Properties and Applications of Thick Film High Temperature Superconductors

Timothy W. Button, Paul A. Smith, Geoffrey Dolman, Carl Meggs, Stephen K. Remillard, James D. Hodge, Stuart J. Penn, and Neil M. Alford

***Abstract*—Melt processed $YBa_2Cu_3O_x$ thick films display low surface resistance, moderate performance in fields and can be applied to three-dimensional (3-D) substrates with ease. The processing and properties of such films are described. Possible applications are examined and prototype devices are described. These include high Q, low frequency resonators for cellular communications filters, low phase noise oscillators, magnetic resonance imaging receiver coils, low noise magnetic shields, coils, flux transformers, and antennas.**

I. Introduction

For some applications of high temperature superconductor (HTS) films it would be advantageous for the HTS layer to be applied over large areas and curved surfaces. Such applications include high Q resonators, antennas, large magnetic resonance imaging (MRI) receiver coils, magnetic shields, coils, and certain flux transformer designs. HTS thin films may be unsuitable if not impossible to manufacture in many of the geometries required and HTS thick films, which can be applied to curved surfaces and over large areas, offer a viable alternative. Such films can have a current density of around 2000 A cm^{-2} at 77 K, possess a far better resistance to magnetic fields than bulk sintered HTS, and have a surface resistance, R_s, of approximately 2 mΩ (10 GHz and 77 K). In this paper we examine possible applications where thick film $YBa_2Cu_3O_x$ (YBCO) could demonstrate a significant improvement over other materials. Particular emphasis is placed on the RF and microwave applications although mention is also made of some of the important magnetic and dc applications.

II. Fabrication

All the devices described in this paper were made by thick film methods [1], [2], involving depositing $YBa_2Cu_3O_7$ on to a 3 mol % yttria stabilized zirconia substrate. First, the superconducting powder was made by mixing $BaCO_3$, CuO, and Y_2O_3 together and heating to ~900°C and then grinding the mixture to a fine powder. The powder was made into a thick ink by mixing with polymers and solvents on a three roll mill. The ink was then deposited onto the zirconia substrate—which could be in the form of wires, coils, tubes, or plates—by screen printing or doctor blading. The coated substrates were then sintered in an oxygen atmosphere at temperatures of around 1000–1050°C. Zirconia substrates were chosen because of their high strength (~800 MPa) and toughness (6 $MPam^{1/2}$). Tolerance to shock and vibration is excellent thus avoiding a key concern with regard to some applications. Although there is a reaction between the substrate and the superconductor which forms mainly barium zirconate this reaction layer does not impair the superconducting properties and does in fact provide an excellent adhesive bond. After firing the thick film body was masked and patterned as necessary.

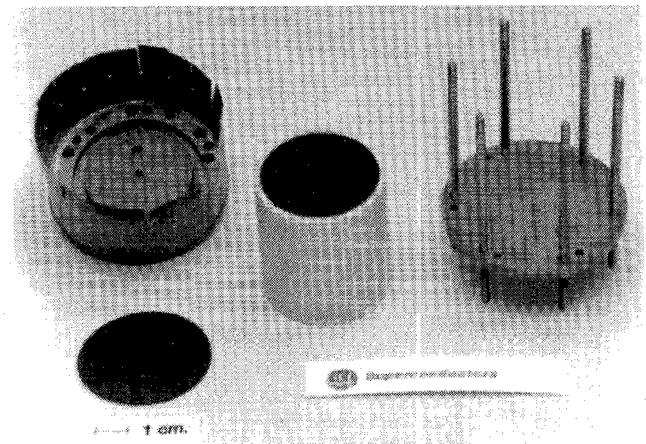


Fig. 1. 10 GHz YBCO thick film cavity (dismantled).

III. Properties and Applications

A. High Q TE_{011} Cavities

At 77 K thick film YBCO has a surface resistance less than copper for frequencies ≤50 GHz [1], and thus the use of the HTS material can be advantageous in certain RF and microwave applications. Thick film YBCO cavity resonators operating in the TE_{011} mode have been constructed. A cavity resonating at 5.66 GHz had an unloaded Q of 715 000 at 77 K, which corresponds to $R_s = 1.09$ mΩ [3]. A 10 GHz cavity has been made to form part of the local oscillator circuit of a cryogenic downconverter system in a collaborative project supported by the U.K. Department of Trade and Industry. The

Manuscript received February 28, 1996; revised March 19, 1996. This work was supported by the U.K. Department of Trade and Industry and Defence Research Agency, the U.S. Department of Commerce, and the HTSSE Programme.

T. W. Button, P. A. Smith, G. Dolman, and C. Meggs are with the IRC in Materials for High Performance Applications, University of Birmingham, Birmingham B15 2TT, U.K.

S. K. Remillard and J. D. Hodge are with the Illinois Superconductor Corporation, Mt. Prospect, IL USA.

S. J. Penn and N. M. Alford are with the SEEIE, South Bank University, London, U.K.

Publisher Item Identifier S 0018-9480(96)04799-0.

TABLE I
PHASE NOISE OF 7.5 GHz OSCILLATORS

Oscillator System	Measurement Temperature (K)	Phase Noise ($dBcHz^{-1}$)	
		1kHz offset	10kHz offset
Cu Cavity	300	-90	-120
Cu Cavity	77	-95	-124
HTS Cavity	77	-108	-135

cavity is shown in Fig. 1. Unloaded Q values of over 10^5 have been measured for the cavity at 77 K, and the complete oscillator, which also incorporates a GaAs HEMT, had phase noise values of -94 and $-120\,dBcHz^{-1}$ at 10 kHz and 100 kHz offsets, respectively, from the carrier frequency [4].

Improvements in close-to-carrier noise of a simple 7.5 GHz oscillator incorporating a thick film HTS resonator have also been measured. The oscillator circuit consisted of an GaAs MESFET amplifier, 3 dB feedback power splitter, a variable attenuator, and a phase shifter with either a TE_{011} mode copper cavity or a high Q, HTS thick film replacement. The TE_{011} cavities each comprised a cylindrical barrel and a pair of closing end plates. Unloaded Q factors (Q_0) for the copper and YBCO cavities were measured to be 65 000 and 500 000, respectively, at 77 K. At a lower temperature of 64 K, Q_0 of the YBCO cavity increased to over 10^6, indicating that the R_s of the YBCO was reduced by a factor of 2. Phase noise measurements were carried out with the entire oscillator circuit at the measurement temperature, either 300 or 77 K, and are summarized in Table I. It should be noted that these phase noise measurements were limited by the noise floor of the measurement system, but the results demonstrate the potential use of high Q HTS resonators in low phase noise systems.

The surface resistance of the thick film materials has been measured at a number of frequencies in the range 5–50 GHz [1], [3]–[5]. In general, these measurements have been made using TE_{01n} cavities constructed either wholly or partly of YBCO thick film elements. The dependence of R_s on frequency is shown in Fig. 2 and demonstrates that the surface resistance exhibits an approximately squared dependence. For comparison, typical data from epitaxial thin films and bulk YBCO are also plotted on Fig. 2.

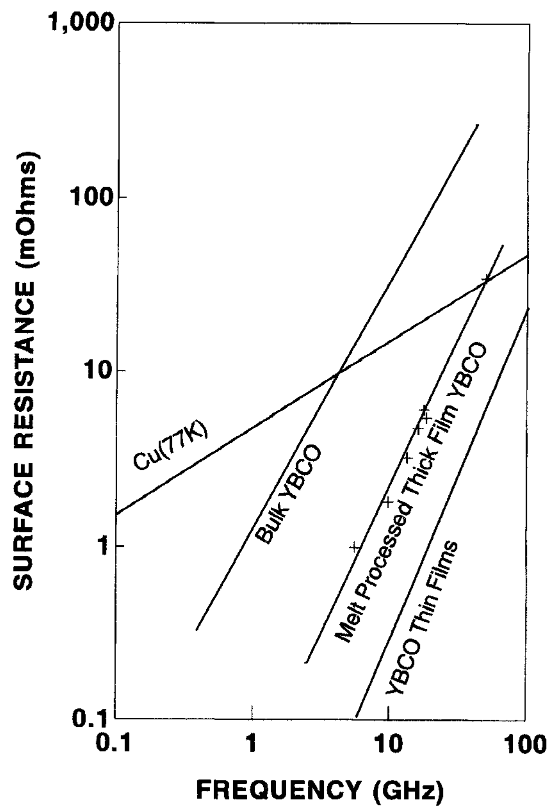


Fig. 2. Frequency dependence of surface resistance for YBCO thick films, bulk materials, and thin films.

B. Lower Frequency Resonators

For lower frequency applications, around 1 GHz, the TE_{011} resonator is not a convenient size to cool, and certainly a series of such resonators constructed to make a filter would not be practical. One alternative geometry would be to use HTS coaxial elements with either a normal metal or HTS outer shield. We have manufactured these and other electrically small, three–dimensional (3-D) resonant structures from thick film YBCO and measured Q values over 86 000. Filters constructed from such resonators demonstrate low insertion loss and good rejection characteristics [6]. A key performance requirement in this application is a low dependence of Q on RF power which can cause nonlinearities in the device and can drastically affect the intermodulation performance [7]. The RF power dependence and excellent intermodulation performance for the thick film materials are shown in Figs. 3 and 4, respectively. Filters incorporating similar thick film resonant elements are currently undergoing field trials.

C. Antennas and MRI Components

Planar antennas [8] and superdirective arrays [9] operating at less than 1 GHz have been demonstrated in thick films. The

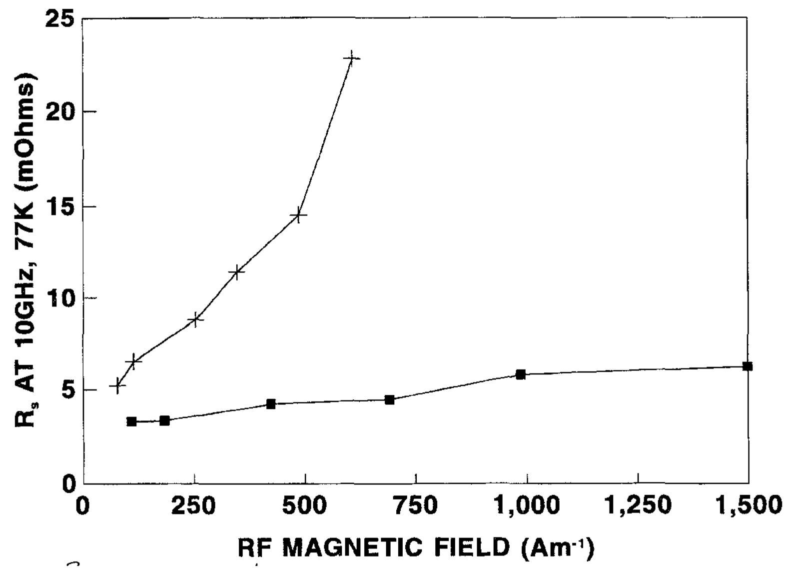


Fig. 3. RF power dependence of standard YBCO (+) and improved melt processed thick films (■).

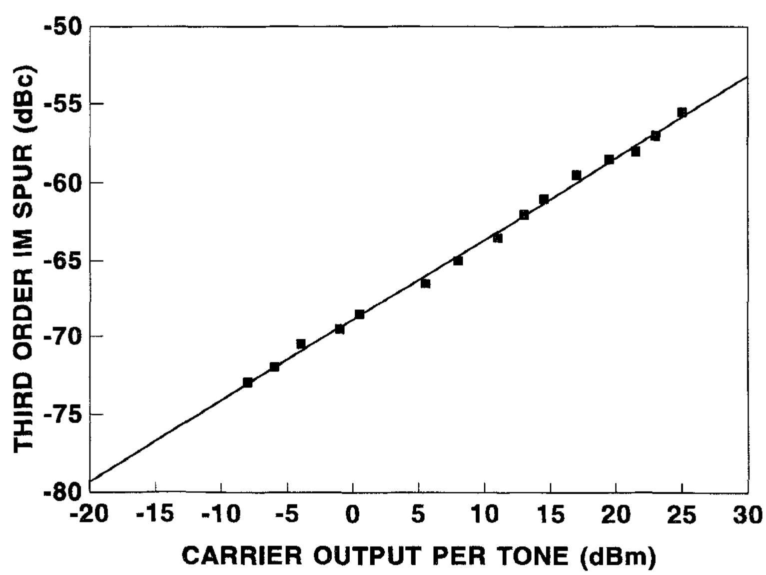


Fig 4. Intermodulation performance of 16-pole GSM receive filter incorporating YBCO thick film elements, measured at 77 K.

reduced loss in the superconductor means that the antenna may be made electrically small without a drastic loss in efficiency. At 500 MHz, a gain of around 6 dB is measured at 77 K for loop and dipole antennas in comparison with copper counterparts. It should be noted that for this application the construction of the matching networks also used thick film HTS. Antenna arrays incorporating patterned HTS thick films on both sides of a 4″ × 4″ substrate are shown in Fig. 5.

An example of a large area, low frequency coil is a receiver coil used in MRI. The use of HTS coils as receiver coils was first suggested by Hall *et al.* [10] who showed an improvement in the signal-to-noise ratio (SNR) of a coil for use in a field of 0.15 T (6.67 MHz). For this application there are two main sources of noise. Coil noise which is influenced by its resistance, and body noise which is due to the electrical conductivity of the body. The body noise increases with frequency, so that if measurements are made at low frequency, i.e., low field, with the correct geometry, the coil noise can be made to dominate. The noise power due to the coil is proportional to 4 kTR, where T is temperature and R is the resistance of the coil. Therefore to reduce the noise, the resistance, temperature or both must be reduced. It should be noted that for ac signals the resistance of the superconductor is not zero but is far less than the resistance of normal metals at the low frequencies used for MRI. We also note that as well as increasing the SNR, the use of a HTS coil also increases the Q as $Q = \omega L/R$, so that reducing R also increases sensitivity. Various designs of HTS thick film MRI receiver coils are currently being examined.

D. Magnetic Properties and Applications

HTS thick film materials can also prove useful in non-RF applications. Superconductors are perfect diamagnetic shields.

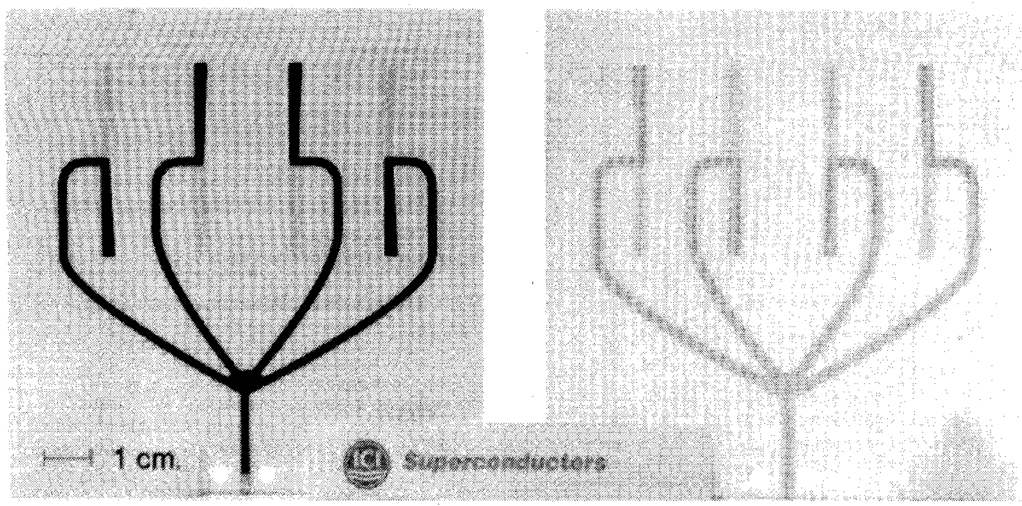


Fig. 5. Antenna arrays on 4″ × 4″ double-sided YBCO thick film substrates.

There are three main issues regarding shields. The first is shielding out background noise and the earth's field. The earth's field is approximately 0.05 mT and there is little problem in constructing thick film shields capable of this level of screening. In fact, the shields made by thick film methods will screen between 0.5 to 1 mT at 77 K [11]. The second is the issue of flux creep and here the behavior of thick film shields has been investigated by Muirhead *et al.* [12] who found that the current density of the shields was of the order 600 A cm^{-2}. For a shielded area of a square centimeter, a creep rate of 10^{-5} flux quanta per second can be shown to correspond to 2×10^{-20} V and, at the lowest voltages, the measurements suggest that the flux creep is adequately low for shield applications. The third issue is the manufacturing route and choice of material. The flux creep performance of YBCO has been demonstrated to be superior to that of BSCCO in our experiments and the method of application onto zirconia substrates appears highly successful. Coatings can be applied to both inside and outside surfaces thereby increasing the performance of the shields.

Exceptionally low noise is required for certain applications where $1/f$ noise and stochastic variation of flux pose problems. In a SQUID, for example, it is clearly important to determine the flux noise in both the thin film component and the screening system ie the shield. The noise properties of YBCO-$SrTiO_3$-YBCO thin film multi-loop magnetometers enclosed within YBCO thick film shields has been measured at 77 K by Ludwig *et al* [13] and found to be very low at 37 $fTHz^{-1/2}$ and 18 $fTHz^{-1/2}$ at 1 Hz and 1 kHz respectively.

Flux transformers and gradiometers have been manufactured using thick film processing techniques and results on both planar and 3-D structures are encouraging. A planar flux transformer consisting of two loops trapped a flux of 25 mG. In an analysis of the creep behavior it was determined that the device worked well down to 10 mHz with a circulating current of 45 mA. Tests at 25 mA, representing a field of 1.5 μT, demonstrated that the device was adequate for most applications. Crossunders using through-substrate vias have also been demonstrated in both planar and 3-D geometries.

IV. Conclusion

The manufacture of high quality thick film artefacts has been described, and several useful devices have been demonstrated. The properties of epitaxial thin film materials will always be potentially superior to those of polycrystalline thick films. However, the main advantages of the thick film materials result from the ability to produce 3-D and large area structures with properties which are more than adequate for many applications. These type of structures cannot be made by thin film techniques.

Thick film resonators have been shown to possess high Q factors, low phase noise, excellent intermodulation performance and reasonable RF power dependence. Thick film shields were seen to have extremely low flux noise characteristics, also useful for the thick film flux transformers and gradiometers. The flux transformers and gradiometers were found to work well down to 10 mHz. Large area, low frequency antennas have been manufactured including MRI receiver coils. The outlook for the application of HTS thick film materials in areas exploiting their large area or 3-D capabilities is encouraging, and cellular communication filters incorporating this technology are already in production.

Acknowledgment

The authors would like to thank their colleagues at the University of Birmingham, U.C. Berkeley, and GEC-Marconi, and A. Abdelmonem, M. Beik, and R. Lithgow of the Illinois Superconductor Corporation.

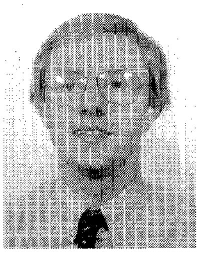
References

[1] N. M. Alford *et al.*, *Nature*, vol. 349, 1991, p. 680.
[2] T. W. Button *et al.*, *IEEE Trans. Magn.*, vol. 27, p. 1434, 1991.
[3] T. W. Button and N. M. Alford, *Appl. Phys. Lett.* vol. 60, p. 1378, 1992.
[4] W. A. Phillips *et al.*, *IEEE Trans. Appl. Superconduct.*, vol. 5, pp. 2283–2286, 1995.
[5] B. A.Tonkin and Y. Proykova, *Applied Superconductivity*, vol 1., H. C. Freyhardt, Ed. Oberursel, Germany: DGM Informationsgesellschaft mbH, 1993, pp. 613–616.
[6] A. Abdelmonem, private communication
[7] S. K. Remillard *et al.*, *Proc. SPIE 1995 Int. Symp. Opt. Sci., Engineering Instrum.*, July 1995, San Diego, CA.

[8] M. J. Lancaster *et al., IEEE Trans. Appl. Superconduct.* vol. 3, p. 2903, 1993.
[9] M. J. Lancaster *et al., Supercond. Sci. Technol.*, vol. 5, p. 277, 1992.
[10] A. S. Hall *et al., Magnetic Resonance in Medicine*, vol. 20, p. 340, 1991.
[11] D. B. Opie *et al., IEEE Trans. Appl. Superconduct.*, vol. 3, p. 189, 1993.
[12] C. M. Muirhead, F. Wellhofer, T. W. Button, and N. M. Alford, *IEEE Trans. Appl. Superconductuct.*, vol. 3, p. 1695, 1993.
[13] F. Ludwig *et al., Appl. Phys. Lett.*, vol. 66, pp. 1418–1420, 1995.

Timothy W. Button received the B.Tech. (honors) and Ph.D. degrees in materials science and technology from the University of Bradford, U.K., in 1978 and 1983, respectively.

He is now a Senior Research Fellow in the Interdisciplinary Research Centre in Materials for High Performance Applications at the University of Birmingham. Prior to 1994 he was Senior Research Scientist at Imperial Chemical Industries (ICI) in a group developing applications of thick film high temperature superconducting (HTS) materials including antennas, high Q cavities and resonators. He led the development of the HTS thick film technology to the point where it is now being used commercially. He has also worked on composite refractory materials and hydrogen storage alloys and has interests in a wide range of materials areas including the fabrication and processing of bulk and thick film ceramics, microstructure-property relationships, and component fabrication and characterization. His current research in functional materials include HTS, ferroelectrics and solid oxide fuel cells, with a particular emphasis on developing materials for applications.



Paul A. Smith received the M.Sc. degree in microwave engineering from Bradford University, U.K., in 1989, and the Ph.D. degree in the microwave properties of HTS in 1991 from the University of Manchester Institute of Science and Technology (UMIST), U.K.

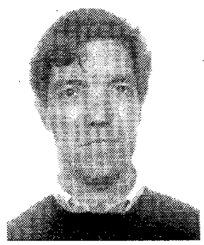
From 1991 to 1993 he was a Research Fellow in the Department of Electrical Engineering and Electronics at UMIST, and at ICI in 1993 before joining the University of Birmingham in 1994. He has published in the field of microwave HTS and microwave dielectrics and is currently working on the preparation dependent properties of thick film HTS.

Goeffrey Dolman is a Research Scientist in the Interdisciplinary Research Centre in Materials for High Performance Applications at the University of Birmingham and his main interests are in the fabrication and characterization of ceramic materials. This involves the development of materials in which both the functional and structural properties are tailored for specific applications. He joined the University in 1994 after a varied 15–year career in the ceramic and chemical industries and has been a key figure in the development of a diverse range of materials and processing technologies including polymer synthesis, high strength, low-defect cement, and high temperature, and high strength ceramics.

Carl Meggs works in the Interdisciplinary Research Centre in Materials for High Performance Applications at the University of Birmingham. His primary interests are in the area of thick film colloidal inks and the development of coating and printing technologies. He has over six years experience in the ceramics and electronics industries and joined Tioxide Specialties Ltd (part of ICI) in 1992 specifically to develop the thick film processes for HTS materials. Since joining the University in 1994 his interests have broadened to include the manufacture of prototype components in the HTS, piezoelectric, and fuel cell areas.

Stephen K. Remillard was born in Galesburg, IL, in 1966. He received the B.S. degree in physics from Calvin College, Grand Rapids, MI, in 1988, and the M.S. and Ph.D. degrees in physics from the College of William and Mary, Williamsburg, VA, in 1990 and 1993, respectively.

His most recent efforts have been focused on the application of HTS films to commercial radio frequency devices. In 1994 he joined Illinois Superconductor Corporation, where he has been developing RF surface resistance measurement techniques for use in optimizing high-temperature superconductor film processing. He is currently managing an effort to develop superconducting RF filters with improved power handling.

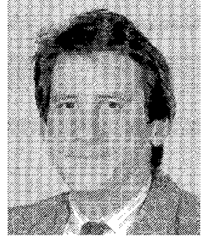


James D. Hodge received the Ph.D. degree in materials science and engineering from the Massachusetts Institute of Technology, Cambridge, MA, in 1980.

He is currently Chief Scientist at Illinois Superconductor Corporation, Mt. Prospect, IL, where he is principally engaged in the commercialization of high-performance RF components incorporating high-temperature superconductors.

Stuart J. Penn received the B.Sc. degree (honors) in physics and the Ph.D. degree from the University of Liverpool, U.K., in 1998 and 1991, respectively.

From 1991 to 1993 he was a Researcher at ICI investigating applications of high temperature superconductors. He is a Research Fellow at South Bank University, London, U.K., where his main research interests are the RF and microwave properties of thick film superconductors and low loss dielectrics for communications applications.



Neil M. Alford was a Divisional Research Associate with ICI from 1981 to 1994. He was responsible for the superconductivity effort at ICI which resulted in the first HTS antenna, the first HTS generator and the lowest surface resistance thick film HTS material measured at microwave frequencies. He is now Professor of Physical Electronics and Materials at South Bank University, London, U.K., and leads a team examining superconductivity and dielectric materials.