes or wires. The conductors are then heat treated at elevated temperatures around 860-900 ºC, for up to seventy-two hours in an oxygen atmosphere *(1)*. This takes a significant amount of time, and does not guarantee high-quality Bi2212. Microwave processing, however, has shown great promise for being able to reduce processing times and result in higher quality products.

Microwave processing has attracted attention due to the potential of reduction in processing time and energy used, and the potential to improve microstructure of the conductor *(2)*. Most promisingly, YBCO has been produced via microwave processing with uniform oxygen content and good densification *(3)*. Additionally, processing was found to take one sixth of the time required for conventional processing *(3)*. Microwave processing can also be used to obtain unusual reactions, such as the anisothermal reactions reported by Peelamedu et. al. *(4)*, which occur due to variations in microwave absorption in the starting materials. Other groups have reported similar results *(5 – 8)*.

The mechanism that allows materials to respond to microwave radiation is not entirely understood, but is likely caused by dipole interaction *(9)*. The material begins to heat at the penetration depth, governed by Equation 1:

$$D = 3\lambda/(8.86\ \pi \tan\delta\ (\varepsilon_r'/\varepsilon_0)^{1/2}) \qquad (1)$$

where λ is the incident wavelength, ε_r' is the relative dielectric constant, and ε_0 is the permittivity of free space. $\tan\delta$ represents the loss tangent, and describes the losses of internal electric field generated within volumes affected by microwave penetration, as expressed in Equation 2:

$$\tan \delta = \sigma / 2\pi f \varepsilon_0 \varepsilon_r' \qquad (2)$$

where σ is the total effective conductivity caused by conduction and f is the frequency (GHz).

The penetration depth for Bi2212 pellets was not calculated because the total effective conductivity of the Bi2212 pellets and their dielectric constant are both unknown. The relative dielectric constant is suspected to be relatively low for unprocessed Bi2212 at room temperature as it is a measure of the polarizability of a material in an electric field, as Bi2212 is an insulator at room temperature and above. The relative dielectric constant and the loss tangent both change as a function of temperature.

Experimental:

Bi2212 was reacted as bulk, made from premixed $Bi_{2.1}Sr_{1.7}Ca_{1.2}Cu_2O_8$ powder obtained from Superconductive Components, which was pressed into pellets using a uniaxial press with four metric tons of pressure. These pellets had a diameter of 7 mm and a thickness between 1.0 and 1.2 mm.

For microwave processing, a microwave oven with a wave frequency of 2.45 GHz and an output power of 1200 watts was obtained. The resultant field was found to be heterogeneous, so a method was needed to find the microwave antinodes. Antinode locations were not calculated because it was unclear exactly where the microwaves were emitted, how the waveguide shaped them as they entered the cavity of the furnace, and what part of the oscillation the standing waves were in as they entered. Therefore, the microwave interior was mapped using a clear acrylic plate about one-quarter of the size of the interior cavity brushed with a layer of egg white, which was microwaved for three seconds. The locations of the cooked areas were recorded with respect to the back left corner of the cavity. This provided a simple way to determine antinode locations. After determining the location of an antinode, several batches of pellets were run one at a time, located on a piece of alumina and ceramic wool for thermal insulation.

Conventional heat treatment was performed in a tube furnace with flowing oxygen and a 32-hour reaction cycle, with a maximum temperature of 887 ºC. This process provided a comparison against microwave treatment.

It is believed that antinode location changed as a function of time. The cavity of the microwave is not symmetric, and it is possible that the waves emitted from the magnetron entered the cavity at random points in any given cycle, rather than always in the same place. Although mapping antinodes provided some insight into pellet placement within the cavity, the constantly changing field probably contributed to the uncertainties and lack of reproducibility in the experiments.

To prevent magnetron overload and terminal damage to the microwave, a block of gypsum was placed in each back corner of the microwave to balance the reflected load.

Each batch had a total of six pellets; one pellet was run from five to thirty minutes in five minute increments. The pellets were compared for phases present and changes in critical temperature relating to changes in the oxygen stoichiometry of the compound. Three batches were run to determine consistency.

Relative amounts of phases present were determined via x-ray diffraction (XRD). Each sample consisted of 1/3 of a pellet ground finely, and run from 2θ: 5-85 degrees, at 0.02 degrees/second. To investigate the phase formation across the sample volume, the outside of the pellet from the third batch was sanded first and those particles collected. Environmental scanning electron microscopy was applied to fractured surfaces of samples that showed pronounced Bi2212 peaks from XRD to locate and identify visible crystalline structures of Bi-Sr-Ca-Cu-O phases.

A Quantum Design SQUID magnetometer was used to determine transition temperature. Four microwaved samples were investigated, two reacted for 20 minutes and two for 30 minutes.

Results:

Bi2212 was identified in every reacted sample, even those microwaved for only five minutes. There were a number of additional peaks that were related to second phases, indicating an incomplete reaction. Generally, the amount of Bi2212 increased as a function of time. Somewhere between 25 and 30 minutes there was a notable increase in the amount of Bi2212 phase formed.

Figure 1 shows a series of XRD data from batch "A" for various reaction times; those run longest produced the most pronounced peaks. Figure 2 shows the data for the batch "B." The first and second batches are not consistent in their trends of intensities of remnant oxides as a function of time.

To study Bi2212 distribution in a sample, XRD was performed on powder ground from the exterior and interior (separately) of a pellet reacted for 30 minutes. The samples had higher relative concentrations of Bi2212 on their exteriors, but there was enough variation that that aspect of the study is inconclusive, as demonstrated in Figure 3, which describes a full batch of pellets run from 5-30 minutes with subsequent interior-exterior separation for analysis.

Observation of pellets as they were processed in the microwave provided some insight into the microwaves' interaction with the Bi2212. Sometimes part of an edge would glow, and then it would spread to the whole circle. Pellets run at full power beneath a constant magnetron would glow after forty seconds, for less than two minutes, and could not be visibly reacted again. Those run beneath an intermittent magnetron (70%+ of the time on) would take the same forty seconds to begin glowing, stop glowing the moment the magnetron turned off, and then start glowing at about twenty seconds after it turned back on. This allowed for repeated and therefore longer (in sum) visible reaction times, but unfortunately no visible effect could be produced at all when the

gypsum was present in the microwave, but long reaction times (>30 min) and lack of an adequate load previously burnt out a magnetron. It was difficult to find how much energy was absorbed by the gypsum, but the pellets did heat, as felt afterwards by touch, and as demonstrated by the subsequent reaction found in analysis of the samples.

Analysis of samples processed in a conventional furnace and in the microwaves revealed variable results on the microscopic level. 2212 phases were positively identified in the product processed conventionally (see Figure 4a). However, the microwaved Bi2212 did not have any phases confirmed visually; pressed powder was all that was observed (see Figure 4b). The surfaces of the pellets were never examined under the ESEM.

Critical temperatures of the samples were found on the to vary between 75 to 85 K, with no certain trend or pattern. The random variation indicates a lack of reproducibility in 2212 quality formed in the microwave. The highest critical temperature was found in a pellet that was microwaved for 20 minutes pellet, and the lowest was a pellet microwaved for 30 minutes. Figure 5 summarizes the SQUID findings.

Analysis:

All microwaved samples are consistent in the intensity of Bi2212 produced increasing with time, which implies that with adequate equipment and sufficient time an entire pellet could fully react. The lesser peaks are believed to represent unreacted material and second phases. Further experimentation is necessary to determine how randomized the sizes of the peaks are.

Every set of data from the XRD has low intensities. Purer phase would have intensities two orders of magnitude higher than we observed. This is likely because the pellets tested were incompletely reacted. It is clear from batch three, in which the inside and outside of each pellet was run separately, rather than together, that large amounts of unreacted Bi2212 were present. The jump in intensity between 25-30 minutes of processing implies that the pellets take a certain amount of time to heat and react beyond the minimal, or possibly allow for heat conduction to the inside of the pellet.

XRD analysis shows that Bi2212 first forms on the outside of the pellet. It is possible that the penetration depth of the microwaves was insufficient to reach the interior of the material. However, even the interior showed some Bi2212, implying that a small reaction took place either caused by penetrating microwaves or mediated by heat conduction.

The experimental observation of glowing/non-glowing pellets clearly indicates that within a microwave it is possible to heat the pellets sufficiently for treatment; the pellets that melted heated beyond the required temperature to react. It is possible that pellets with lower thicknesses might react fully. Additionally, there was never any experimentally confirmed explanation for why pellets run under full, constant power

would simply stop glowing after a while; it was theorized that this was from lack of available oxygen (the original furnace did not have an oxygen source). There was no additional load in the microwave when these pellets glowed, beyond the alumina chip and a small amount of steel-wool insulation.

In the ESEM study, no Bi2212 was confirmed visually in the microwaved pellets. The problem is presumably that the pellets were only partially reacted, and the relatively random portion that we viewed under the microscope were unreacted. A consistent presence of Bi2212 in the XRD data implies that Bi2212 was present. We studied only fracture surfaces down the center of the pellets, rather than their surfaces; later discoveries of Bi2212 on the exterior of pellets may explain why no crystalline microstructure was found on the interior.

The critical temperatures found in SQUID analysis were in the lower ranges typical for Bi2212, indicating oxygen underdoping of the samples. Furthermore, the shallow transition indicates the presence of non-superconducting phase as well as Bi2212. The lack of a trend indicates that oxygen content in each pellet was highly variable.

Future Work:

To refine the microwave processing technique, more information and more ways to collect data during the process itself are needed. A way to monitor the temperature of the sample within the microwave is important: an infrared thermometer may be a solution.

It would be best for the resistive material to be eliminated altogether, and another failsafe put into place to prevent the magnetron from burning out; that way the sample would receive the maximum amount of power.

Additionally, to ensure that the sample is getting a controlled amount of microwaves, a more homogeneous field is needed. A kitchen appliance microwave, like the one used in these experiments, produces an insufficiently homogeneous field. There are, however, potential improvements that can be made to an existing microwave. If the waves could be properly located, a waveguide (made out of copper or another reflecting metal) could be positioned in the microwave to bend and interfere with the waves as needed. One good use for the waveguide would be to reflect standing waves back onto themselves, the interference created a more constant. The price of consistency would be amplitude, as no such field created could match an antinode's strength. Samples could then be placed in such a waveguide. Another such guide could direct more waves at one area, increasing the direction and number of waves coupling to the sample.

Conclusions:

These initial results are encouraging, as they demonstrate that it is possible to produce Bi2212 via microwave processing. There is a definite trend, with more Bi2212 being produced with increased reaction time, particularly on the exterior of the bulk samples. However, these experiments should be repeated with larger numbers of batches

and longer reaction times. Screening could be overcome by regrinding a microwaved sample, pressing it back into pellet form, and re-reacting it. During reaction times longer than half an hour, a method must be developed to safeguard the microwave generator without sacrificing the amount or radiation or power reaching the sample. In addition, related research should be done to better determine the physics of microwave/material interaction, as well as basic research on fundamental material properties of reacted and unreacted Bi2212.

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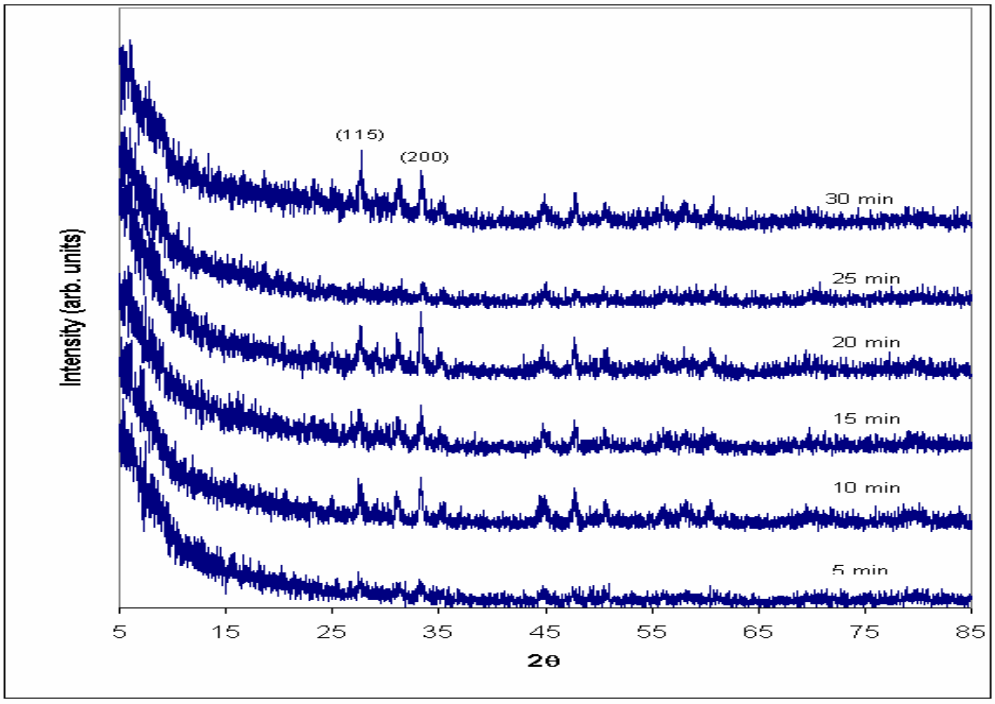
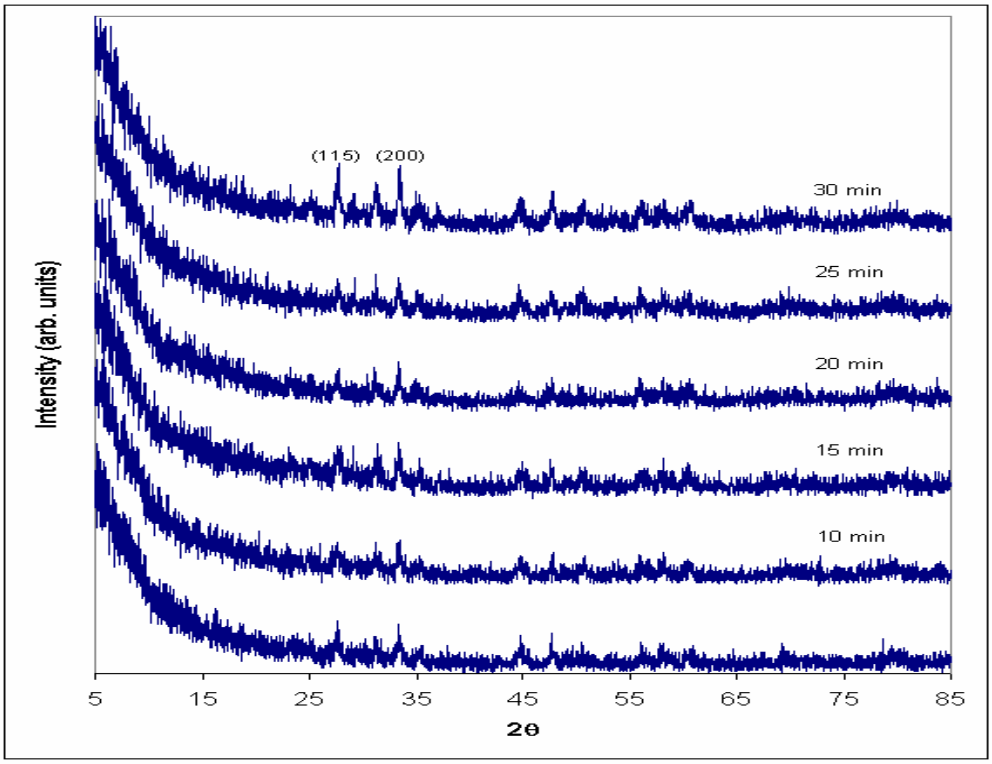
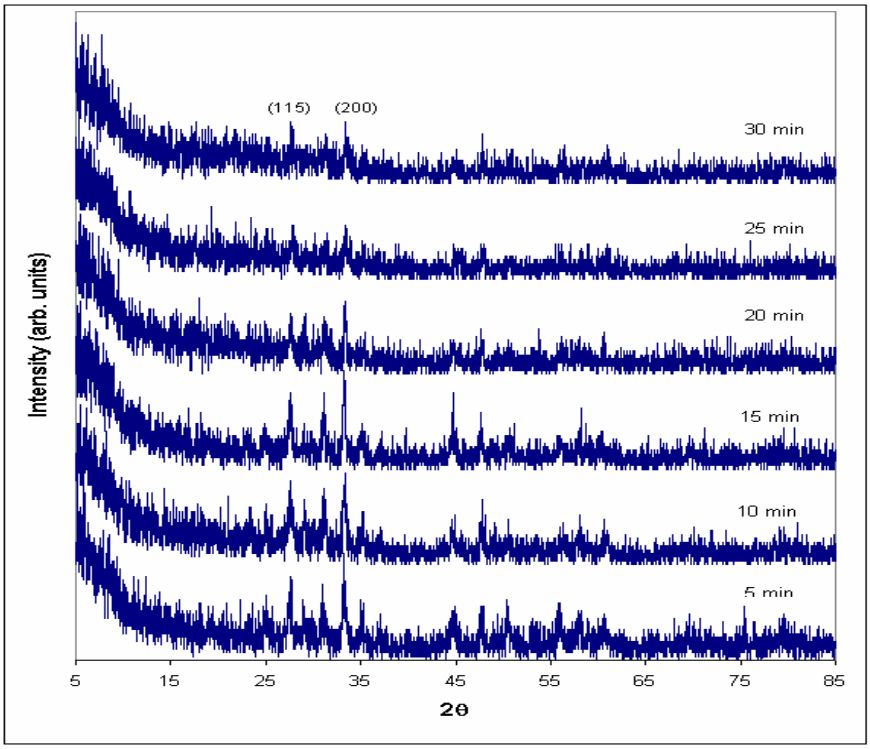
Appendix: Figures

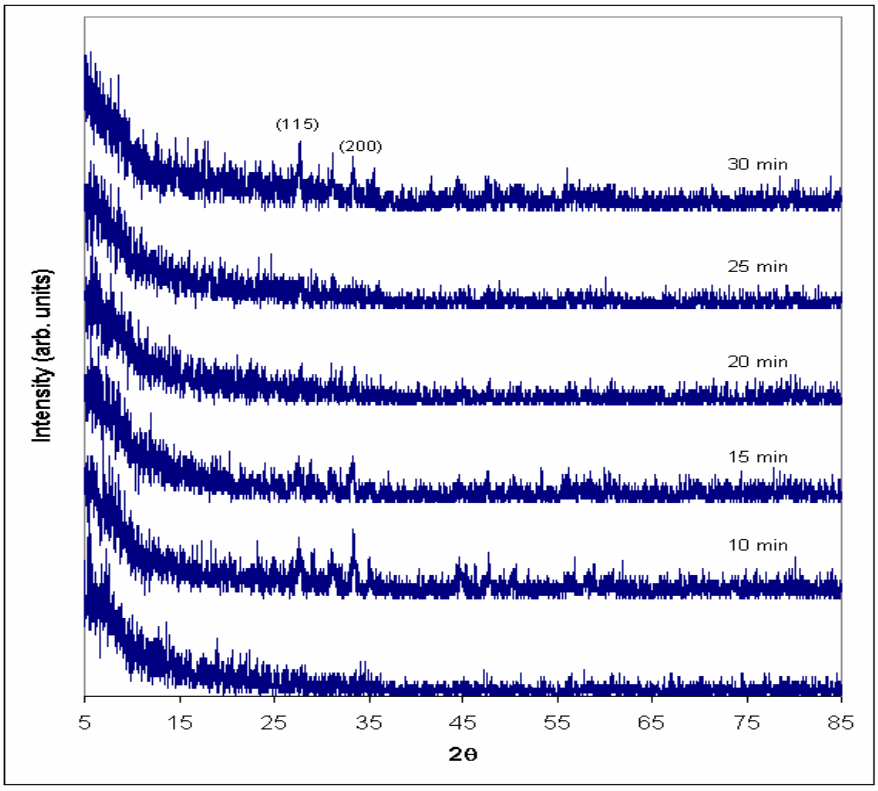
Figure 1 (top) and Figure 2 (bottom): "A" and "B" run XRD data, respectively. Both figures demonstrate a trend of increasing 2212 as a function of time. Notice the especially dominant peaks at 27 and 33, indicative of 2212. Other peaks are different oxides, such as Cu-Sr oxides.





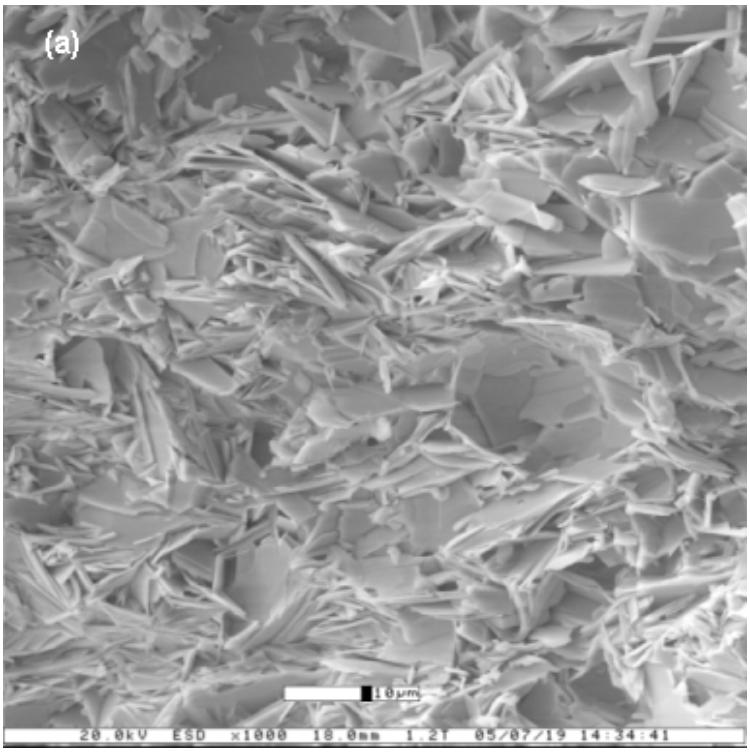
Below: Figures 3a and 3b, the exterior and interior respectively of six pellets run from 5-30 minutes.





Figures 4a and 4b, ESEM photography. 4a: 2212 crystalline microstructure in a conventionally processed pellet. 4b: the packed powder found inside a microwaved pellet. No indication of crystal growth was

found.



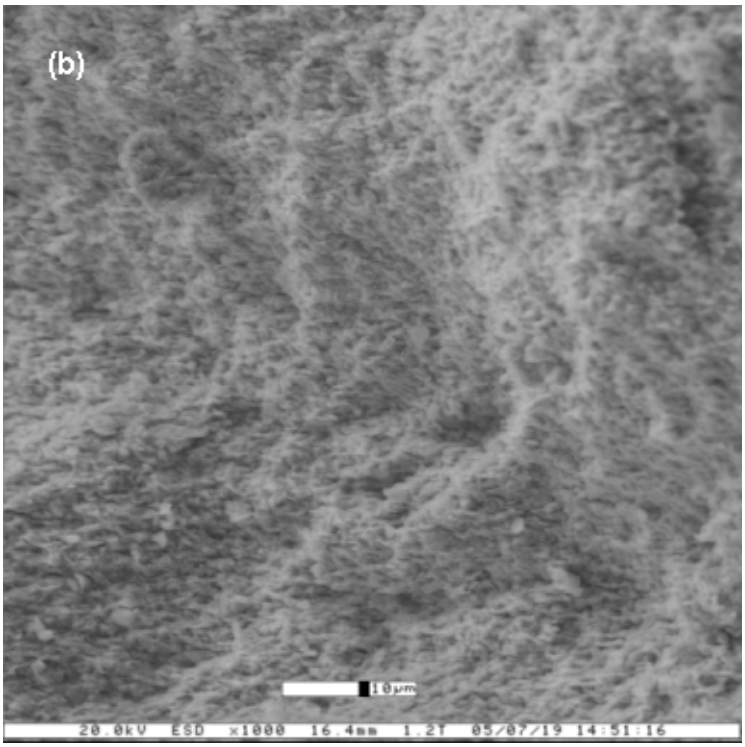
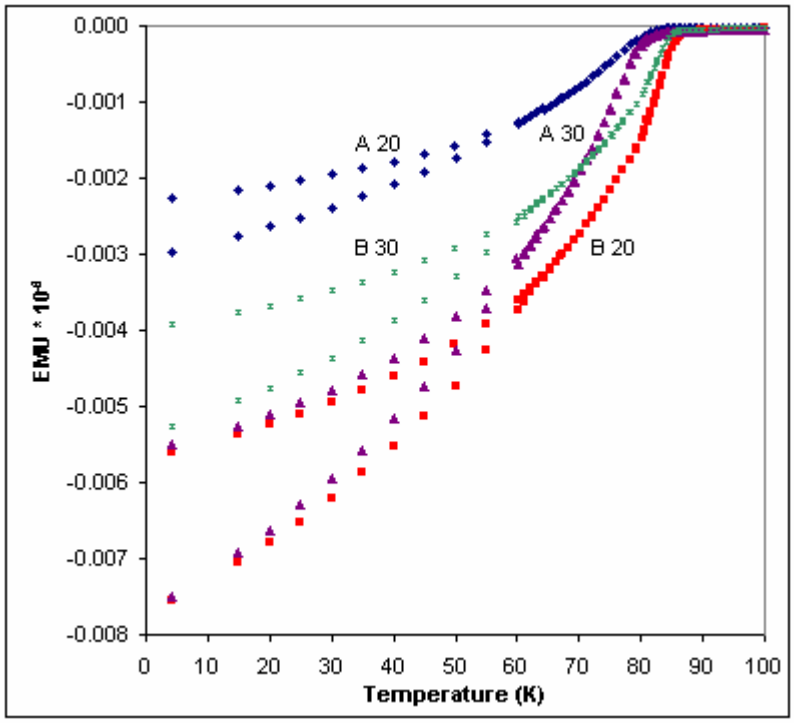


Figure 5: SQUID data. A20 means "Batch A, 20-minute pellet," and so forth. There is little visible hysteresis, suggesting a poor signal due to interference from lots of unreacted, non-superconducting product.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