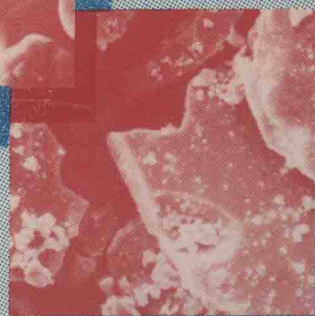
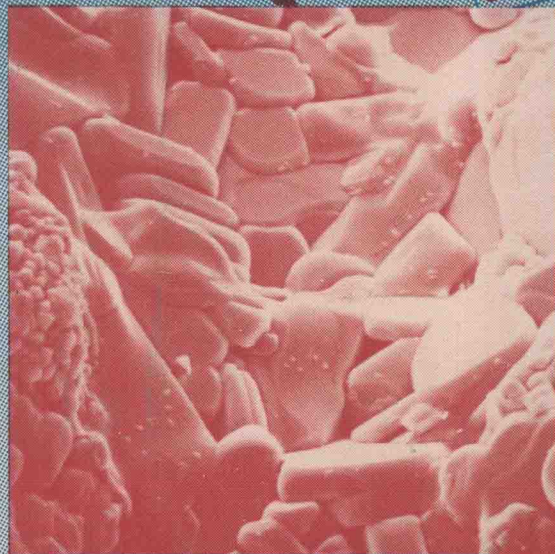


Research
Update, 1988

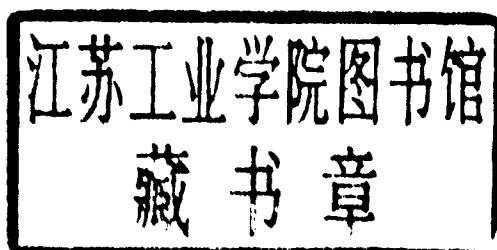
CERAMIC SUPERCONDUCTORS II



Man F. Yan
Editor

Research
Update, 1988

C E R A M I C
SUPERCONDUCTORS
II



Man F. Yan
Editor

Published by:
The American Ceramic Society, Inc.
Westerville, Ohio
USA

Copyright © 1988, The American Ceramic Society, Inc. All rights reserved.

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the publisher.

Printed in the United States of America

1 2 3 4 5—95 94 93 92 91 90 98 88

Introduction

In the past eighteen months, there has been a phenomenal interest in ceramic superconductors. Scientific and technological contributions of ceramists to this fast growing field have been widely reported. In recognition of this increasing interest, the American Ceramic Society has held three different technical symposia on ceramic superconductors during the annual and fall meetings in the past year. The latest symposium on ceramic superconductors was held in Cincinnati, OH, on May 1-5, 1988. The timeliness and continued interest in this field was attested to by the total of 161 invited and contributed papers, which were scheduled into seventeen sessions. The plenary lecture by Dr. J. George Bednorz, the 1987 Nobel Laureate in Physics, attracted over 1000 attendees.

Based on the high level of interest on the part of the attendees, the American Ceramic Society decided to solicit papers from this symposium and from researchers working with ceramic superconductors and to publish these papers in a timely fashion. This volume is the result of that solicitation. It contains 62 papers, each of which was reviewed by at least one reviewer and many of which were revised prior to acceptance for publication. This volume is the second publication by the American Ceramic Society devoted to ceramic superconductors—the first was published in *Advanced Ceramic Materials* as Volume 2, Number 3B, July 1987.

Several papers in this volume report the recent advances in crystal chemistry and phase equilibria of the different classes of novel ceramic superconductors. A significant interest has been shown in oxidation kinetics and high temperature defect chemistries, which are important considerations in ceramic processing and superconducting properties. Magnetic and electrical properties of the ceramic superconductors have been documented in this book; these properties are also correlated with different chemical compositions and processing conditions. Conductivity data at microwave frequencies have been characterized. Mechanical properties of these ceramic superconductors and their interactions with the environment are addressed in several papers. The extensive material characterizations also provide a useful scientific basis for their technological applications.

Processing of these novel superconductors remains the primary focus of this volume. New crystal growth techniques, novel powder synthesis methods, ceramic densification, and microstructural development are described in depth. The fabrication and properties of polymer/ceramic composites are also reported; these composites may provide a new degree of freedom in the design and application of ceramic superconducting devices. Other diverse processing techniques are illustrated by papers on magnetron sputtering, screen printing, tape casting, and sol-gel spin coating methods to fabricate thin and thick film superconductors.

The low critical current density of ceramic superconductors is probably the most important factor in limiting their applications. Thus, a significant research effort has focused on increasing the critical current density of these superconductors, and many papers in this volume are devoted to solutions to this problem. For example, the Melt-Textured-Growth process for bulk ceramics and the Liquid-Gas-Solidification process for thick and thin films are described. These two methods provide microstructural configurations which have the highest critical current densities yet reported. Hot forging, hot pressing, and magnetic casting techniques are also shown to enhance the texture development and increase the critical current density in ceramic superconductors. Furthermore, several papers in this book provide useful analytical data to elucidate the effects of compositions, microstructures, and grain boundary chemistry on the critical current density of these novel ceramics.

The success of this volume is the result of the efforts of many people. I gratefully acknowledge the contributions of Ilhan Aksay, Harlan Anderson, Helen Chen, Dudley Chance, Ye Chou, Uma Chowdhry, David Johnson, Ronald Loehman, Donald Murphy, Mani Nair, Roger Poeppel, Catharine Rice, Jenifer Taylor, Harry Tuller, and Wayne Young in serving as session chairs at the symposium. Manuscripts submitted for publication were also reviewed by John Blendell, Allen Bruce, Daniel Button, Helen Chen, Yet Chiang, William Coblenz, Timothy Dinger, Stephen Freiman, Rosario Gerhardt, Andreas Glaeser, Gideon Grader, Michael Gyorgy, John Halloran, Carol Handwerker, Mark Harmer, Shin-Ichi Hirano, Jau Jean, Sung-ho Jin, David Johnson, Lynn Johnson, Hung Ling, Robert Newnham, Henry O'Bryan, George Peterson, Roger Poeppel, Ahmad Safari, Tom Shaw, Donald Smyth, Jenifer Taylor, Robert Vest, Eva Vogel, and Wayne Young. Furthermore, I am pleased to acknowledge the efforts of John Blum, Edwin Fuller, Cornelius Moynihan, Catherine Simmons, and Nancy Tighe in coordinating the co-sponsorship of this symposium among the Electronics, Basic Science, and Glass Divisions of the American Ceramic Society. I also thank Jan Graham and Bill Douglas for organizing the symposium, Pam Achter for managing the publication of this volume, and Su Yan for coordinating the correspondence with authors and reviewers. Their help is sincerely appreciated.

Man F. Yan
AT&T Bell Laboratories
Murray Hill, NJ 07974-2070

Contents

Structural Patterns in High T_c Superconductors D.M. Smyth	1
Phase Equilibria in the System Ba-Y-Cu-O- CO_2 in Air R.S. Roth, C.J. Rawn, F. Beech, J.D. Whitley, and J.O. Anderson	13
Structural Phase Transitions of $\text{Ba}_2\text{RCu}_3\text{O}_{6+x}$ Superconductors W. Wong-Ng, L.P. Cook, C.K. Chiang, L.J. Swartzendruber, and L.H. Bennett	27
Low Temperature Phase Relations and Decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Precursors S.J. Keating, I-Wei Chen, and T.Y. Tien	43
Phase Transformations and Thermodynamic Behavior of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ System Via EMF Measurements M. Tetenbaum, A. Brown, and M. Blander	51
Direct Observations of Transitions in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Controlled by Oxygen Loss J. Chen, Y.W. Chang, A. Zangvil, T.A. Friedmann, and D.M. Ginsberg	59
Localized Electrons in Tetragonal $\text{YBa}_2\text{Cu}_{2.93}\text{O}_{6.38}$ Z. Inoue, S. Sasaki, S. Dallaire, N. Iyi, and S. Takekawa	69
Processing Induced Variations of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Microscopic Structure: A PAC Study H.T. Su, A.G. McKale, S.S. Kao, L.L. Peng, W.H. Warnes, J.A. Gardner, and J.A. Sommers	80
Oxidation Kinetics of $\text{Ba}_2\text{YCu}_3\text{O}_x$ H.M. O'Bryan and P.K. Gallagher	89
High Temperature Defect Structure and Transport in Rare Earth-Alkaline Earth-Copper Oxide Superconductors M.-Y. Su, K. Sujata, and T.O. Mason	99
Lattice and Defect Properties of La_2CuO_4 , Pr_2CuO_4 , Nd_2CuO_4 , and Al_2CuO_4 Related to High T_c Superconductivity N.L. Allan and W.C. Mackrodt	115
Prediction of Possible Other Alternate Candidate High T_c Non-Cuprate Superconductors in Perovskite-Structure Across-the-Periodic-Table Electron-Supercarrier Metalloids Edward Siegel	125
Growth of Single Crystals of High T_c Superconductors L.F. Schneemeyer, J.V. Waszczak, R.B. van Dover, A.E. White, and K.T. Short	136
Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ From Homogeneous Metal Alkoxide Solution W.G. Fahrenholtz, D.M. Millar, and D.A. Payne	141
YBCO Superconductor via Nitrates B.I. Lee, V. Modi, and M.D. Sherrill	148
Synthesis of Y-Ba-Cu-O Powders via Evaporative Decomposition of Solutions P.A. Fuierer, T.T. Srinivasan, and R.E. Newnham	156
Preparation of Superconducting $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Powders by Ball Milling and Their Properties N. Ichinose and T. Motai	162
Feasibility of Synthesis of Anisotropic Morphology $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ Powder by Molten Salt Technique C.T. Decker, V.K. Seth, and W.A. Schulze	169
Synthesis Variability and Syntactic Intergrowths in the BCSCO System J.J. Ratto, R.M. Housley, J.R. Porter, and P.E.D. Morgan	177

A Critical Comparison of Various Processing Methods for Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ S. Baik, J.H. Moon, K.W. Moon, and H.M. Jang	186
Superconducting Properties of $\text{LaBa}_2\text{Cu}_3\text{O}_x$ and $\text{YBa}_2\text{Cu}_3\text{O}_y$ U. Balachandran, K.C. Goretta, D. Shi, R.B. Poeppel, and N.G. Eror	198
Reaction Sintering of $\text{YBa}_2\text{Cu}_3\text{O}_x$ in Different Oxygen Partial Pressures P. Sarkar, T.B. Troczynski, K.J. Vaidya, and P.S. Nicholson	204
The Relation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Properties to Densification Technique R.H. Moore, M.O. Eatough, T.J. Gardner, W.F. Hammetter, S.J. Lockwood, R.E. Loehman, R.G. Tissot, Jr., and E.L. Venturini	216
Process-Microstructure-Property Relations in Ceramic Superconductors N.McN. Alford, J.D. Birchall, W.J. Clegg, M.A. Harmer, and K. Kendall	232
Reaction Sintering High-Density, Fine-Grained $\text{Ba}_2\text{YCu}_3\text{O}_{6.5+x}$ Superconductors Using $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ J.S. Wallace, B.A. Bender, S.H. Lawrence, and D.J. Schrodt	243
Small Radius Ion Substitution Effect in Ceramic Superconductors K. Niwa, K. Yamanaka, A. Tanaka, N. Kamehara, and T. Uzumaki	252
Impurity Effects on the Properties of Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ S.X. Dou, A.J. Bourdillon, C.C. Sorrell, H.K. Liu, J.P. Zhou, X.Y. Sun, H.J. Logren, E.M. Lindh, and K.E. Easterling	263
Critical Current Density and Fabrication of the Polycrystalline Y-Ba-Cu-O Superconductor S. Jin, R.C. Sherwood, T.H. Tiefel, R.B. van Dover, S. Nakahara, and R.A. Fastnacht	272
Processing of Superconducting Ceramics for High Critical Current Density K. Sawano, A. Hayashi, T. Ando, T. Inuzuka, and H. Kubo	282
Influence of Composition on the Critical Current Density of $\text{Ba}_2\text{YCu}_3\text{O}_{6+x}$ J.E. Blendell and M.D. Vaudin	294
Critical Current Density in Bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ S.M. Johnson, M.I. Gusman, D.L. Hildenbrand, K.B. Schwartz, C.B. Eom, and T.H. Geballe	300
Grain Size Effects on the Transport Critical Current Density of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ A. Roshko, Y.-M. Chiang, J.S. Moodera, and D.A. Rudman	308
Texture Development in $\text{Ba}_2\text{YCu}_3\text{O}_{6+x}$ Through Sinter-Forging L.C. Stearns, M.D. Vaudin, C.P. Ostertag, J.E. Blendell, and E.R. Fuller, Jr.	315
Texturing of $\text{RBa}_2\text{Cu}_3\text{O}_x$ Superconductors K.C. Goretta, A.J. Schultz, D.W. Capone, II, T.L. Tolt, U. Balachandran, J.T. Dusek, M.T. Lanagan, R.B. Poeppel, J.P. Singh, D. Shi, R.L. McDaniel, D.S. Applegate, J.K. Degener, and J.S. Kallend	323
Alignment of Superconducting Grains by Magnetic Casting C.P. Ostertag, R.D. Shull, M.D. Vaudin, J.E. Blendell, L.C. Stearns, and E.R. Fuller, Jr.	332
Texture Development During Pressing and Sintering of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ M.R. De Guire, C.J. Kim, W.-H. Lu, D.E. Farrell, and D. Boyne	343
Crystallite Alignment of Polycrystalline $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ A.F. Hepp, J.R. Gaier, G.A. Landis, and S.G. Bailey	356
Hot Forging and Hot Pressing of Ba-Y-Cu-O Superconductors J.J. Balducci, V.K. Seth, and W.A. Schulze	367
Structure and Properties of the Grain-Oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ Superconductors Fabricated Using Tape Casting S.S. Kim, T.T. Srinivasan, T.R. Shrout, and R.E. Newnham	381

Strong Texture Formation During the Electrodischarge Compaction of Superconductor Composites M.E. Saum, K. Okazaki, R.J. De Angelis, J.W. Brill, D.R. Zint, W.D. Arnett, and C.E. Hamrin, Jr.	390
Novel Method of Making High T_c Material: Liquid-Gas-Solidification Processing H.S. Chen, S.H. Liou, A.R. Kortan, L.C. Kimerling, and G.S. Indig	400
Melt Processing of Bi-Ca-Sr-Cu-O Superconductors E.D. Zotto, J.P. Cronin, B. Dutta, B. Samuels, S. Subramoney, G.L. Smith, G. Dale, T.J. Gudgel, G. Rajendran, E.V. Uhlmann, M. Denesuk, B.D. Fabes, D.R. Uhlmann, V.G. Vasquez, J. Makous, and C. Falco	406
Bi-Ca-Sr-Cu-O Superconductors of (2122) Composition by Melt Processing T.J. Gudgel, E.D. Zotto, G.L. Smith, G. Dale, S. Subramoney, E.V. Uhlmann, M. Denesuk, J. Cronin, B. Dutta, G. Rajendran, B. Fabes, and D.R. Uhlmann	419
Polymer Composite Comprising Superconducting $YBa_2Cu_3O_{7-x}$ Particles N.McN. Alford, J.D. Birchall, W.J. Clegg, M.A. Harmer, K. Kendall, C.E. Gough, C.M. Muirhead, D.A. O'Connor, and F. Wellhofer	428
Electrical, Magnetic, and Physical Properties of $YBa_2Cu_3O_{7-x}$ Superconductor/Polymer Composites P.A. Fuierer, T.T. Srinivasan, and R.E. Newnham	438
Organometallic Precursors for the Fabrication of High T_c Superconducting Fibers R.M. Laine, K.A. Youngdahl, W.M. Carty, G. C. Stangle, C. Han, R.A. Kennish, S. McElhaney, T.K. Yin, T. Yogo, and M. Sarikaya	450
Fabrication of Screen-Printed High T_c Superconducting Oxide Thick Films on Several Substrates J. Tabuchi, Y. Shimakawa, A. Ochi, and K. Utsumi	464
Synthesis and Characterization of High T_c Screen-Printed Y-Ba-Cu-O Films on Alumina N.P. Bansal, R.N. Simons, and D.E. Farrell	474
Preparation of $YBa_2Cu_3O_{7-x}$ and $ErBa_2Cu_3O_{7-x}$ Superconducting Thin Films by Rf-Magnetron Sputtering T. Aida, T. Fukazawa, A. Tsukamoto, S. Takayama, K. Takagi, and K. Miyauchi	483
Citrate-Derived Spin-On Films of High T_c Superconductors S.L. Furcone, Y.-M. Chiang, J.A.S. Ikeda, and D.A. Rudman	490
Wet Chemical Processing of High T_c Superconducting Films B. Dutta, B. Samuels, J.P. Cronin, G. Dale, G. Teowee, G. Rajendran, E.D. Zotto, E.V. Uhlmann, T. Gudgel, G. Smith, S. Subramoney, M. Denesuk, B. Fabes, D.R. Uhlmann, and S. Dey	501
Wet Chemistry-Derived Barrier Layers for Ceramic Superconductor Films J.P. Cronin, T.J. Gudgel, L. Zotto, B. Dutta, G.P. Rajendran, G. Dale, E.D. Zotto, E.V. Uhlmann, G.L. Smith, M. Denesuk, B.D. Fabes, D.R. Uhlmann, J.A. Leavitt, and J.R. Martin	511
A Simple Magnetic Balance Technique for Determining Transition Temperatures of High T_c Superconducting Powders T. Takamori and D.B. Dove	524
Impedance of Ceramic Superconducting Strips Over the Frequency Range from 20 Hz to 25 MHz G.E. Peterson, C.R. Kurkjian, R.P. Stawicki, and U.C. Paek	531
A Comparative Study of Different Processing Methods and Microwave Surface Conductivity of 1-2-3 Superconducting Ceramics H.G.K. Sundar, C. Wilson, D. Horzog, M.S. Hegde, R. Caracciolo, A. Safari, J.B. Wachtman, Jr., A. Fathy, D. Kalokitis, and E. Belohoubek	543
Magnetic Separation of High T_c Powders M. Barsoum, D. Patten, and S. Tyagi	554
Magnetization Study of Weak Links in $RBa_2Cu_3O_7$ ($R = Y, Dy, Ho$) S. Gotoh, N. Nakamura, M. Ishida, H. Shishido, and M. Shimotomai	562

Measurement of Residual Stress in a Ba-Y-Cu-O Superconductor J.S. Park, J.F. Shackelford, and D.M. Boyd.....	570
Young's Modulus Measurement of Polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Superconductor G.C.S. Chang, S.J. Burns, A. Goyal and P.D. Funkenbusch.....	580
Deformation Characteristics of Textured $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_2\text{O}_{8+x}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Polycrystals P.E. Reyes-Morel, X. Wu, and I-W. Chen.....	590
An XPS Study of $\text{YBa}_2\text{Cu}_3\text{O}_x$ Surface Corrosion R.K. Brow.....	598
Grain Boundary Segregation and Critical Current Density in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Superconductors Y.-M. Chiang, J.A.S. Ikeda, and A. Roshko.....	607

STRUCTURAL PATTERNS IN HIGH T_c SUPERCONDUCTORS

D. M. Smyth
Materials Research Center,
Coxe Lab #32
Lehigh University, Bethlehem, PA 18015

ABSTRACT

It is proposed that the basic structural features of all of the high T_c superconducting oxides discovered so far can be described in terms of an extended Ruddlesden-Popper series of structures having the general formula $mAO \cdot nABO_3$, where A is some combination of large cations (Ba, Bi, Ca, Sr, or Tl) and B is Cu. This extension accommodates a variable number of AO layers in a sequence having the NaCl structure separating two-dimensional slabs having a variable number of ABO_3 layers with the perovskite structure. The superconducting compositions can be characterized in terms of different values of the integers m and n, and their structures in terms of the corresponding numbers of sequential NaCl and perovskite layers.

INTRODUCTION

The number of high temperature superconducting oxide compositions has recently increased. In addition to the original $La_{2-x}Sr_xCuO_4$, and the subsequently discovered $YBa_2Cu_3O_{6+x}$, there have now been added Bi-containing and Tl-containing compositions. All of these have highly defective structures, relative to fully occupied prototypes, and are thus of immediate interest to the defect chemist. It is important to note any structural patterns that exist in these materials. In the absence of a detailed theoretical model for superconductivity in these oxides, such patterns can assist in the search for additional superconducting oxides, and may even contribute to the development of a better theoretical understanding. Almost all of the presently known high T_c superconductors fit either the basic perovskite formula ABO_3 or are large-cation-rich relative to this composition. It will be shown that the structures of these materials can be related to a generalized form of the Ruddlesden-Popper (R-P) series of compounds (1), in which two-dimensional perovskite-like slabs are separated by layers of excess large-cation oxide in the NaCl structure. The approach will emphasize general patterns of the structures and will ignore deviations from ideality that result from minor distortions and displacements.

COHERENCY BETWEEN THE PEROVSKITE AND NaCl STRUCTURES

Thirty years ago, Ruddlesden and Popper described a series of structures in the Sr-Ti-O system that can be related to the general formula $\text{SrO} \cdot n\text{SrTiO}_3$, or $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$, where n is an integer from 1 to ∞ (1). Members of the series thus include Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}_4\text{Ti}_3\text{O}_{10}$, ----- SrTiO_3 , where the first member has the K_2NiF_4 structure, and the last member has the ideal perovskite structure. The structures can be described as two-dimensional slabs of perovskite-like structure, n unit cells thick, separated by a single layer of SrO in the NaCl structure. The structure of $\text{Sr}_3\text{Ti}_2\text{O}_7$ is shown in Fig. 1. This homologous series of structures is an example of the persistence with which materials try to retain the essence of the perovskite structure, even when the composition differs widely from the ideal ABO_3 stoichiometry (2).

The R-P structural series depends on a coherent relationship between the perovskite and NaCl structures. Two alternative unit cells for the perovskite structure are shown in Fig. 2. The top and bottom planes of both cells are emphasized with heavy lines and show that in version (A) they consist of aligned squares containing A_4O , centered on O with A at the corners. In version (B), these top and bottom planes are squares containing AO_4 , centered on A with O at the corners. The actual stoichiometric content of the layers containing these squares is AO in both cases. It is seen in Fig. 3 that these same types of squares exist in the NaCl structure, but that in this case they alternate back and forth from AO_4 to A_4O . In the NaCl structure the AO_4 and A_4O squares follow directly after one another, with no intervening material. In the perovskite structure, the AO_4 or A_4O squares are separated by the BO_2 part of the perovskite composition. The commonality of the AO_4 and A_4O structural components makes it possible to switch from the perovskite structure to the NaCl structure, and vice versa, in a coherent way that is the essence of the R-P structures.

Examination of Fig. 1 shows that within the bottommost perovskite slab, the unit cell is defined by a vertical sequence of SrO_4 squares, centered on the Sr. Between the slabs, there is a lateral shift such that this transforms within the next perovskite slab into a vertical sequence of Sr_4O squares, centered on the O. The sequence alternates from one perovskite slab to the next, and the slabs are alternately shifted laterally back and forth. Between the slabs, the shift from SrO_4 to Sr_4O corresponds to the NaCl structure, as shown in Fig. 3. The insertion of this extra layer of SrO into the perovskite structure serves as a phase-shifter that displaces each perovskite slab laterally from its nearest neighbors. In the following discussion, it will be seen how the structures of the high T_c superconductors can be fit into this structural pattern.

La-Sr-Cu-O

The 35 K superconductors, $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$ with x about 0.15, can be viewed as acceptor-doped La_2CuO_4 , with the latter in the first R-P ($n=1$), or K_2NiF_4 , structure. An early view of a very similar

composition is shown in Fig. 4 (3). The material appears to maintain a nearly full O sublattice, so that the acceptor doping, i.e. Sr^{+2} substituted for La^{+3} , results in an elevation of the formal oxidation state of the Cu above the undoped value of +2. This is probably best considered as the formation of the equivalent number of holes that support the p-type conductivity of the material. In this case, the insertion of the alternate layers of large cation oxide having the NaCl structure gives an inherent layering of the structure that separates the Cu-O planes that are thought to contribute to the superconductivity.

Y-Ba-Cu-O

The ideal perovskite YCuO_3 , with all of the Cu in the trivalent state, can be viewed as the prototype for the 95 K superconducting material commonly known as 1-2-3, and this is shown in Fig. 5a in the form of three successive unit cells, $\text{Y}_3\text{Cu}_3\text{O}_9$. This is then very heavily acceptor-doped, i.e. 2/3 of the Y^{+3} is replaced by Ba^{+2} , with a corresponding reduction of the O-content to $\text{YBa}_2\text{Cu}_3\text{O}_8$, since the elevation of the oxidation state of the Cu above $+3$ is not a viable alternative. As shown in Fig. 5b, the oxygen that is missing relative to the perovskite structure is localized around the Y, which much prefers to be 8-coordinated, since it is too small for 12 coordination [the ionic radius for 8-coordination for Y^{+3} is 0.1155 nm, compared with 0.156 nm for Ba^{+2} (4)]. It is important for the Y and Ba to order themselves in the sequence shown so that this localized oxygen deficiency separates the structure into the layers that seem to be essential for superconductivity. It is not possible to maintain the Cu in the +3 state at atmospheric pressure, so an additional oxygen is lost, giving the structure shown in Fig. 5c for the composition $\text{YBa}_2\text{Cu}_3\text{O}_7$. This oxygen is lost from the top and bottom planes of the structure. If the vacancies are disordered within these planes, the structure is tetragonal, and the material is not superconducting; if they are ordered in parallel lines as shown, the structure is orthorhombic, and the material is superconducting. In order to obtain a superconducting material, it is necessary to anneal the oxide at low temperatures (near 500°C) in pure O_2 , both to raise the oxygen content to nearly O_7 (actually to about $\text{O}_{6.92}$) and to give the orthorhombic, ordered structure. At this composition, the average oxidation state of the Cu is +2.33 ($2\text{Cu}^{+2} + 1\text{Cu}^{+3}$), but again, these do not correspond to individual species with different ionic charges, but to a corresponding concentration of hole species. The orthorhombic structure has both planes and chains of Cu-O, and it has been proposed that the latter are related to the high T of this structure. It is possible to further reduce the material to $\text{YBa}_2\text{Cu}_3\text{O}_6$, in which all of the oxygen is missing from the top and bottom planes, as shown in Fig. 5d (5). This is a remarkably oxygen-deficient version of the perovskite structure, with Ba^{+2} ions facing each other in adjacent subcells through a layer of Cu without intervening oxygens. This composition represents a phase boundary for the system, since further reduction results in irreversible decomposition. It has been shown that this is the stoichiometric composition for this system, from a thermodynamic point of view, and that the superconducting compositions are oxygen-excess, p-type versions of this reference state (6).

The Bi-Containing Materials

There have been reports of various superconducting compositions in the Bi-alkaline earth-Cu-O system. The earliest example had the approximate formula $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ and a T_c of about 20 K (7). Major interest in this system was stimulated by the discovery of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ with a T_c of 85 K (8-11). More recently, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ and $\text{BiSrCaCu}_2\text{O}_x$ (12,13) have been reported with T_c s of about 110 K.

The structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has been described as orthorhombic with a and b about 5.4 Å, and c about 30 Å (9,11). In some cases a superstructure has been noted that extends the b axis to $5 \times 5.4 = 27$ Å (9-11). A notable feature of the structures of all of these materials is the presence of double Bi-O layers. This is not a new structural feature as indicated by the following quote from the fourth edition (1975) of "Structural Inorganic Chemistry", by A. F. Wells (14): "--series of complex oxides with tetragonal or pseudotetragonal symmetry which all have the a dimension of the unit cell close to 3.8 Å, and are based on sequences of Bi_2O_2 layers---interleaved with portions of perovskite-like structure." These so-called Bi-layer compounds have been of interest for some time for their piezoelectric properties. It will be seen that this quotation is a useful description of the Bi-containing superconductors, since the tetragonal symmetry can be viewed as an approximate subcell of the orthorhombic unit cell in the same way that the A_2O and AO_4 squares define a subcell of the NaCl structure ($3.8 \times \sqrt{2} = 5.4$).

Tarascon et al. have described the structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ in terms of the tetragonal subcell with $a = 3.817$ Å and $c = 30.6$ Å as shown in Fig. 6 (10). All of the investigators agree on the cation sequence along the c axis, although they differ somewhat on details of the symmetry. In this version, the Ca at the midpoint of the cell defines a mirror plane between the top and bottom halves that each contain the unit $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. The Ca serves a similar purpose here as the Y does in the 1-2-3 compound, in that every layer that contains Ca localizes a layer of missing oxygens at that level within an otherwise normal cubic perovskite cell, because of its preference for a coordination number of less than 12. Above and below the central perovskite-like cell centered on Ca is a layer of SrO, much like the SrO layers in the R-P series. However, rather than reverting then to another perovskite layer, the SrO layer is followed by two successive BiO layers. The SrO-BiO-BiO sequence follows a NaCl structural pattern of squares, SrO_4 - BiO_4 - BiO_4 , before there is then a terminal perovskite-like cell centered on Cu, and with Sr on the top corners and Ca on the bottom corners. The oxygen that would normally be at the center of the bottom, Ca-containing plane is missing (as is the one that would be in the center of the topmost plane of the full unit cell). The sequence along the c axis is then: two successive Ca-Sr-Cu perovskite-like units, centered on the Cu, then a triple R-P type sequence of BiO-BiO-SrO, then a Ca-Cu perovskite-like unit, centered on Ca, then three more R-P layers, etc. The R-P layers, in the NaCl pattern, serve as lateral structural shifters, just as they do in the SrO-nSrTiO_3 R-P series. The first layer would shift the next

perovskite unit laterally, the second will shift it back into alignment, and the third one shifts it again, so that in this structure, successive perovskite units are laterally shifted. This structure shares a feature in common with the Y-Ba-Cu-O material, in that there are two successive Cu-O planes, rather than only a single one as in La-Sr-Cu-O.

The structural pattern described above suggests that we should consider a more generalized version of the R-P formula, namely, $m\text{AO}-n\text{ABO}_3$, where there can be multiple NaCl-type layers, as well as multiple perovskite-type layers. The homologous series based on $\text{SrO}-n\text{SrTiO}_3$ is then a special case with $m = 1$. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ can then be derived from the ideal prototype $3\text{SrO}-2\text{SrCuO}_3$, where the Cu is formally +4. This is relieved to Cu+3 by replacing 2SrO with 2BiO^+ , where the Bi+3 acts as a donor dopant. Another oxygen is lost, giving $\text{SrO}-2\text{BiO}-2\text{SrCuO}_{2.5}$, and SrO is replaced by CaO to localize part of the missing oxygen. The oxidation state of the Cu is then formally +2, and to obtain the superconducting material it is raised to about +2.2 by oxidizing the material from O_8 to $\text{O}_{8.2}$ (9).

$\text{Bi}_2\text{Sr}_2\text{CuO}_6$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ have similar structures except that the two-dimensional perovskite-like slabs are only one perovskite unit thick in the former, and are three units thick in the latter. Their ideal prototypical formulas are then $2\text{BiO}\cdot\text{SrO} - \text{SrCuO}_3$ and $2\text{BiO}\cdot\text{SrO}-\text{SrCa}_2\text{Cu}_3\text{O}_9$, or $3\text{AO}-\text{ABO}_3$ and $3\text{AO}-3\text{ABO}_3$.

There has been a very recent report of a superconducting cubic perovskite that contains no Cu (15). Its formula was given as $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ with a T_c of 30 K.

The Tl-Containing Materials

The Tl analogs of the Bi-containing materials have also been prepared, and they fit the same structural pattern, i.e. $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ ($3\text{AO}-\text{ABO}_3$), $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ($3\text{AO}-2\text{ABO}_3$), and $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($3\text{AO}-3\text{ABO}_3$) (16-18). Once again, the smaller Ca^{++} serves to localize planes of missing oxygen relative to the filled perovskite structure.

SUMMARY

It is suggested that almost all of the high temperature superconducting oxides reported to date can be treated as members of an extended version of the Ruddlesden-Popper family of structures that provides for a variable number of AO layers in sequence as well as the usual variable number of ABO_3 layers in sequence. The generalized formula is then $m\text{AO}-n\text{ABO}_3$, and the stoichiometries of the superconducting compounds correspond to four different combinations of m and n along with some systematically missing oxygens. These compounds are summarized below:

Compound	ideal prototype $m\text{AO}-n\text{ABO}_3$	m:n	% missing oxygen	T_c
$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$	$\text{AO}-\text{ABO}_3$	1:1	0	35 K
$\text{YBa}_2\text{Cu}_3\text{O}_7$	ABO_3	0:1	22	95 K
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	$3\text{A}'\text{O}-\text{A}''\text{BO}_3$ $3\text{A}' = \text{Bi}_2\text{Sr}$ $\text{A}'' = \text{Sr}$	3:1	0	12 K
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$	$3\text{A}'\text{O}-2\text{A}''\text{BO}_3$ $3\text{A}' = \text{Bi}_2\text{Sr}$ $2\text{A}'' = \text{SrCa}$	3:2	11	85 K
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	$3\text{A}'\text{O}-3\text{A}''\text{BO}_3$ $3\text{A}' = \text{Bi}_2\text{Sr}$ $3\text{A}'' = \text{SrCa}_2$	3:3	17	110 K
$\text{Tl}_2\text{Ba}_2\text{CuO}_6$	$3\text{A}'\text{O}\cdot\text{A}''\text{BO}_3$ $3\text{A}' = \text{Tl}_2\text{Ba}$ $\text{A}'' = \text{Ba}$	3:1	0	84 K
$\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$	$3\text{A}'\text{O}-2\text{A}''\text{BO}_3$ $3\text{A}' = \text{Tl}_2\text{Ba}$ $2\text{A}'' = \text{BaCa}$	3:2	11	110 K
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	$3\text{A}'\text{O}-3\text{A}''\text{BO}_3$ $3\text{A}' = \text{Tl}_2\text{Ba}$ $3\text{A}'' = \text{BaCa}_2$	3:3	17	125 K
$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$	ABO_3	0:1	0	30 K

All of the materials contain Cu-O planes that in most cases are separated from one another by a plane that contains only a relatively small cation, Y^{+3} or Ca^{+2} , and no oxygen. The Cu in the Cu-O planes is (at least) 4-coordinate, although in $La_{1-x}Sr_xCuO_4$ there are essentially complete octahedra around each Cu. In the other compounds there is a fifth, more distant, oxygen that could be considered to give an approximate 5-coordination in a square pyramidal configuration. It should be noted that none of the Bi and Tl-containing compounds have the Cu-O chains that had been thought to be important for high T_c superconductivity in the 1-2-3 compound. It has more recently been suggested that the number of successive Cu-O planes is an important factor in determining T_c .

The one high T_c oxide reported to date that does not seem to fit this structural pattern is $YBa_2Cu_3O_{7-x}$ with a T_c of 80 K. This material is BO_2 -rich relative to ABO_3 , and thus does not correspond to the AO-rich R-P composition. The structure is still somewhat related, however, in that it contains double layers of perovskite-like structure, centered on Cu, with Y and Ba as the large cations. These are separated by double Cu-O layers with square planar Cu sharing edges within the layer. Thus Cu is serving the dual purpose of centering the perovskite cells, and of separating the perovskite layers in a way that is roughly analogous to that of the Bi and Tl. It is thus related to the $3A'O-2A''BO_3$ structures with $3A' = Cu_2Ba$ and $2A'' = BaY$ and has a formal structural relationship with $Bi_2Sr_2CaCu_2O_8$. It has a T_c that is typical of those structures that have two adjacent perovskite cells.

There is a developing tendency to relate the T_c 's with the number of successive Cu-O "planes" in the structure. This is equivalent to the number of perovskite cells in sequence, since each perovskite cell has a CuO_2 plane across its middle. The two descriptions are thus interchangeable.

ACKNOWLEDGEMENT

The authors are grateful for support from the Division of Materials Research, NSF, and from the Lehigh University Consortium for Superconducting Ceramics.

REFERENCES

1. S. N. Ruddlesden and P. Popper, "The Compound $Sr_3Ti_2O_7$ and Its Structure," *Acta Cryst.*, 11, 54-55 (1958).
2. D. M. Smyth, "Defects and Order in Perovskite-Related Oxides," pp. 329-357 in *Annual Review of Material Science*, 15. Edited by R. A. Huggins, J. A. Giordmaine, and J. B. Wachtman, Jr., Annual Reviews, Inc., Palo Alto, CA (1985).
3. N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, "Oxygen Defect K_2NiF_4 - Type Oxides: The Compounds $La_{2-x}Sr_xCuO_{4-x/2+8}$," *J. Solid State Chem.*, 39, 120-127 (1981).

4. R. D. Shannon and C. T. Prewitt, "Effective Ionic Radii in Oxides and Fluorides," *Acta Cryst.*, Sect. B, 25, 925-946 (1969).
5. A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. Schneemeyer, and J. V. Waszczak, "The Structure and Properties of $\text{Ba}_2\text{YCu}_3\text{O}_6$," *Mat. Res. Bull.*, 22, 1007-1013 (1987).
6. E. K. Chang, D. J. L. Hong, A. Mehta, and D. M. Smyth, "Equilibrium Conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_x$," accepted by *Materials Letters*.
7. C. Michel, M. Hervieu, M. M. Bovel, A. Grandiu, F. Deslandes, J. Provost, and B. Raveau, "Superconductivity in the Bi-Sr-Cu-O System," *Z. Phys. B*, 68, 421-423 (1987).
8. C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Hue, "Superconductivity up to 114K in the Bi-Al-Ca-Sr-Cu-O Compound System without Rare-Earth Elements," *Phys. Rev. Lett.*, 60 (10), 941-943 (1988).
9. M. A. Subramaniam, C. C. Torardi, J. C. Calabrese, J. Gapalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, "A New High Temperature Superconductor: $\text{Bi}_{2-x}\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{8+y}$," *Science* 239, 1015-1017, February 26, 1988.
10. J. M. Tarascon, Y. LePage, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, "Crystal Substructure and Physical Properties of the Superconducting Phase $\text{Bi}_4(\text{Sr,Ca})_6\text{Cu}_4\text{O}_{16+x}$," submitted to *Phys. Rev.*
11. S. A. Sunshine, et al., "Structure and Physical Properties of Single Crystals of the 84K Superconductor $\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8+\delta}$," submitted to *Phys. Rev.*
12. I. K. Gapalakrishnan, P. Sastry, K. Gangadharan, J. V. Yakhnu, G. M. Phatak, and R. M. Tyer, "High Temperature Superconductivity in Bismuth-Alkaline Earth-Copper-Oxygen System," *Pramana-J. Phys.* 30 (5), 1-3 (1988).
13. K. Togano, H. Kumakura, H. Maeda, K. Takahashi, and M. Nakao, "Preparation of High-T Bi-Sr-Ca-Cu-O Superconductors," submitted to *Jap. J. of Applied Physics*.
14. A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford (1975), p. 713.
15. R. J. Cava, B. Batlogy, J. J. Krajewski, R. C. Farrow, L. W. Rupp, Jr., A. E. White, K. T. Short, W. F. Peck, Jr., and T. Y. Kometani, "Superconductivity Near 30K Without Copper: $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ Perovskite," *Nature* Vol. 332, 814-816, 28 April, (1988).

16. Z. Z. Sheng and A. M. Hermann, "Superconductivity in the Rare-Earth-Free Tl-Ba-Cu-O System Above Liquid-Nitrogen Temperature," *Nature*, 332, 55-58 (1988).
17. M. A. Subramaniam, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. Chowdhry, and A. W. Sleight, "Crystal Structure of a New High Temperature Superconductor: $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$," *Nature* 332, 420-422, March 31, (1988).
18. R. M. Hagen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, C. G. Hadjilacos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, A. El Ali, and A. M. Hermann, "100K Superconducting Phases in the Tl-Ca-Ba-Cu-O System," *Phys. Rev. Lett.*, 60, (16), 1657-1660 (1988).