



Springer Series in Materials Science

Advisors: M. S. Dresselhaus · K. A. Müller

Editors: U. Gonser · A. Mooradian · R. M. Osgood · M. B. Panish · H. Sakaki

Managing Editor: H. K. V. Lotsch

- 1 **Chemical Processing with Lasers**
By D. Bäuerle
 - 2 **Laser-Beam Interactions with Materials**
Physical Principles and Applications
By M. von Allmen
 - 3 **Laser Processing of Thin Films and Microstructures**
Oxidation, Deposition and Etching of Insulators
By I. W. Boyd
 - 4 **Microclusters**
Editors: S. Sugano, Y. Nishina, and S. Ohnishi
 - 5 **Graphite Fibers and Filaments**
By M. S. Dresselhaus, G. Dresselhaus, K. Sugihara, I. L. Spain, and H. A. Goldberg
 - 6 **Elemental and Molecular Clusters**
Editors: G. Benedek, T. P. Martin, and G. Pacchioni
 - 7 **Molecular Beam Epitaxy**
Fundamentals and Current Status
By M. A. Herman and H. Sitter
 - 8 **Physical Chemistry of, in and on Silicon**
By G. F. Cerofolini and L. Meda
 - 9 **Tritium and Helium-3 in Metals**
By R. Lässer
 - 10 **Computer Simulation of Ion-Solid Interactions**
By W. Eckstein
 - 11 **Mechanisms of High Temperature Superconductivity**
Editors: H. Kamimura and A. Oshiyama
 - 12 **Dislocation Dynamics and Plasticity**
By T. Suzuki, S. Takeuchi, and H. Yoshinaga
 - 13 **Semiconductor Silicon**
Materials Science and Technology
Editors: G. Harbeke and M. J. Schulz
 - 14 **Graphite Intercalation Compounds I**
Structure and Dynamics
Editors: H. Zabel and S. A. Solin
 - 15 **Crystal Chemistry of High T_c Superconducting Copper Oxides**
By B. Raveau, C. Michel, M. Hervieu, and D. Groult
 - 16 **Hydrogen in Semiconductors**
By S. J. Pearton, M. Stavola, and J. W. Corbett
 - 17 **Ordering at Surfaces and Interfaces**
Editors: A. Yoshimori, T. Shinjo, and H. Watanabe
 - 18 **Graphite Intercalation Compounds II**
Transport and Electronic Properties
Editors: S. A. Solin and H. Zabel
 - 19 **Laser-Assisted Microtechnology**
S. M. Metev, V. P. Veiko
 - 20 **Microcluster Physics**
S. Sugano
-

B. Raveau C. Michel
M. Hervieu D. Groult

Crystal Chemistry of High- T_c Superconducting Copper Oxides

With 320 Figures

Springer-Verlag
Berlin Heidelberg New York
London Paris Tokyo
Hong Kong Barcelona
Budapest

Professor Dr. Bernard Raveau
Professor Dr. Claude Michel
Professor Dr. Maryvonne Hervieu
Professor Dr. Daniel Groult

Lab. de Cristallographie et Sciences des Matériaux
Boulevard du Maréchal Juin, F-14050 Caen Cedex, France

Series Editors:

Prof. R. M. Osgood

Microelectronics Science Laboratory
Department of Electrical Engineering
Columbia University
Seeley W. Mudd Building
New York, NY 10027, USA

Prof. Dr. U. Gonser

Fachbereich 12/1
Werkstoffwissenschaften
Universität des Saarlandes
W-6600 Saarbrücken, Fed. Rep. of Germany

M. B. Panish, Ph. D.

AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974, USA

A. Mooradian, Ph. D.

Leader of the Quantum Electronics Group, MIT
Lincoln Laboratory, P. O. Box 73
Lexington, MA 02173, USA

Prof. H. Sakaki

Institute of Industrial Science
University of Tokyo
7-22-1 Roppongi Minato-ku
Tokyo 106, Japan

Managing Editor: Dr. Helmut K. V. Lotsch

Springer-Verlag, Tiergartenstrasse 17
W-6900 Heidelberg, Fed. Rep. of Germany

ISBN-13:978-3-642-83894-1 e-ISBN-13:978-3-642-83892-7

DOI: 10.1007/978-3-642-83892-7

Library of Congress Cataloging-in-Publication Data. Crystal chemistry of high T_c superconducting copper oxides / B. Raveau ... [et al.]. p. cm. – (Springer series in materials science; v. 15) Includes bibliographical references and index. ISBN-13:978-3-642-83894-1

1. High temperature superconductors. 2. Copper oxide superconductors. I. Raveau, B. (Bernard), 1940 –. II. Series. QC611.98.H54C79 1991 537.6'231-dc20 91-15165

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1991
Softcover reprint of the hardcover 1st edition 1991

The use of registered names, rademark, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

This text was prepared using the PSTM Technical Word Processor and printed by a Hewlett-Packard Laser Jet III
54/3140-543210 – Printed on acid-free paper

Preface

The recent discovery of high-temperature superconductivity in copper-based oxides is an event of major importance not only with respect to the physical phenomenon itself but also because it definitely shows that solid state chemistry, and especially the crystal chemistry of oxides, has a crucial place in the synthesis and understanding of new materials for future applications. The numerous papers published in the field of high T_c superconductors in the last five years demonstrate that the great complexity of these materials necessitates a close collaboration between physicists and solid state chemists.

This book is based to a large extent on our experience of the crystal chemistry of copper oxides, which we have been studying in the laboratory for more than twelve years, but it also summarizes the main results which have been obtained for these compounds in the last five years relating to their spectacular superconducting properties. We have focused on the structure, chemical bonding and nonstoichiometry of these materials, bearing in mind that redox reactions are the key to the optimization of their superconducting properties, owing to the importance of the mixed valence of copper and its Jahn-Teller effect. We have also drawn on studies of extended defects by high-resolution electron microscopy and on their creation by irradiation effects.

Our objective is to reach a very broad audience: students and teachers, physicists and solid state chemists, whether directly or only indirectly involved in the field of superconductivity. Nonspecialists may skip over many details but will find here the main structural types and the main features which govern the nonstoichiometry of copper oxides, and in this way this book will be useful to students and also to "pure" physicists who are more concerned with the physics of superconductivity. Although far from comprehensive, the lists of references will allow solid state chemists working in this field to find basic tools for their investigations.

Such a book could be written not only for copper oxides but also for many other complex oxides, which have already been synthesized and for which one day surprising physical properties will probably be discovered. For these reasons, we would like to recognize here the tremendous pioneering work which has been done before us by solid state chemists and crystallographers in the field of nonstoichiometric oxides.

The first draft of this book was written during August 1988. We are grateful to our families for the sacrifices they made during those holidays and also at other times before and after the discovery of high-temperature superconductivity.

Caen
June 1991

B. Raveau
C. Michel
M. Hervieu
D. Groult

Contents

1. Introduction: Superconductivity in Oxides Before 1986	1
2. Phases of the Systems A-La-Ca-Cu-O and A-Y-Ca-Cu-O (A = Ca, Sr, Ba): Structural Aspects	7
2.1 Copper Chemistry in Oxides: Oxidation States and Coordination	7
2.2 The Ternary Systems La-Cu-O and A-Cu-O (A = Ca, Sr, Ba) .	11
2.3 The Pseudoternary Systems A-La-Cu-O (A = Ca, Sr, Ba)	16
2.3.1 Phases with Oxygen-Deficient Perovskite Structures	17
a) $\text{BaLa}_4\text{Cu}_5\text{O}_{13+\delta}$	17
b) $\text{La}_{8-x}\text{Sr}_x\text{Cu}_8\text{O}_{20}$	20
c) $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14}$ and $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$	21
2.3.2 The Intergrowths Between Perovskite and Rock-Salt-Type Structures	22
a) The Oxides $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-x/2+\delta}$	22
b) The Oxides $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6-x/2+\delta}$	28
c) $\text{La}_{4-2x}\text{Ba}_{2+2x}\text{Cu}_{2-x}\text{O}_{10-2x}$	31
2.4 The Pseudoternary System Y-Ba-Cu-O	32
2.4.1 The Orthorhombic 92 K Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.	32
2.4.2 The Tetragonal Phases $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	34
2.4.3 Problems of Microtwinning in the Orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	43
2.4.4 The "Green Phase" Y_2BaCuO_5	47
2.4.5 Other Phases of the System Y-Ba-Cu-O	48
2.5 The Systems Ln-Sr-Cu-O (Ln \neq La)	48
3. Electron Transport Properties Connected with Oxygen Nonstoichiometry	52
3.1 Electron Transport Properties in Cuprates Related to the Perovskite: General Considerations	52
3.2 Oxides with the K_2NiF_4 -Type Structure	55
3.2.1 La_2CuO_4	55
a) "Normal" Properties	55
b) Superconducting Properties	57
3.2.2 The Oxides $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-x/2+\delta}$ (A = Ba, Ca, Sr)	58
a) Electron Transport Properties Above 77 K	59
b) Superconducting Properties	64

3.2.3	Substitutions for Lanthanum in the Superconducting Oxide $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-y}$	67
	a) Rare-Earth Substitutions	67
	b) Bismuth Substitution	68
3.2.4	Other Cuprates with the K_2NiF_4 Structure	70
3.3	Oxides with the Oxygen-Deficient $\text{Sr}_3\text{Ti}_2\text{O}_7$ -Type Structure	71
3.3.1	The Oxides $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6-x/2+\delta}$ ($\text{A} = \text{Sr}, \text{Ca}$)	71
3.3.2	The Oxides $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6-x/2}$	73
	a) $\text{Ln} = \text{Pr}, \text{Nd}; x = 0.14$	74
	b) $\text{Ln} = \text{Eu}, \text{Sm}, \text{Gd}; x = 0.9$	74
3.4	Oxides with the Oxygen-Deficient Perovskite Structure	74
3.4.1	Nonsuperconducting Oxides	74
	a) LaCuO_3	74
	b) $\text{BaLa}_4\text{Cu}_5\text{O}_{13+\delta}$ and $\text{La}_{8-x}\text{Sr}_x\text{Cu}_8\text{O}_{20-\epsilon}$	75
	c) $\text{Ba}_3\text{La}_3\text{Cu}_6\text{O}_{14+\delta}$	77
3.4.2	Superconducting Oxides: Properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	80
	a) The "Stoichiometric" Oxide	80
	b) Influence of the Oxygen Nonstoichiometry	82
	c) Substitution for Yttrium and Barium	86
4.	Substitutions in La_2CuO_4-Type and $\text{YBa}_2\text{Cu}_3\text{O}_7$-Type Superconductors	91
4.1	Substitution on the Rare-Earth Sites	91
	4.1.1 La_2CuO_4 -Type Oxides	91
	4.1.2 $\text{YBa}_2\text{Cu}_3\text{O}_7$ -Type Oxides	93
4.2	Substitution on the Copper Sites	94
	4.2.1 La_2CuO_4 -Type Oxides	96
	4.2.2 $\text{YBa}_2\text{Cu}_3\text{O}_7$ -Type Oxides	98
	a) Nickel Substitution	98
	b) Iron Substitution	101
	c) Other Transition Element Substitutions	109
	d) Other Substitutions	110
4.3	Substitutions on Other Sites	112
	4.3.1 Substitution for Barium	112
	4.3.2 Fluorination of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	112
5.	Bismuth, Thallium and Lead Superconducting Cuprates	113
5.1	Bismuth Alkaline-Earth Superconducting Cuprates	113
5.2	Thallium Alkaline-Earth Superconducting Cuprates	123
5.3	Lead Alkaline-Earth Superconducting Cuprates	140
5.4	Layered Cuprates Involving Double Fluorite-Type Layers	145
5.5	Structural Relationships	150
6.	Extended Defects in Superconducting Oxides: High-Resolution Electron Microscopy	155
6.1	$\text{YBa}_2\text{Cu}_3\text{O}_7$ -Type Superconductors: Ordering in the Perovskite Framework	156

6.1.1	YBa ₂ Cu ₃ O _{7-δ}	156
	a) HREM Images	156
	b) 92 K Orthorhombic Superconductor (0≤δ≤0.1)	159
	c) Order-Disorder Phenomena: The 60 K Superconductor YBa ₂ Cu ₃ O _{7-δ} (0.37≤δ≤0.45)	174
	d) Nonsuperconducting Tetragonal Phases YBa ₂ Cu ₃ O _{7-δ}	184
	e) Ordering of Oxygen Vacancies: Concluding Remarks	188
6.1.2	La _{3-x} Ba _{3+x} Cu ₆ O _{14+y} Phases	189
	a) LaBa ₂ Cu ₃ O _{7-δ}	189
	b) La ₃ Ba ₃ Cu ₆ O _{14+y}	192
6.2	Nature and Ordering of the Stacked Layers: Intergrowth Mechanisms	198
6.2.1	Structural Considerations for HREM Studies	198
6.2.2	The Bismuth Family	201
6.2.3	Thallium Families: The Classical Defects	207
	a) Perovskite Layers	207
	b) Rock-Salt-Type Layers	211
6.2.4	The Nonsuperconducting TlBa ₂ NdCu ₂ O ₇ : A New Mechanism	215
	a) Classical Defects	218
	b) Variations in the Fluorite-Type Layers	219
6.2.5	Lead Oxides	222
6.2.6	The Rare Earth Oxides	227
6.3	Layer Interconnections	232
6.4	Extra Spots in ED Patterns: An Amazing Variety	239
6.4.1	Substituted Bismuth Oxides	240
6.4.2	Thallium Oxides	247
6.4.3	Lead Oxides	249
6.5	Domains and Boundaries	256
7.	Irradiation Effects in the High-T_c Superconducting Oxides	263
7.1	Radiation Damage in Solids	264
7.1.1	Electronic and Nuclear Stopping Powers	264
7.1.2	Material Modifications	266
	a) Electronic Energy Loss Effects	267
	b) Nuclear Energy Loss Effects	267
7.2	Radiation Damage by Electrons and Fast Neutrons in Copper Oxide Superconductors	269
7.2.1	Defect Structures Produced by Electron Irradiation	269
7.2.2	Changes Induced by Fast Neutron Irradiation	273
7.3	Phase Transformations Induced by Fast Heavy Ions in the High-T _c Copper Oxides	277
7.3.1	Improvement of T _c in the Grain Surface Superconductor La ₂ CuO ₄	278

7.3.2	Heavy-Ion-Induced Changes of Superconducting and Normal Properties of Polycrystalline Ceramics $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$	281
7.3.3	Ion Implantation Effects in Thin Films of Copper Oxide Superconductors	290
7.4	Conclusions	294
8.	Concluding Remarks	296
8.1	Low Dimensionality of the Structure	296
8.2	Mixed Valence of Copper and Hole Delocalization	296
8.3	The Model of Copper Disproportionation	297
8.4	Role of the Lone Pair Cations and of the Alkaline Earth Elements	300
	References	303
	Subject Index	327