

ADVANCED CERAMIC MATERIALS

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SPECIAL SUPPLEMENTARY ISSUE

Ceramic Superconductors



The 89th Annual Meeting of The American Ceramic Society was held in Pittsburgh, PA, on April 26-30, 1987. At this meeting, a technical session on Ceramic Superconductors was held; organized by David R. Clarke, IBM, this one-day session attracted over 1000 attendees. Based on the high level of interest on the part of the attendees, the decision was made to solicit additional papers and to publish these papers in a timely fashion. As a result, a Call for Papers was distributed to attendees and was subsequently mailed to all members of the Basic Science and Electronics Divisions. This Special Supplementary Issue of Advanced Ceramic MaterialsTM, our quarterly publication devoted to advanced ceramics, is the result of that special session and the response to the Call for Papers.

Rapid strides are being made in advances of superconducting ceramics and their processing to produce materials which exhibit superconductivity at reasonable temperatures. In order to obtain the rapid publication essential in a field which changes weekly, we have departed from our normal format for this periodical and have chosen to print camera-ready copy as submitted by authors.

David R. Clarke, IBM, and David W. Johnson, Jr., AT&T Bell Labs, agreed to serve as the Coordinating Editors of this issue. Authors sent their papers directly to them, and each paper was read and evaluated by a minimum of two people. Assisting in the evaluation efforts were George Onoda, IBM, Man Yan, AT&T Bell Labs, and a group of specially qualified readers when the subject matter required additional expertise. Each paper was evaluated and those included in this special issue were felt to be suitable for publication by the American Ceramic Society.

The editors of this issue have grouped the contributions into four general categories: Phase Equilibria, Processing and Fabrication, Properties and Characterization, and Theory. These categories are not always clear-cut, however, and it is particularly difficult to separate Processing from Characterization. When overlap occurs, it is often in these areas. In addition, readers are reminded that due to the rapidly changing nature of the field, some of the findings reported here are necessarily of a preliminary nature.

We plan to continue to keep our readers informed of new developments in ceramic superconductors via the regular, quarterly issues of Advanced Ceramic MaterialsTM. We welcome your contributions, support, and interest.

Dr. William J. Smothers, Editor

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SPECIAL ISSUE

Ceramic Superconductors

Advanced Ceramic Materials™ reports on the development, fabrication, and application of advanced ceramic and composite materials of technological and commercial potential.

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Table of Contents

The Development of High T_c Ceramic Superconductors: An Introduction D. R. Clarke	273
Section I. Phase Equilibria	293
Phase Compatibilities in the System Y_2O_3 -BaO-CuO K. G. Frase and D. R. Clarke	295
Phase Equilibria and Crystal Chemistry in the System Ba-Y-Cu-O R. S. Roth, K. L. Davis, and J. R. Dennis	303
950 °C Subsolidus Phase Diagram for Y_2O_3 -BaO-CuO System in Air G. Wang, S.-J. Hwu, S. N. Song, J. B. Ketterson, L. D. Marks, K. R. Poeppelmeier, and T. O. Mason	313
Section II. Processing and Fabrication	327
Powder Processing for Microstructural Control in Ceramic Superconductors M. J. Cima and W. E. Rhine	329
Preparation of Superconducting Powders by Freeze-Drying S. M. Johnson, M. I. Gusman, D. J. Rowcliffe, T. H. Geballe, and J. Z. Sun	337
Properties of Superconducting Oxides Prepared by the Amorphous Citrate Process B. Dunn, C. T. Chu, L.-W. Zhou, J. R. Cooper, and G. Gruner	343
Rapid Solidification of Oxide Superconductors in the Y-Ba-Cu-O System J. McKittrick, L.-Q. Chen, S. Sasayama, M. E. McHenry, G. Kalonji, and R. C. O'Handley	353
Fabrication of Ceramic Articles from High T_c Superconducting Oxides D. W. Johnson, Jr., E. M. Gyorgy, W. W. Rhodes, R. J. Cava, L. C. Feldman, and R. B. van Dover	364
Manufacture and Testing of High- T_c Superconducting Materials B. Yarar, J. Trefny, F. Schowengerdt, N. Mitra, and G. Pine	372
Sinter-Forged $YBa_2Cu_3O_{7-\delta}$ Q. Robinson, P. Georgopoulos, D. L. Johnson, H. O. Marcy, C. R. Kannewurf, S.-J. Hwu, T. J. Marks, K. R. Poeppelmeier, S. N. Song, and J. B. Ketterson	380
Problems in the Production of $YBa_2Cu_3O_x$ Superconducting Wire R. W. McCallum, J. D. Verhoeven, M. A. Noack, E. D. Gibson, F. C. Laabs, D. K. Finnemore, and A. R. Moodenbaugh	388

Thermal Spraying Superconducting Oxide Coatings	401
J. P. Kirkland, R. A. Neiser, H. Herman, W. T. Elam, S. Sampath, E. F. Skelton, D. Gansert, and H. G. Wang	
Plasma Sprayed High T_c Superconductors	411
W. T. Elam, J. P. Kirkland, R. A. Neiser, E. F. Skelton, S. Sampath, and H. Herman	
Large Area Plasma Spray Deposited Superconducting $YBa_2Cu_3O_7$ Thick Films	422
J. J. Cuomo, C. R. Guarnieri, S. A. Shivashankar, R. A. Roy, D. S. Yee, and R. Rosenberg	
Superconducting Oxide Thin Films by Ion Beam Sputtering	430
P. H. Kobrin, J. F. DeNatale, R. M. Housley, J. F. Flintoff, and A. B. Harker	
High T_c Y-Ba-Cu-O Thin Films Prepared by DC Magnetron Sputtering	436
B. Y. Jin, S. J. Lee, S. N. Song, S.-J. Hwu, J. Thiel, K. R. Poeppelmeier, and J. B. Ketterson	
Fabrication, Mechanical Properties, Heat Capacity, Oxygen Diffusion, and the Effect of Alkali Earth Ion Substitution on High T_c Superconductors	444
G. W. Crabtree, J. W. Downey, B. K. Flandermeier, J. D. Jorgensen, T. E. Klippert, D. S. Kupperman, W. K. Kwok, D. J. Lam, A. W. Mitchell, A. G. McKale, M. V. Nevitt, L. J. Nowicki, A. P. Paulikas, R. B. Poeppel, S. J. Rothman, J. L. Routbort, J. P. Singh, C. H. Sowers, A. Umezawa, B. W. Veal, and J. E. Baker	
Superconductivity and the Tailoring of Lattice Parameters of the Compound $YBa_2Cu_3O_x$	457
I-W. Chen, S. Keating, C. Y. Keating, X. Wu, J. Xu, P. E. Reyes-Morel, and T. Y. Tien	
Synthesis and Characterization of $YBa_2Cu_3O_{7-x}$ Superconductors	471
W. J. Weber, L. R. Pederson, J. M. Prince, K. C. Davis, G. J. Exarhos, G. D. Maupin, J. T. Prater, W. S. Frydrych, I. A. Aksay, B. L. Thiel, and M. Sarikaya	
High T_c Superconductivity in Y-Ba-Cu-O System	480
S. N. Song, S.-J. Hwu, F. L. Du, K. R. Poeppelmeier, T. O. Mason, and J. B. Ketterson	
Processing Study of High Temperature Superconducting Y-Ba-Cu-O Ceramics	492
A. Safari, J. B. Wachtman, Jr., C. Ward, V. Parkhe, N. Jisrawi, and W. L. McLean	
Processing and Superconducting Properties of Perovskite Oxides	498
J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, B. G. Bagley, E. M. Vogel, and Y. LePage	
Processing and Properties of the High T_c Superconducting Oxide Ceramic $YBa_2Cu_3O_7$	506
B. Bender, L. Toth, J. R. Spann, S. Lawrence, J. Wallace, D. Lewis, M. Osofsky, W. Fuller, E. Skelton, S. Wolf, S. Qadri, and D. Gubser	
Processing-Property Relations for $Ba_2YCu_3O_{7-x}$ High T_c Superconductors	512
J. E. Blendell, C. K. Chiang, D. C. Cranmer, S. W. Freiman, E. R. Fuller, Jr., E. Drescher-Krasicka, W. L. Johnson, H. M. Ledbetter, L. H. Bennett, L. J. Swartzendruber, R. B. Marinenko, R. L. Myklebust, D. S. Bright, and D. E. Newbury	
Low Temperature Thermal Processing of $Ba_2YCu_3O_{7-x}$ Superconducting Ceramics	530
C. K. Chiang, L. P. Cook, S. S. Chang, J. E. Blendell, and R. S. Roth	

Synthesis, Characterization, and Fabrication of High Temperature Superconducting Oxides	539
E. C. Behrman, V. R. W. Amarakoon, S. R. Axelson, A. Bhargava, K. G. Brooks, V. L. Burdick, S. W. Carson, N. L. Corah, J. F. Cordaro, A. N. Cormack, D. G. DiCarlo, A. Dwivedi, G. S. Fischman, J. Friel, M. J. Hanagan, R. L. Hexemer, M. Heuberger, K.-S. Hong, J.-Y. Hsu, W.-D. Hsu, P. F. Johnson, W. C. LaCourse, J. R. LaGraff, M. Lakshminarasimha, J. W. Laughner, A. V. Longobardo, P. F. Malone, P. H. McCluskey, D. M. McPherson, T. J. Mroz, C. W. Rabidoux, J. S. Reed, P. Sainamthip, S. C. Sanchez, C. A. Sheckler, W. A. Schulze, V. K. Seth, J. E. Shelby, S. H. M. Shieh, J. J. Simmins, J. C. Simpson, R. L. Snyder, D. Swiler, J. A. T. Taylor, R. Udaykumar, A. K. Varshneya, S. M. Vitch, and W. E. Votava	
Studies on Ceramic Superconductors	556
A. C. D. Chaklader, G. Roemer, W. N. Hardy, J. H. Brewer, J. F. Carolan, and R. R. Parsons	
Section III. Properties and Characterization	563
X-Ray Powder Characterization of $Ba_2YCu_3O_{7-x}$	565
W. Wong-Ng, R. S. Roth, L. J. Swartzendruber, L. H. Bennett, C. K. Chiang, F. Beech, and C. R. Hubbard	
Comparisons of Transport Properties, Electron Deficiency, and Superconducting T_c in the $La_{2-x}Sr_xCuO_{4-d}$ System and $YBa_2Cu_3O_{9-d}$	577
T. Penney, M. W. Shafer, B. L. Olson, and T. S. Plaskett	
Transport Critical Current in Bulk Sintered $Y_1Ba_2Cu_3O_x$ and Possibilities for Its Enhancement	586
J. W. Ekin	
Microstructural Effects on the Magnetization of Superconducting $YBa_2Cu_3O_{7-x}$ in Fields Below the Lower Critical Field	593
M. R. De Guire and D. E. Farrell	
The Bulk Modulus and Young's Modulus of the Superconductor $Ba_2Cu_3YO_7$	601
S. Block, G. J. Piermarini, R. G. Munro, and W. Wong-Ng	
Fracture Properties of Polycrystalline $YBa_2Cu_3O_x$	606
R. F. Cook, T. M. Shaw, and P. R. Duncombe	
Electrical, Mechanical, and Ultrasonic Properties of a Sintering-Aid Modified $YBa_2Cu_3O_x$ High- T_c Superconductor	615
N. D. Patel, P. Sarkar, T. Troczynski, A. Tan, and P. S. Nicholson	
X Ray Studies of Helium-Quenched $Ba_2YCu_3O_{7-x}$	624
W. Wong-Ng and L. P. Cook	
Characterization of $Ba_2YCu_3O_x$ as a Function of Oxygen Partial Pressure Part I: Thermoanalytical Measurements	632
P. K. Gallagher	
Characterization of $Ba_2YCu_3O_x$ as a Function of Oxygen Partial Pressure Part II: Dependence of the O-T Transition on Oxygen Content	640
H. M. O'Bryan and P. K. Gallagher	

Oxygen Stoichiometry in $\text{Ba}_2\text{YCu}_3\text{O}_x$, $\text{Ba}_2\text{GdCu}_3\text{O}_x$, and $\text{Ba}_2\text{EuCu}_3\text{O}_x$ Superconductors as a Function of Temperature G. S. Grader and P. K. Gallagher	649
Thermal Analysis of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ at 700-1000 °C in Air L. P. Cook, C. K. Chiang, W. Wong-Ng, and J. Blendell	656
The Orthorhombic and Tetragonal Phases of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{9-y}$ D. J. Eaglesham, C. J. Humphreys, W. J. Clegg, M. A. Harmer, N. McN. Alford, and J. D. Birchall	662
Microstructure, Crystal Symmetry, and Possible New Compounds in the System $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{9-x}$ C. M. Sung, P. Peng, A. Gorton, Y. T. Chou, H. Jain, D. M. Smyth, and M. P. Harmer	668
A Microstructural Study of Phases in the Y-Ba-Cu-O System A. I. Kingon, S. Chevachoenkul, J. Mansfield, J. Brynstad, and D. G. Haase	678
A Study of Mixed Phase Behavior in the Lanthanide-Substituted Superconducting Oxide $\text{ErBa}_2\text{Cu}_3\text{O}_7$ H. W. Zandbergen, G. F. Holland, P. Tejedor, R. Gronsky, and A. M. Stacy	688
Environmental and Solvent Effects on Yttrium Barium Cuprate ($\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$) K. G. Frase, E. G. Liniger, and D. R. Clarke	698
Reactions of Barium-Yttrium-Copper Oxides with Aqueous Media and Their Applications in Structural Characterization A. Barkatt, H. Hojaji, and K. A. Michael	701
Section IV. Theory	711
Superconductivity and the Metal-Semiconductor Transition A. W. Sleight and U. Chowdhry	713
Electronic Structure of High T_c Oxide Superconductors M. E. McHenry, C. Counterman, G. Kalonji, K. H. Johnson, A. Collins, M. Donovan, and R. C. O'Handley	719
Computation of Oxygen 1s Core Energy Difference and Density of States for La_2CuO_4 R. V. Kasowski and W. Y. Hsu	733

THE DEVELOPMENT OF HIGH-T_c CERAMIC SUPERCONDUCTORS: AN INTRODUCTION

1

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Abstract.

The development of the new superconducting oxide ceramics is chronicled in this introductory contribution. Following an outline of the crystal structure, phase equilibria and properties of the lanthanum strontium cuprate and the yttrium barium cuprate superconductors, a number of the challenges facing the ceramics community are described.

Introduction.

The last year has seen a startling development in ceramics that has the potential, in the view of many, to alter our way of life in much the same way as the steam engine, the telephone or the computer. All of a sudden, ceramics have been thrust into the limelight as new progress on the ceramic superconductors has been made. The latest advances have appeared in newspapers, such as The New York Times, The Washington Post and The Wall Street Journal, and major articles have appeared in mass circulation periodicals such as Time, Business Week and Fortune [1,2] as well as in general science journals [3]. Whether the new superconducting ceramics will have the revolutionary impact that previous ceramics, bricks and whitewares, have had remains to be seen but the potential has set an unprecedented race in laboratories around the world to investigate the properties of these new materials and to search for materials with yet higher superconducting transition temperatures.

The remarkable developments of the last year date from the discovery by Bednorz and Müller [4-6] of a new class of ceramics which exhibit superconductivity to unprecedentedly high temperatures. The radical advance triggered by this discovery and that of the subsequent yttrium substituted materials can be appreciated by considering the development of the superconducting transition temperature since

¹ Adapted from the author's opening remarks to the Basic Science Division Special Session on Ceramic Superconductors, April 29th during the 89th Annual Meeting of the American Ceramic Society

the phenomenon of superconductivity was discovered by Onnes [7]. From figure 1 it can be seen that the discovery of new materials has been responsible for the superconducting transition temperature (T_c) rising at a steady value of about 4 degrees Kelvin per decade since Onne's discovery of superconductivity in mercury in 1911.² In the context of the steady but pedestrian progress indicated by the figure, the increases in T_c brought about by the recent discoveries are extraordinary, and being exhibited by a ceramic, revolutionary. Extrapolating the progress being made up until the beginning of last year, materials having a superconducting transition above liquid nitrogen temperature (77°K) so that they could be operated using relatively cheap³ liquid nitrogen rather than liquid helium, would not have been reached until the year 2100. Instead, the liquid nitrogen barrier was broken early this year, apparently independently, by several groups around the world [11-14].

The breakthrough by Bednorz and Müller (figure 2) was really two-fold. One, the demonstration of a new, previously unrecognized, class of superconducting materials. The other, a big advance in the superconducting transition temperature to a value believed by many theorists to be the limiting temperature for the operation of the electron-phonon interaction that is the basis of the BCS theory [15] of superconductivity.⁴

Chronology:

Although the discovery by Bednorz and Müller was submitted to the German periodical *Zeitschrift fur Physik* in mid-April and appeared later in the year [4] it received little attention until the Materials Research Society meeting in December 1986. There, their findings were substantiated by a University of Houston group under Professor Chu [16] and by a University of Tokyo group [17,18] under the direction of Professors Kitazawa and Tanaka. The Tokyo group also reported succeeded in making single phase samples of lanthanum barium cuprate, $La_{2-x}Ba_xCuO_{4-y}$. By the turn of the year at least five groups, University of Tokyo, The Institute of Physics in Beijing [19], ATT Bell Laboratories [20], Bell Communications Research [21], and IBM Zurich Laboratories [22] had demonstrated that by substituting strontium for barium the transition temperature T_c could be raised to approximately 40°K . The

² Not shown on the figure are the discovery of superconductivity in three oxide materials, reduced $SrTiO_3$ [8], $LiTiO_3$ [9], and the $BaPb_{1-x}Bi_xO_3$ [10]. These discoveries indicated that superconductivity was not restricted to elemental materials and metallic alloys but since their transition temperatures (0.3, 13.7 and 13°K respectively) were lower than that of the metallic alloys of the time they otherwise attracted little attention outside of their proponents.

³ By one comparison, the cost of a gallon of liquid nitrogen is about the same as a gallon of milk.

⁴ It is clear that the somewhat tentative tone of the original paper was due to the authors wishing to be absolutely certain of discovering superconductivity before claiming to have done so. Over the last decade there have been many claims, later discounted, of superconductivity in a variety of new materials. Perhaps the cautionary tone was also due to the fact that the authors were aware of the positive temperature coefficient (PTC) effect in certain doped, polycrystalline perovskites ceramics. It is tempting to speculate that a number of claims for onsets above 100°K may be due to a PTC effect, a phenomenon apparently not widely known to many in the superconducting physics community.

basis for substituting strontium (and calcium) was the knowledge that the Ca^{2+} , Sr^{2+} and Ba^{2+} could all substitute into the La^{3+} site in the La_2CuO_4 structure and thereby modify its transport properties. The finding that Sr^{2+} would substitute for the La^{3+} and still give rise to superconductivity allowed Bednorz et al. [22] to conclude that the origin of superconductivity produced by the doping was due to a direct electronic mechanism rather than an ion size effect. The University of Houston group then reported [23] that the application of high pressure (1.2 GPa) shifted the onset of the superconducting transition up to an astonishing 52°K. A number of groups also reported that the transition temperature was sensitive to the sintering and annealing atmospheres with the changes in T_c with oxygen content being reversible down to temperatures of at least 350°C.

The next dramatic breakthrough came with reports that superconductivity had been observed in polyphase materials at temperatures above that of liquid nitrogen. The first announcement in the USA was from the National Science Foundation on February 16th that Chu's group at the University of Houston had observed transition onset temperatures as high as 92°K. Soon after it became evident that a number of groups around the world, the Institute of Physics in Beijing [12], the Indian Institute of Science, Bangalore [13], had independently observed the same transition above liquid nitrogen temperatures in similar materials. In each case, the investigators had substituted the rare-earth yttrium in place of the lanthanum in the La-Ba-Cu-O material and obtained a polyphase material with indications of a critical temperature in excess of 90°K -- the liquid nitrogen barrier was finally broken. In retrospect it appears that a number of the groups were making a straightforward substitution of Y for La under the assumption that the compound Y_2CuO_4 analogous to La_2CuO_4 exists. Whilst the Bangalore group, for one, clearly understood that there was not such a Y analog, the result of the yttrium substitution was the formation of a polyphase material having an unprecedented superconducting transition temperature.

Immediately a race began to identify the phase responsible for the 90°K superconductivity. Amid reports that the polyphase material described by Chu was a mixture of a green phase and a black phase, groups from several laboratories [25-28] identified, in a matter of days, that the superconducting phase was the black phase and was a yttrium barium cuprate having a composition of $Y_1Ba_2Cu_3O_{9-x}$. The green, non-superconducting phase was later recognized as being one of the phases synthesised earlier by Michel and Ravueau [24] and having the composition $Y_2Ba_1Cu_1O_5$.

Next the race was on to determine the crystal structure of the superconducting phase and how it depended on the processing of the material, in particular on the oxygen content of the atmosphere. Some groups used conventional X-ray diffraction analysis to determine the crystal structure whilst others used a combination of X-ray diffraction and transmission electron microscopy techniques [29-31]. Figure 3, drawn from the joint IBM Yorktown - Almaden laboratories investigation, is the first high resolution electron atomic structure image showing the position of the atoms in the yttrium barium cuprate structure. The positions of the Y and Ba atoms are

clearly delineated, being well within the resolution capabilities of the microscope used, and the unit cell is outlined in the figure. From images such as these, the techniques of convergent beam electron diffraction, X-ray diffraction and neutron diffraction, the structure is now believed to be as shown in figure 4 and discussed in a following section. No structural phase transition has been reported to occur at the superconducting transition temperature.

As part of the search for the superconducting phase, several groups established its compatibility relations. By the time of the American Physical Society meeting [32] -- a mere three weeks after the announcement in the United States of Chu's work -- it had been established that the superconducting phase was compatible with CuO , BaCuO_2 and the green phase Y_2BaCuO_5 . It is now known [33] that the phase compatibility relations (the phase behavior diagram) are as indicated in figure 5, and that in addition to the new superconducting yttrium barium cuprate, there is a new K_2NiF_4 type perovskite with a composition Ba_2CuO_3 , a ABO_3 perovskite of composition $\text{YBa}_3\text{Cu}_2\text{O}_9$, and an additional phase of composition Ba_3CuO_4 . (It is now also known that the superconducting yttrium barium cuprate phase is only stable over a narrow range of oxygen partial pressures and so an appropriate representation of the phase diagram is as shown in figure 6).

Since the identification of the superconducting yttrium barium cuprate, work has diverged as some groups have focussed their efforts on the structure of the material, others have sought to explore the superconducting properties and still others have concentrated on potential applications of the new superconducting ceramics.

Structure Of The Lanthanum Strontium Cuprate:

Following the tentative identification by Bednorz and Müller that a perovskite of the potassium nickel fluoride (K_2NiF_4) type was responsible for the observed high T_c , workers at the University of Tokyo [18] confirmed that the phase has indeed the tetragonal symmetry of K_2NiF_4 with the stoichiometry $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. The structure of these perovskites has been well established by Longo and Raccach [34], and more recently for the Sr series, by Nguyen et al. [35,36]. Such oxygen defect perovskites can be thought of as consisting of alternating intergrowths of perovskite- and sodium chloride type layers. The structure is made up of planes of CuO_6 octahedra sharing corners, separated by (La,Sr)O layers within which the La and Sr are ninefold coordinated to oxygen. As a result, the copper-oxygen bonding is distorted with the copper assuming a planar fourfold coordination with oxygen. In the La_2CuO_4 , all the copper is Cu^{2+} and the structure has a slight orthorhombic distortion. Substitution of Ba or Sr for La oxidizes some of the copper to Cu^{3+} by ordering of oxygen vacancies to give a mixed valence compound and decreases the orthorhombicity of the K_2NiF_4 structure. A number of groups have explored the superconductivity as a function of the degree of substitution x and have found that the superconducting transition is a maximum at a value of $x=0.15$ [21,22]. This corresponds to being near to what is believed to be a metal-insulator transition, a finding similar to that dis-

covered for the $BaPb_{1-x}Bi_xO_3$ system, and discussed in this special issue by Sleight and Chowdhry.

Structure Of The Yttrium Barium Cuprate:

The structure (figure 4) of the $Y_1Ba_2Cu_3O_7$ yttrium barium cuprate phase can be described in a number of essentially equivalent ways. The first reports refer to the structure as having a tripled unit cell along the c-axis consisting of a sequence of Ba-Y-Ba atoms separated by two-dimensional CuO_2 planes. On the basis of such a description the formula unit can be written as $YBa_2Cu_3O_{9-x}$ since if all the available oxygen sites were occupied the number of oxygen ions per unit cell would be 9. More recently, it has become recognized that a better description may be in terms of a class of defect perovskites studied by Er-Rakho et al. [37] and Michel and Raveau [36]. On such an assignment there are no oxygen atoms in the yttrium plane and there are ordered oxygen vacancies in the CuO_2 plane separating the planes containing the barium ions. The number of oxygen ions per unit cell would then be 7, hence the tendency in recent papers to refer to the superconducting phase as being $YBa_2Cu_3O_{7-x}$ or $YBa_2Cu_3O_7$ rather than $YBa_2Cu_3O_{9-x}$. The Er-Rakho phase features many of the characteristics that are now thought to be particularly important in the structure of the superconducting phase, ordered arrays of vacancies, mixed valence Cu^{2+} and Cu^{3+} states, and pyramidal and square-planar coordination of the copper ions. Recently, Shafer et al. [38] have argued that since these materials, and the lanthanum strontium copper oxides, are metallic it is more appropriate to describe the conduction in terms of [Cu-O] complexes rather than in terms of the valence state of the copper ions. This is discussed, together with evidence for the conduction mechanism being electron hole conduction, in a contribution to this volume by Shafer and colleagues.

Rare-earth and Alkali Substitution:

One of the early surprises to many was the finding that any rare-earth element (other than La) could be used to substitute, wholly or in part, for the yttrium without markedly altering the superconducting transition temperature [39,40]. Particularly surprising was the finding that the magnetic rare-earth elements, such as Dy, Er and Ho, did not affect the superconductivity. In previous classes of superconductors, the magnetic moments of the rare-earth ions interact with the conduction electrons and break the Cooper pairs thereby destroying, or at the very least suppressing superconductivity. It has also been found that the Ba ion can be partially substituted for by Ca and/or Sr, but in each case complete substitution cannot be achieved.

Processing:

The oxygen deficient perovskites, including the $La_{2-x}Sr_xCuO_4$ and the perovskites related to the newly discovered yttrium barium cuprate, have been known for some time to exhibit sensitivity to oxygen and were, in fact, investigated as possible oxygen sensors and gauges. For this reason it is not surprising that one of the key observa-

tions made in the last few months has been the importance of the processing atmosphere and annealing treatments in attaining good superconductivity. This sensitivity is illustrated with four representative resistance versus temperature curves for single phase, polycrystalline samples of yttrium barium cuprate (figure 7). The sharpest transition occurs after slow cooling in oxygen and is degraded by either annealing in too high an oxygen partial pressure (curve c) or in too low an oxygen partial pressure (curve b). Quenching from too high a temperature, even in oxygen, adversely affects the transition (curve d). The changes in oxygen content, and their reversibility, have been followed by a number of workers [41,42] using thermogravimetric analysis as reproduced by the data of figure 8 taken from the work of Tarascon et al. [41]. Other examples of this intercalation and removal of oxygen from ceramic samples of the yttrium barium cuprate are presented in contributions to this special volume.

The intercalation of oxygen and the effect of annealing treatments as well as quenching can be interpreted in structural terms primarily as affecting the oxygen occupancy on the copper plane lying between the barium ions. This is based on the results of neutron diffraction and supports the idea that there is an optimum oxygen stoichiometry for high temperature superconductivity. The prevailing view at the present time is that it is the perfection of the CuO_2 "ribbons" or "chains" created by oxygen vacancy ordering in the basal plane of figure 4 that is critical for high values of the superconducting transition temperature T_c . In this interpretation, deviations from the ideal structure of figure 4 caused by the addition (high oxygen pressure) or removal (low oxygen pressure) of oxygen from the copper-oxygen plane between the barium ions will result in lowering of the transition temperature. This is consistent with the results, reproduced in figure 7, referring to the change in resistance of a single phase $YBa_2Cu_3O_7$ sample after being subject to a variety of annealing and quenching treatments.

One of the consequences of the processing atmosphere and temperature is that the orthorhombic distortion of the unit cell alters (figure 9). Above a certain temperature the unit cell becomes tetragonal and samples quenched from this tetragonal state do not exhibit 90°K superconductivity. Using neutron diffraction, it has been established that the orthorhombic-to-tetragonal transition occurs when the oxygen stoichiometry falls to a value of 6.5, and that the temperature at which this transition occurs depends on the oxygen partial pressure of the experiment. In terms of the unit cell description, as oxygen leaves the Cu-O-Cu chains in the orthorhombic cell the stoichiometry falls until at a value of 6.5 the oxygen ions disorder between sites in the basal plane in the a and b axes making them equivalent and thereby causing the cell to become tetragonal. Thus, if a sample is quenched from above the phase transition temperature, the oxygen ions will not form the Cu-O-Cu chains and superconductivity will be lost.

A rather dramatic illustration of the importance of processing is that the single phase La_2CuO_4 material has been known for many years to be insulating, yet recently groups at both IBM Almaden [43] and Grènoble [44] have shown that it can be converted to exhibit superconductivity with an onset as high as 40°K by annealing

in air at about 950°C. Furthermore, the superconductivity can be reversibly created and destroyed by alternating heat treatments in an oxidizing and reducing atmosphere

Single Crystals:

Many groups have attempted to grow large single crystals of the yttrium barium cuprate in order to make measurements of the crystallographic dependence of fundamental properties of these new materials. The majority of attempts have been frustrated because of the reactivity of the material with most crucible materials (only single crystal magnesium oxide, strontium titanate and silver appear not to react) and by the peritectic melting of the cuprate at approximately 1030°C. Nevertheless, two groups have reported successfully growing single crystals, Argonne National Laboratory and IBM Yorktown Heights. The Argonne's crystals are reported to have been grown by a vapor transport method whilst those of the IBM group were grown by a combined vapor/liquid technique [45]. In addition, several groups of workers have been successful in growing large (several millimeter sized) plate shaped crystals from the molten region of the $CuO - BaCuO_2 - YBa_2Cu_3O_7$ compatibility region (figure 5) by slowly cooling the melt but have had difficulties in removing the crystals from the solidified melt since no preferential etch has yet been discovered. A collection of such single crystals is shown in figure 10 taken from the work of reference 46.

Mechanical Properties:

In the majority of applications foreseen for the new ceramic superconductors it is likely that they will be subject to mechanical stresses. For instance, in current high field superconducting magnets one of the design limitations on the attainable magnetic field is the mechanical strength of the superconducting material. The presently used superconductors, the transition element alloys such as niobium-tin and niobium-titanium, have relatively low strength (and are quite brittle) but the difficulty experienced in producing dense samples of the yttrium barium cuprate has precluded a comparison with these materials. The strength values reported to date are unlikely to be close to the attainable strength since they are undoubtedly limited at the present time by their large porosity.

There will also, as in other applications of ceramic materials, be particular applications that are truly strength limited and others that are fracture toughness limited. Recent measurements [47] of the fracture toughness of single crystals of the yttrium barium cuprate indicate that the value (approximately 1.1 MPa $m^{1/2}$) are relatively low in comparison with other single crystals of ceramics. One other potentially important finding is that in addition to having a relatively poor fracture toughness, the yttrium barium cuprate is also susceptible to the phenomenon of moisture enhanced

slow crack growth.⁵ The low fracture toughness and susceptibility to slow crack growth, make the material analogous in these respects to soda-lime glass and suggest that mechanical design with the new superconducting oxides will probably require particularly conservative design procedures in the absence of toughening. The susceptibility to moisture enhanced crack growth suggests that the material be protected by the use of impermeable coatings, much as optical glass fibers are today, from exposure to such stress corroding atmospheres. Less protection may be necessary if the material is to spend its entire life at liquid nitrogen temperatures since slow crack growth is generally a thermally activated process.

Thin Films:

As soon as the yttrium barium cuprate was identified as the superconducting phase, a number of investigators began attempts to grow thin films of the material. Although thin films of approximately the correct composition were relatively easy to grow, great difficulty was experienced in processing them so that they would become superconducting above 77°K. The first films to exhibit complete superconductivity above liquid nitrogen were prepared by electron beam evaporation through a partial pressure of oxygen onto sapphire and MgO substrates maintained at typically 450°C [48]. The early films, typically 1µm thick, were polycrystalline and, after annealing in oxygen, were fully superconducting by 87°K. More recently a number of groups have been successful in producing thin films by d.c. magnetron sputtering [49,50] and also by ion beam sputtering. The formation of thin, superconducting films has opened the door to the manufacture of viable electronic devices operating in the liquid nitrogen range. The first such devices, superconducting quantum interference devices (SQUID's), were recently fabricated at IBM Yorktown Laboratories [51].

Wires and Fibers:

Also within a matter of weeks of the yttrium barium cuprate being identified, a number of groups, including those from Argonne National Laboratory, ATT Bell Laboratories and Toshiba, announced that they had fabricated superconducting wires. In the ATT Bell Laboratories' process [52], pre-reacted yttrium barium cuprate is packed into a silver metal tube, extruded to a small diameter and then heated at temperatures of approximately 900°C to sinter the superconducting material. Early results indicate that the wires exhibit a sharp transition temperature and are capable of carrying critical currents in excess of 1000 A/cm². The Toshiba process appears to be quite similar, but using what is believed to be a Cu-Ni alloy for the tube material rather than silver. Although not as advanced, a number of other groups have attempted to form fibers, for instance by pulling fibers from a gel and then firing them to convert the gel to the superconducting form. There is considerable precedent for this approach, not simply from the formation of graphite fibers

⁵ Various known as static fatigue, stress corrosion cracking, or sub-critical crack growth this is the phenomenon in which cracks grow with time in the presence of moisture.

but also from the work of the ICI group in manufacturing fibers of alumina and zirconia.

Large Area Applications:

In a number of potential applications, such as electrical and magnetic screening and the coating of wires, it will be necessary to be able to apply the superconducting materials rapidly and evenly over large areas, and onto a variety of surfaces. One such process has recently been demonstrated with the announcement from IBM that the yttrium barium cuprate material could be applied by the technique of plasma spraying [53]. This type of approach is described in three contributions to this volume.

Challenges To The Ceramics Community:

The development of the new superconducting ceramics has, until recently, been largely in the hands of the physicists and structural chemists. However, it is likely that the further development of these materials and process optimization will require all the talents of the ceramics community. This is particularly so since the principal problems are ones that have long been familiar in the development of other ceramic materials, namely: a) how to densify the material, b) how to increase the strength and fracture toughness, c) how to control the processing to produce a desired microstructure and d) how to control the chemistry and properties of the grain boundaries. The principal challenges at the present time are how to make large, dense pieces of the material and how to raise the critical current density to values that will make them useful.

As in other ceramic materials full density is required so that the material's strength is maximized and not unduly limited by the presence of large pores. In addition, however, it is expected that pores, unless they are exceptionally small, will invariably reduce the attainable critical current. To date the majority of samples exhibiting superconductivity at 90°K have had densities of 90% (of theoretical) or less. Samples having greater densities have been made, but it appears that in the majority of cases they have not exhibited bulk superconductivity throughout but rather only near the surface where oxygen has been able to diffuse into the material. As larger pieces of material are made, the problems of simultaneously achieving full density and equilibrating at an oxygen partial pressure for 90°K superconductivity will be exasperated. Densification of the yttrium barium cuprate is discussed in several papers in this volume, but with the exception of sinter-forging full density has not been attained. It might be thought from the low densities reported in the published literature that the yttrium barium cuprate is in some way especially resistant to densification. However, to put this in perspective it is reasonable to ask how many crystalline ceramics can be sintered to full density at below 1000°C ?⁶ Clearly, experience tells

⁶ Sintering at a higher temperature than 1000°C is not feasible since the yttrium barium cuprate undergoes a peritectic melting reaction at approximately 1030°C

us that very few can be densified without a sintering aid, and so the challenge is to discover a sintering aid that does not affect the superconducting properties of the material. With the possible exception of the work described in this issue by Patel et al., no such aid has yet been found. One of the more successful strategies used in the past to readily produce ceramics having a high density, namely ball milling in alumina mills so as to deliberately incorporate alumino-silicates from the mill that can act as liquid phase sintering aid, is unacceptable. We have found in our own work that such an approach leads to the formation of a remnant glass intergranular films (as in many other ceramics) but that the materials do not exhibit bulk superconductivity presumably because the intergranular films insulate and isolate the superconducting grains.

The low fracture toughness of both the lanthanum strontium cuprate and the yttrium barium cuprate provides an additional challenge, namely how to increase the fracture toughness of these materials without diluting the bulk superconductivity or decreasing the critical current carrying capability of the material. The limited compatibility of the yttrium barium cuprate with other materials also will restrict the available reinforcements, probably to the noble metals. (We have had some initial success in toughening the material through the use of silver wires [54], as have our colleagues at ATT Bell Laboratories).

One of the critical problems likely to be encountered in trying to use polycrystalline, ceramic materials of the yttrium barium cuprate in applications is the small values of current they can conduct before transforming from their superconducting to their normal condition. Values of the order of 10-100 A/cm² have been reported compared to values for commercial niobium based liquid helium temperature materials of typically 10⁶ A/cm², and the fundamental limit imposed by the "depairing current density"⁷ calculated to be approximately 10⁷ A/cm². The problem is thrown into further relief by the recent critical current measurements made on epitaxial thin films (deposited on single crystal strontium titanate substrates) that show that the material is capable of carrying critical current densities in excess of 10⁵ A/cm² at 77°K [55].

This unfavorable comparison implicates the grain boundary regions as being responsible for the low critical current densities. Indeed, low magnetic field measurements of both the lanthanum strontium copper oxides [56] and the yttrium barium cuprate [57] suggest that the magnetic behavior of these polycrystalline materials is that of individual superconducting granules separated by normal, resistive boundaries. This interpretation is supported by the finding that the size of the granular regions deduced from the magnetization data is approximately the same as the grain size in the materials investigated. What is causing the grain boundaries to remain normal or to become normal at low currents has yet to be established, but clearly

⁷ The current density at which the kinetic energy of an electron Cooper pair equals its superconductor condensation energy.