Keywords
superconductor,
multilayered
packaging,
cofired ceramics,
YBCO

Deposition and Single-Step Processing of YBCO Thick Films for Multilayered Electronics

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Abstract

The goal of this project was to successfully cofire a screen-printed yttrium barium copper oxide (YBCO) superconductor onto a low-temperature cofired ceramic (LTCC) substrate. The purpose was to investigate the compatibility of thick-film, high-temperature superconductors with multilayered ceramic (MLC) packages for cryogenic applications. Paste consisting of standard organics and YBCO powder of -325 mesh particle size was screen-printed onto Dupont 951 Green Tape. The system was cofired at temperatures ranging from 925°C to 975°C. The quality of the cofired system was characterized in several ways: Meissner diamagnetism, scanning electron microscopy, x-ray diffraction, and AC susceptibility tests were performed to determine the superconducting capability of the system. Samples cofired at 950°C retained some superconductivity after firing and showed the best compromise between sintering and degradation.

1. Introduction

Many of today's electronics depend on multilayered ceramic (MLC) packaging technology.[1] This technology allows a circuit to be constructed in three dimensions and consists of a process in which metallic conductor film is screen-printed onto a ceramic substrate, the printed substrates are stacked one on top of another, and the system is cofired.[2] An electronic package suitable for a variety of applications is the result.

Two important types of MLC substrates are high-temperature cofired ceramics (HTCC) and low-temperature cofired ceramics (LTCC).[1] The former and more outdated substrate uses a ceramic fired at high temperatures with a low-conductivity refractory metal as a conductor. The latter was developed because high-conductivity metals cannot be fired to temperatures required for sintering HTCC substrates. Important properties of LTCC substrates include low dielectric loss and the capability of being cofired with high-conductivity conductors.[1]

High-temperature superconductors (HTS), such as yttrium barium copper oxide (YBCO), are being incorporated into microwave/RF devices because of their low resistivity.[2] Thick-film YBCO is not used as a standard conductor with LTCC substrates, but the incorporation of YBCO with LTCC-based MLC packages constitutes an interesting approach to making MLC devices.

Ceramic high-temperature superconductors, though nonmetallic, meet a key requirement for MLC conductors: excellent electrical conductivity. This project investigated HTS materials as printed conductors in order to improve the conductivity of circuitry in MLC packages.

The technology of cofired MLC packages is based on the ability to cofire the conductor and the substrate without harming their respective properties. Therefore, the first step in this investigation was to demonstrate that YBCO could be cofired with a suitable, low-loss LTCC substrate.

The following is a list of objectives for the investigation:

- Deposit superconductor thick film onto unfired dielectric tape
- Evaluate the effects of conventional processing on substrate/HTS system
- Characterize the samples
- Optimize the processing parameters

2. Experimental Procedure

A screen-printable paste was developed using $YBa_2Cu_3O_{7-x}$ (YBCO) powder, a common superconductor compound, and standard organics. The YBCO powder (-325 mesh) was manufactured by SCI Engineered Materials. The organics were acetone, Heraeus RV-912 thinner, Heraeus RV-914 binder, and Sigma-Aldrich Menhadden fish oil. A silk screen and hand-squeegee were used to print a 1 in x 1 in square pattern of the paste onto the substrate.

The LTCC tape used for this experiment was DuPont 951 Green Tape with a 10 mil thickness. To increase thickness, a Dake press was used to laminate unfired tapes together.

A Thermolyne 1400 tabletop box furnace with manual temperature control was used for the cofiring operation. Due to the oxygen-sensitive nature of YBCO, the furnace was equipped with an oxygen lance that entered the furnace through a small opening in the door.

The samples were comprised of four layers of YBCO printed onto a substrate consisting of three laminated tapes. A drying step was included between printing each YBCO layer. Experimentation consisted of an evaluation of the effect of different cofiring times and temperatures on the system. Figure 1 shows the firing profile.

Combinations of three peak times (5, 10, and 15 min.) and temperatures (925°C, 950°C, and 975°C) were used, giving a total of nine different combinations. Two samples were fired at each time/temperature combination. Processing times were controlled as closely as possible, but since a manual furnace was used, some variations of time from the nominal values occurred.

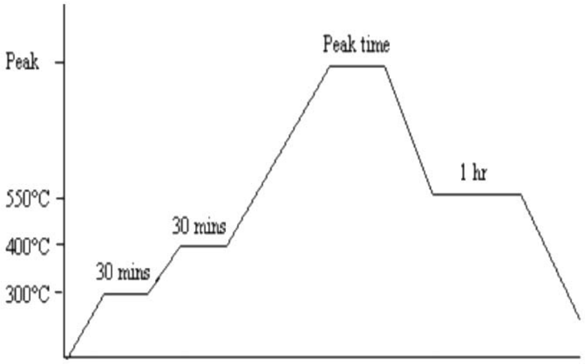

Figure 1. Firing profile for time/temperature investigation

3. Results and Discussion

3.1 Meissner Effect and Adhesion

Qualitative Meissner analysis was performed on all the samples cofired according to the above schedule. The testing consisted of scraping off particles from the film surface into a dish of liquid nitrogen and observing if the particles were repelled when introduced to a magnetic field (the Meissner effect). Table 1 shows the results. A “Yes” indicates the presence of the Meissner effect.

All samples fired at 925°C exhibited the Meissner effect, indicating that they were superconducting. Only the two samples held at 950°C for shorter times were superconducting. None of those fired at 975°C exhibited this effect. The sample fired at 975°C for 15 minutes yielded no powder for analysis because it was very hard and well-bonded to the substrate. From this qualitative analysis, it appeared that the lower time/temperature combinations provided the best results for superconductivity.

Temperature also appeared to be proportional to hardness and adhesion of the film. At 925°C, powder was readily removed when scraped for Meissner testing. In contrast, it was very difficult to get any part of any film fired at 975°C to separate from the tape. This resistance to scratching was attributed to better sintering at higher temperatures. Unfortunately, higher temperatures, while providing good bonding

Table 1. Results of Meissner test

	Time (min)		
Temperature(°C)	5	10	15
925	Yes	Yes	Yes
950	Yes	Yes	No
975	No	No	-

in the film, had a negative effect on the superconducting properties, as discussed.

A theory was devised relating the opposite effects on adhesion and diamagnetism to the four layers of YBCO paste that were deposited. At lower temperatures, the first couple of layers acted as a barrier to the glassy phase coming through from the substrate, leaving a poorly bonded pure-phase YBCO layer on top. At higher temperatures, sintering was driven at much faster rates and the glassy phase from the substrate was able to creep up and contaminate all four YBCO layers. Further research into this theory was carried out with scanning electron microscopy.

3.2 Microscopy

Microscopy was performed using a Jeol scanning electron microscope. The use of SEM provided a number of interesting details about the structure. In Figure 2, the microstructural evolution for samples held at peak temperature for 10 minutes is shown.

In Figure 2a, unsintered YBCO particles on the order of 1mm diameter are shown. Figure 2b reveals that these particles formed necks by 925°C. Figure 2c shows substantial coarsening of YBCO particles at 950°C. Finally, Figure 2d reveals very large grains at 975°C.

The microstructure of samples fired at 925°C was fairly uniform. Some cracks were visible under 2000x magnification, leaving islands of isolated material with approximate diameter of 500 nm. These cracks had a width of approximately 1µm. At 950°C, the islands were still present; however, the crack width was much smaller and barely visible at 2000x magnification. At 975°C, no cracks were visible.

As shown in Figure 2d, samples fired at 975°C contained very large grains, but some of these large regions appeared to be glassy. As time and tempera-

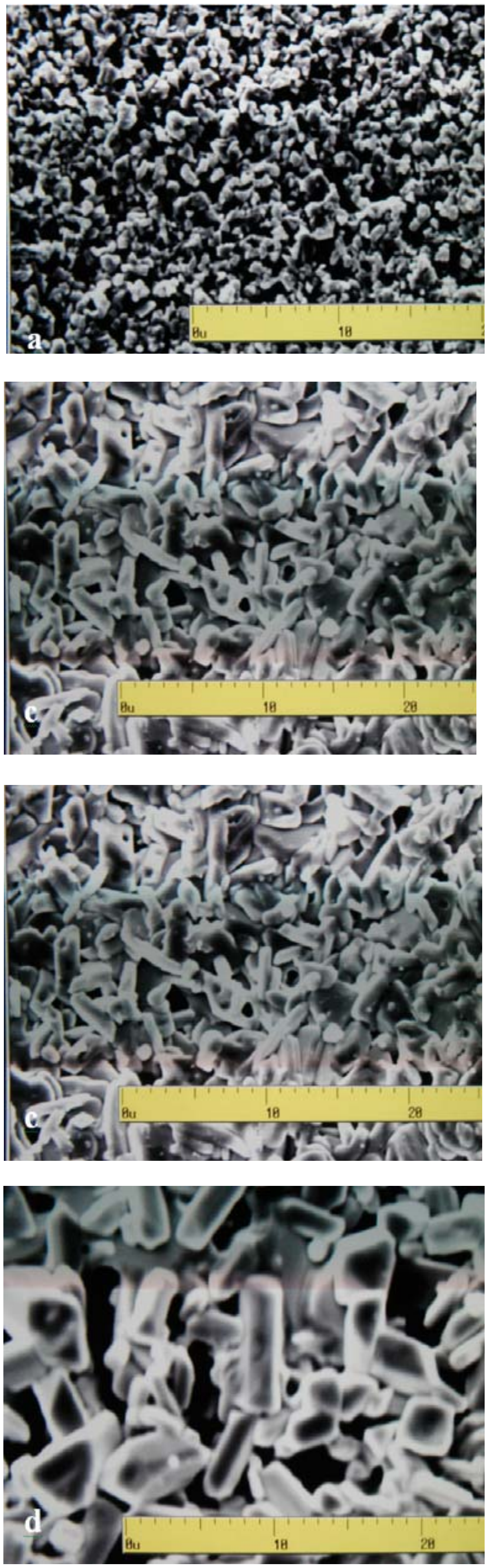

Figure 2. Difference in microstructure at various temperatures. The scale is in microns. (a) Unfired YBCO layer. (b) 925°C, 10 min. (c) 950°C, 10 min. (d) 975°C, 10 min.

ture were increased, these regions grew and became more abundant within the microstructure.

The dielectric tape contained alumina and glass frit, the latter of which was used to lower the sintering temperature. Films cofired on this substrate at 975°C had a glassy appearance and did not easily yield particles from scraping for the Meissner test. This effect was attributed to the glass frit interacting with the YBCO particles, as shown above. The same glassy phase was not observed in the YBCO samples fired at 925°C.

3.3 X-ray Analysis

X-ray powder diffraction was performed on the surface of YBCO films using a Scintag XDS 2000 diffractometer. Figure 3 shows the diffraction peaks for various samples. These peaks change with time and temperature, indicating crystallographic evolution of the film.

The sample held at 925°C for 5 minutes (Figure 3b) produced a diffraction pattern closely resembling that of phase-pure YBCO powder (Figure 3a). The diffraction pattern of the sample fired at 950°C for 10 minutes (Figure 3c) has the peak characteristics of YBCO, but peaks from another phase are visible in the region of 42-46°. The diffraction pattern of the sample fired at 975°C for 15 minutes (Figure 3d) is very cluttered and presents many non-YBCO peaks.

The diffraction data suggest that increasing time and temperature caused degradation of the YBCO film. This result was in agreement with the Meissner test and microscopy, which suggested that the lack of the Meissner effect correlated with the presence of a non-YBCO glassy phase at higher times and temperatures.

3.4 AC Susceptibility

The AC susceptibility measurements were performed on samples fired for five minutes at each temperature. Figure 4 shows the variation of m´, the real part of susceptibility, with temperature at a frequency of 100 Hz.

The superconducting transition occurs when m´ deviates from zero, indicating the expulsion of magnetic flux from superconducting regions.[3] Figure 4 shows that the transition temperature of the samples fired at 925°C and 950°C was approximately 92K, the value expected for pure YBCO, and the transition of the sample fired at 975°C was approximately 86K.

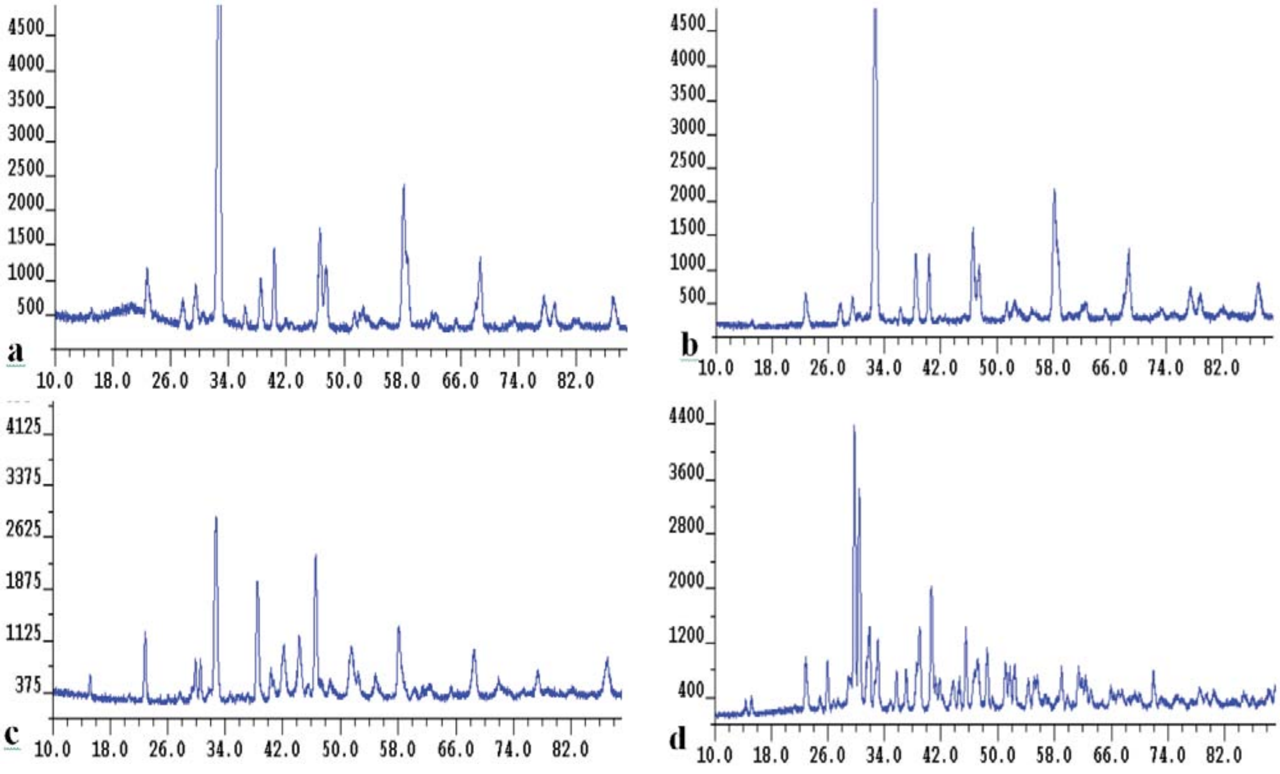

Figure 3. Diffraction patterns for (a) Pure YBCO and samples fired at (b) 925°C, 5 min. (c) 950°C, 10 min. and (d) 975°C, 15 min.

While all samples showed some degree of diamagnetism, the sample fired at 950°C had the most significant value of m´ at lower temperatures, indicating better superconducting properties. The sample fired at 975°C showed a poorer response than the other two samples.

4. Conclusions

The evidence suggests that cofiring YBCO and DuPont 951 Green Tape, while not resulting in an optimum system, is feasible. Cofiring at 950°C produced the best compromise between film sintering/adhesion and the preservation of the YBCO film properties. Firing at a higher temperature resulted in a severely degraded YBCO layer, as shown by x-ray diffraction and microscopy. This degradation translated into inferior superconducting properties, demonstrated by the Meissner test. Firing at a lower temperature produced a film that was superconducting but lacked the sintering and adhesion required for MLC packaging.

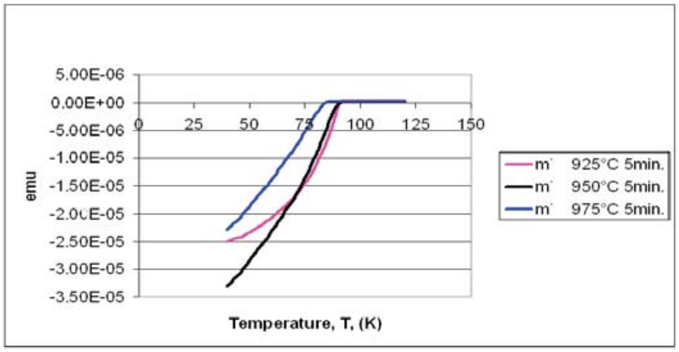

Figure 4. AC susceptibility measurements for samples fired at 5 minutes

5. Future Work

This work has demonstrated that YBCO can be cofired with a commercially available, unfired dielectric tape with some preservation of superconducting properties. An area of extension for this work includes protecting the YBCO film from degradation. Protection could be achieved by printing a buffer layer onto the tape prior to firing, thus restricting interaction between the superconductor and glass from the tape.

Acknowledgements

The authors thank Patrick Smith, Michael Smith, and John Crumpton of DuPont; Jesus Calata and Zachary Zhang, graduate students at Virginia Tech, for providing materials and insight. The authors also thank Drs. Guangbin Wang and Gordon Yee of Virginia Tech for assistance with susceptibility measurements and Dr. Marie Paretti of Virginia Tech for project guidance.

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