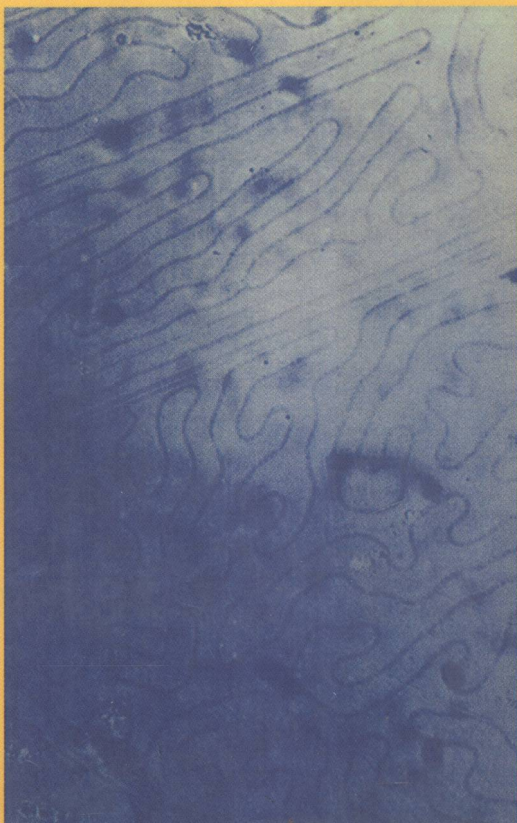


CHEMISTRY
OF
SOLID
STATE
MATERIALS

Magnetic ceramics

RAUL VALENZUELA



TM284
V161

Magnetic ceramics

Raul Valenzuela

*Instituto de Investigaciones en Materiales,
National University of Mexico*



E2010001095



CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS

Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press

The Edinburgh Building, Cambridge CB2 2RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org

Information on this title: www.cambridge.org/9780521364850

© Cambridge University Press 1994

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 1994

This digitally printed first paperback version 2005

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication data

Valenzuela, Raul.

Magnetic ceramics / Raul Valenzuela.

p. cm. — (Chemistry of solid state materials)

Includes bibliographical references.

ISBN 0-521-36485-X

1. Ceramic materials—Magnetic properties. 2. Ferrites—Magnetic properties. I. Title. II. Series.

TK7871.15.C4V35 1994

620.1'404297—dc20 93-43325 CIP

ISBN-13 978-0-521-36485-0 hardback

ISBN-10 0-521-36485-X hardback

ISBN-13 978-0-521-01843-2 paperback

ISBN-10 0-521-01843-9 paperback

Magnetic ceramics describes the structure, preparation techniques, magnetic properties and applications of iron-based oxides, also known as ferrites. The main purpose of the book is to provide an up-to-date overview of the relevant aspects of ferrites. These cover a wide range of magnetic properties and applications such as high-frequency transformer cores, permanent magnets, microwave telecommunication devices, magnetic recording tapes and heads. The subject is approached by emphasising its interdisciplinary nature. Synthesis and fabrication methods and crystal structures are covered alongside the theoretical basis of magnetic properties. This book fills a gap in the ceramics literature. It has been written to appeal to the international community of materials scientists, including researchers in industry and graduate students.

Magnetic ceramics

Chemistry of Solid State Materials

Series editors:

Bruce Dunn, Department of Materials Science and Engineering,
UCLA

John W. Goodby, School of Chemistry, University of Hull

A. R. West, Department of Chemistry, University of Aberdeen

Titles in this series:

David Segal, *Chemical synthesis of advanced ceramic materials*

Philippe Colomban (ed.), *Proton conductors*.

Alan Wilson and John Nicholson, *Acid base reaction cements*

Raul Valenzuela, *Magnetic ceramics*

Peter Bruce (ed.), *Solid state electrochemistry*

Preface

Excellent reviews of various aspects of ferrites (Smit & Wijn, 1961; Smit, 1971; Wohlfarth, 1980, 1982; Goldman, 1990) and magnetism (Cullity, 1972; Jiles, 1991) have been published; however, the need for a monograph covering recent developments on ferrites, such as new preparation technologies, the now-established correlations between polycrystalline structure and magnetic properties, and the most recent applications in magnetic recording, at an introductory level, was felt. The aim of this book is to satisfy that need.

The book corresponds to a final-year undergraduate or graduate level in solid-state chemistry, solid-state physics, or materials science, but is expected to be useful also for the researcher specialising in other areas who is interested in a basic overview of magnetic ceramics. It is hoped, additionally, that it will be helpful for the development engineer concerned with the science of ferrites which underpins their applications.

The book was conceived to cover all the important aspects of ferrites. The different crystalline structures are described in Chapter 2, with brief discussions on cation site occupancy and the basic features of the polycrystalline state. Chapter 3 is devoted to preparation methods for powders, ceramics, thin films and single crystals, including classical solid-state sintering as well as new techniques involving the manipulation of small particles. Magnetic properties are discussed in Chapter 4; the approach is developed from the microscopic scale (magnetic moments localised on atoms) to the macroscopic level (domains, granular and shape effects). Electrical and magnetooptic properties are also briefly discussed. Chapter 5 describes the basis of the well-established applications such as permanent magnets and high-frequency transformers, more complex devices based on ferrites, such as magnetic recording heads and media, as well as some of the most promising developments,

Preface

such as perpendicular recording media and magnetooptic recording materials. Finally, a brief overview of other types of magnetic materials, mostly metallic alloys, is given in Chapter 6, including 'classic' materials such as soft and hard magnets, magnetic recording media and heads, miscellaneous materials and applications, and superconductors. In each chapter, an extensive list of references is provided for readers interested in having access to the full details of the original papers.

SI-Sommerfeld units are used throughout this book, since it is essentially addressed to newcomers to magnetism. It is expected that the SI unit system will eventually be fully adopted by the magnetism research community. The definitions of the basic parameters and the conversion factors are given in Tables 4.6–4.8.

Most of this book was written during a sabbatical leave at the Department of Chemistry, University of Aberdeen, with a Research Fellowship from the European Commission; I thank the Mexican authorities at SRE and at the University of Mexico (DGAPA-UNAM). I especially acknowledge the invitation and encouragement from Professor Anthony West to write this book, as well as his invaluable help with the intricacies of the English language! I am indebted to the staff of the IIM-UNAM (Mexico) and Queen Mother (Aberdeen) Libraries for providing many scientific publications. I thank my wife Patricia, not only for her understanding and encouragement to achieve this task, but also for her technical help (she drew most of the figures!). Finally, I hope that my son Alejandro will be interested in this book in the near future.

University of Mexico
July 1993

Raúl Valenzuela

References

- Cullity, B. D. (1972). *Introduction to Magnetic Materials*, Addison-Wesley, Massachusetts.
- Goldman, A. (1990). *Modern Ferrite Technology*, Van Nostrand Reinhold, New York.
- Jiles, D. (1991). *Introduction to Magnetism and Magnetic Materials*, Chapman and Hall, London.
- Smit, J. (1971). *Magnetic Properties of Materials*, McGraw-Hill, New York.

Preface

- Smit, J. & Wijn, H. P. J. (1961). *Les Ferrites*, Bibliotheque Technique Philips, Dunod, Paris.
- Wohlfarth, E. P. (Ed.) (1980). *Ferromagnetic Materials*, Vol. 2. North-Holland, Amsterdam.
- Wohlfarth, E. P. (Ed.) (1982). *Ferromagnetic Materials*, Vol. 3. North-Holland, Amsterdam.

Symbols

A	exchange constant
A, A'	constant
A	cross-sectional area
A	angular momentum
a	nucleation-rate factor
a	unit cell parameter
$B(J, \alpha')$	Brillouin function
B	magnetic induction
B_d	demagnetised induction
B_r	remanent induction
$(BH)_{\max}$	maximum energy product
b	growing phase dimensionality factor
C	capacitance
C	domain wall mobility
C_v, C_c	vacancy concentrations
C_v	heat capacity at constant volume
c	cell parameter
D	divalent cation
D	average grain size
D_0, D_c	diffusion coefficients
Dq	energy difference (crystal field)
d_{xy}	atomic orbitals
d	density
E	activation energy
E_c	kinetic energy
E_f	Fermi energy
E_K	anisotropy energy
E_{ex}	exchange energy
E_m	magnetostatic energy
E_n	electron energy
E_p	magnetic potential energy
e	electron charge
e_g	electron orbital doublet
F	Lorentz force

Symbols

f	frequency
g	Landé factor
H	intensity of magnetic field
H_c	coercivity
H_c	critical field (superconductors)
H_{c1}, H_{c2}	critical fields (superconductors)
H_{cr}	critical field
H_{eff}	effective anisotropy field
H_c	coercive field measured from B-H curves
H_c	intrinsic coercive field
H_K	anisotropy field
H_n	nucleation field
H_p	pinning field
H_p	propagating field
H_T	total field
H_w	molecular or Weiss field
ΔH	resonance linewidth
h	ac magnetic field
h	Planck's constant
h_{rf}	radio frequency magnetic field
$I(K)$	interference function
J	total angular quantum number
J_{ex}	exchange integral
K	Arrhenius-type constant
K	geometric constant
K	Kundt's constant
K	total anisotropy constant
K	scattered density
K_s	shape-anisotropy constant
K_1, K_2	magnetocrystalline anisotropy constants
k	constant
k	Boltzmann constant
L	inductance
L	total angular quantum number
$L(\alpha)$	Langevin function
l	angular momentum quantum number
M	magnetisation
M	metaloid
Me	divalent cation
M_r	remanent magnetisation
M_s	saturation magnetisation
\mathcal{M}	magnetic dipolar momentum
m	reduced magnetisation
m	mass
m	effective domain wall mass
m_l	magnet quantum number

Symbols

N	number of atoms per volume unit
N_d	demagnetisation factor
N_0	Avogadro's number
n	Avrami exponent
n	integer
n	number of Bohr magnetons per formula unit
n	total number of electrons 3d + 4s
P_e	eddy-current loss
P_h	hysteresis energy loss
$P(r)$	atomic distribution function
P_T	total energy loss
P_0	average atomic density
ΔP	change in properties
ΔP	pressure difference
p	growth mechanism factor
p_s	spin angular momentum
p_0	angular momentum
Q	electric charge
q	electric charge
R	gas constant
R	rare-earth cation
R	resistance
R_O	oxide ion radius
$RDF(r)$	radial distribution function
R	wave function in spherical coordinates
r	distance between atoms
r	heating rate
r	particle radius
r	pore radius
r_0	interatomic equilibrium distance
S	total spin
s	spin quantum number
s_p	particle separation
T	temperature
T	trivalent cation
TM	transition metal
T_C	Curie temperature
T_f	fictive temperature
T_g	glass transition temperature
T_m	melting temperature
T_N	Néel temperature
T_x	crystallisation temperature
T_{comp}	compensation temperature
t	thickness
t	reduced temperature
t	time

Symbols

t_{2g}	electron orbital triplet
u	deformation parameter
V	unit cell volume
V	electrostatic potential
\mathbf{v}	velocity
v	volume
x	composition
x	crystallised fraction
x	domain wall displacement
W	formula weight
W_h	area of hysteresis loop
Z	atomic number
Z^*	complex impedance
α	Fe bcc crystal phase
α	Langevin factor
α	optical absorption coefficient
α	restoring force coefficient
$\alpha_1, \alpha_2, \alpha_3$	angle cosines
β	viscous damping factor
γ	gyromagnetic ratio
γ	surface energy
γ	Fe fcc crystal phase
γ_w	domain wall energy
Δ	energy difference (crystal field)
δ	degree of inversion
δ_w	domain wall thickness
ε	permittivity
η	geometrical factor
\ominus	extrapolated temperature (antiferromagnetics)
\ominus	wave function in spherical coordinates
θ	angle
θ_F	Faraday rotation angle
λ	molecular field coefficient
λ	wavelength
λ_s	saturation magnetostriction constant
μ_i	relative initial permeability
μ_{\max}	relative maximum permeability
μ_0	permeability of free space
ρ	electrical resistivity
σ_g	greenbody strength
τ	relaxation time
Φ	wave function in spherical coordinates
Φ_0	magnetic quantum flux
ϕ	magnetic flux
ϕ_v	solid volume fraction

Symbols

χ	magnetic susceptibility
χ^*	complex susceptibility
χ', χ''	real and imaginary parts of the susceptibility
χ_0	low-frequency susceptibility
χ_{\perp}	perpendicular magnetic susceptibility
χ_{\parallel}	parallel magnetic susceptibility
Ψ	wave function
ψ	time-independent wave function
ω	angular frequency
ω_L	Larmor frequency
ω_s	resonance frequency
ω_x	angular relaxation frequency

Contents

Preface	<i>xi</i>
Symbols	<i>xv</i>

1	Introduction	<i>1</i>
	References	<i>2</i>

2	The crystal structures of magnetic ceramics	<i>3</i>
2.1	Spinel	<i>3</i>
2.1.1	<i>The spinel structure</i>	<i>3</i>
2.1.2	<i>Normal and inverse spinels: cation distribution</i>	<i>6</i>
2.1.3	<i>Spinel solid solutions</i>	<i>16</i>
2.1.4	<i>Distorted spinels, magnetite and maghemite</i>	<i>19</i>
2.2	Garnets	<i>24</i>
2.2.1	<i>The garnet structure</i>	<i>24</i>
2.2.2	<i>Cation substitutions</i>	<i>28</i>
2.2.3	<i>Garnet solid solutions</i>	<i>29</i>
2.3	Hexagonal ferrites	<i>30</i>
2.3.1	<i>Crystal structures</i>	<i>30</i>
2.3.2	<i>Cation substitutions</i>	<i>34</i>
2.4	Microstructure	<i>36</i>
2.4.1	<i>The polycrystalline state</i>	<i>36</i>
	References	<i>38</i>

3	Preparation of magnetic ceramics	<i>44</i>
3.1	Introduction	<i>44</i>
3.2	Powder preparation	<i>46</i>
3.2.1	<i>Coprecipitation</i>	<i>48</i>
3.2.2	<i>Precursor methods</i>	<i>49</i>
3.2.3	<i>Sol-gel methods</i>	<i>50</i>
3.2.4	<i>Spray-drying</i>	<i>53</i>
3.2.5	<i>Freeze-drying</i>	<i>54</i>
3.2.6	<i>Combustion synthesis</i>	<i>55</i>

Contents

3.2.7	<i>Glass crystallisation</i>	56
3.2.8	<i>Other methods</i>	57
3.3	<i>Greenbody forming</i>	57
3.3.1	<i>Compaction</i>	57
3.3.2	<i>Pressing</i>	59
3.3.3	<i>Casting</i>	60
3.4	<i>Sintering</i>	62
3.4.1	<i>Solid-state reactions</i>	66
3.4.2	<i>Densification</i>	69
3.4.3	<i>Hot press sintering</i>	74
3.4.4	<i>Microwave sintering</i>	75
3.5	<i>Permanent magnet technology</i>	76
3.6	<i>Preparation of ferrite thin films</i>	79
3.6.1	<i>Liquid phase epitaxy</i>	79
3.6.2	<i>Sputtering techniques</i>	81
3.6.3	<i>Other methods</i>	83
3.7	<i>Preparation of ferrite single crystals</i>	88
	<i>References</i>	92
4	<i>Magnetic properties of ferrites</i>	98
4.1	<i>Origin of magnetic moments</i>	98
4.1.1	<i>Electronic structure</i>	98
4.1.2	<i>Bonding</i>	106
4.2	<i>Magnetic order</i>	111
4.2.1	<i>Diamagnetism and paramagnetism</i>	111
4.2.2	<i>Exchange</i>	116
4.2.3	<i>Molecular field theory</i>	121
4.2.4	<i>Ferrimagnets</i>	128
4.2.5	<i>Anisotropy and magnetostriction</i>	137
4.3	<i>Domains and domain walls</i>	142
4.3.1	<i>Domain structure</i>	142
4.3.2	<i>Magnetisation processes and hysteresis</i>	148
4.4	<i>Soft ferrites</i>	162
4.4.1	<i>Initial permeability</i>	162
4.4.2	<i>Disaccommodation and magnetic annealing</i>	163
4.5	<i>Hard ferrites</i>	167
4.5.1	<i>Magnetisation rotation</i>	167
4.5.2	<i>The $(BH)_{\max}$ product</i>	171
4.6	<i>Magnetisation dynamics</i>	173
4.6.1	<i>Domain wall dynamics</i>	173
4.6.2	<i>Ferromagnetic resonance</i>	177
4.7	<i>Electrical properties</i>	179
4.8	<i>Magneto-optical properties</i>	182
	<i>References</i>	185

Contents

5	Applications of ferrites	191
5.1	Permanent magnet devices	191
5.2	Linear response applications	194
5.3	Power applications	199
5.4	Magnetic recording	201
5.4.1	Core memories and bubbles	201
5.4.2	Magnetic recording processes	203
5.4.3	Magnetic recording heads	207
5.4.4	Magnetic recording media	209
5.4.5	Magneto-optical recording	211
5.5	Microwave components	213
5.6	Other applications	217
	References	219
6	Other magnetic materials	223
6.1	Soft magnetic materials	223
6.1.1	Crystalline alloys	224
6.1.2	Amorphous alloys	243
6.2	Hard magnetic materials	257
6.2.1	Coercivity mechanisms	258
6.2.2	Alnico alloys	260
6.2.3	Sm-Co magnets	263
6.2.4	Nd-Fe-B magnets	267
6.2.5	Nitrides and carbides	270
6.3	Materials for magnetic recording	272
6.4	Materials for magneto-optical recording	277
6.5	Special magnetic materials and applications	279
6.5.1	Molecular magnets	280
6.5.2	Magnetic imaging	282
6.5.3	Non-destructive evaluation	285
6.6	Superconductors	289
	References	299

Index	309
-------	-----