Springer Series in Materials Science

Volume 177

For further volumes:
http://www.springer.com/series/856

The Springer Series in Materials Science covers the complete spectrum of materials physics, including fundamental principles, physical properties, materials theory and design. Recognizing the increasing importance of materials science in future device technologies, the book titles in this series reflect the state-of-the-art in understanding and controlling the structure and properties of all important classes of materials.

M.D. Glinchuk • A.V. Ragulya
Vladimir A. Stephanovich

Nanoferroics

Springer

M.D. Glinchuk
Department of Functional Oxide Materials
Institute of Material Science NAS
Kiev
Ukraine

A.V. Ragulya
Department of Physical Chemistry
Institute of Material Science NAS
Kiev
Ukraine

Vladimir A. Stephanovich
Department of Physics
Opole University
Opole
Poland

ISSN 0933-033X
ISBN 978-94-007-5991-6 ISBN 978-94-007-5992-3 (eBook)
DOI 10.1007/978-94-007-5992-3
Springer Dordrecht Heidelberg New York London

Library of Congress Control Number: 2013937616

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Modern rapid development of nanotechnology imposes an increased interest on studies of subtleties of fabrication technology and physical properties of nanosized materials. Although the physical properties of any material crushed down to nanometer size are interesting by themselves, the most intriguing are, in our view, the properties of so-called ferroic (i.e. ferroelectric, ferroelastic, ferromagnetic or multiferroic combining different kind of orderings) substances. The point is, that generally speaking, a nanosized particle of any material would have the properties absent in corresponding bulk sample due to excessive role of a surface. Such properties are strongly dependent on the particle shape (and boundary conditions on its surface) and are due to the effects of geometrical confinement, which have been well studied, e.g., for thin films. At the same time, any bulk ferroic obligatorily has a phase transition, where its long-range ordering appears. The simplest common examples are temperature phase transitions in ferroelectrics (ferromagnets) where spontaneous polarization (magnetization) emerges. More complicated ferroics may have many different kinds of phases, both pure like ferroelectric, ferroelastic and/or ferromagnetic (so-called primary ferroics) and their mixture (secondary ferroics). In the vicinity of phase transition points the ferroics have anomalous properties, which, for nanosized samples, are superimposed on the above effects of geometrical confinement. It can be easily imagined that interplay of these effects is “disastrous” – many weak effects related to phase transitions in a bulk sample, can be overamplified in a nanosized one. Conversely, many effects, absent in a bulk ferroic, may appear in a sample consisting of one or several nanosized particles. Latter effects are extremely important for possible nanotechnological applications of ferroics. Our present monograph is devoted to the comprehensive studies of physical properties of nanosized ferroics which we call nanoferroics. The results of such studies, generating the knowledge of physical properties of nanoferroics, permit to improve substantially the corresponding fabrication technology, which has also been discussed in the present book.

The book consists of five chapters. The first chapter has introductory character. It contains the general definitions and classification of primary and secondary ferroics with the listing of different ferroic materials. For the sake of generality, we discuss briefly the properties of spin, dipole and quadrupolar glasses as well as superparaelectric, superparamagnetic, and relaxor phases. The multiferroics (or secondary ferroics) like ferromagnetic ferroelectrics have also been considered. In these substances, one can control the magnetic properties by the application of electric fields and conversely.

The main results of experimental studies of size effects in nanoferroics are presented in second chapter. In particular, we collect the extensive experimental data about size effects in nanoparticles and thin films of ferroelectrics, ferroelastics and magnetically ordered ferroics. The data have been collected for different nanoparticles geometries like spherical and cylindrical as well as for nanowires, nanotubes and nanopills. As for nanosizes the local properties play a decisive role, we pay attention to the results of electron spin resonant measurements, which are sensitive to the local properties. To obtain the reliable information about the physical properties of the entire nanostructure, the above local methods should be augmented by other experimental techniques like dielectric, magnetic and optical methods. We hope that our collection of available experimental data will give the idea about both local and average static and dynamic properties of nanostructures.

In the third chapter, we discuss the existing theoretical approaches to describe the size effects in nanoferroics. Based on Landau-Ginzburg-Devonshire (LGD) formalism, augmented by corresponding surface terms and boundary conditions, we present the comprehensive theoretical approach suitable for nanoferroics and compare its results with experiment. In many cases, the solution of corresponding Euler-Lagrange equation, obtained by the minimization of LGD free energy functional can be done analytically. This permits to derive analytical (at least asymptotic) expressions for physical properties of nanoparticles of different morphology as well as for thin films on different substrates. The important factor of nanoparticle sizes distribution has also been taken into consideration. The above LGD formalism permits to consider the interesting question about the influence of domain structure on the physical properties of thin ferroelectric (ferromagnetic) films and multilayers near phase transition temperature. The specific analysis has been performed for ferro – paraelectric multilayers and very good coincidence with experimental data has been achieved. We also consider an important question about the behavior of so-called superparamagnetic ensembles of nanoparticles. We show that weak intergranular interaction in such system leads either to superferromagnetic or super spin glass behavior.

The fourth chapter is devoted to the properties, which are specific to nanosized ferroics and absent in corresponding bulk samples. As we have discussed above, such specific properties are generated by the effects of geometrical confinement in nanosized ferroics. In other words, they are due to dominant surface influence. We present vast experimental evidence on these effects, which have recently been revealed for the films and nanoparticles. Also, the comprehensive theoretical analysis of the available experimental data is presented. In this chapter, more attention has been paid to multiferroics, where ferroelectric and ferromagnetic long-range orders coexist. Latter substances have been considered in the form of thin films on substrate or nanowires. Detailed symmetry consideration of the physical properties with respect to effects of geometrical confinement has been presented. The particular attention has been paid for such interesting phenomenon as so-called spontaneous flexoeffect which occurs only in nanoferroics and is absent in bulk samples. The direct flexoeffect is the appearance of order parameter (polarization, magnetization or elastic stress) in primary ferroics in response to inhomogeneous mechanical impact, i.e. strain gradient. The origin of spontaneous flexoeffect in nanosized ferroics is the mechanical strain gradient which appears spontaneously due to above effects of geometrical confinement.

The fifth chapter presents detailed review of technological aspects of ferroic nanoparticles fabrication. We present the detailed information about methods of chemical synthesis of above nanoparticles. Among them are hydrothermal, sol-gel and coprecipitation methods. We also present the method of unstable compounds decomposition. The combined synthesis methods have also been discussed. Namely, we consider mechanochemical, sonochemical and template synthesis methods. The main idea of these methods is to control the dispersity and agglomeration degree of nanoparticles by inspection of nucleation and growth of a new phase. Self-assembly and self-organization of ferroic nanoparticles as well as composites formation on their base by means of colloidal processes have also been considered.

Our monograph is written on the base of results of our original investigations and those of other authors. Also, the material of the monograph has been widely presented in the form of lectures in Kiev Taras Shevchenko National University, Kiev Polytechnic University (Ukraine), Opole University, Wroclaw Polytechnic University (Poland) as well as many other universities from Ukraine, Russia, Poland, Czech Republic, France, Germany, Italy, Slovenia, USA, Canada, Japan, South Korea and Egypt.

We are indebted to many our colleagues for long-lasting collaboration on subjects which are relevant to our present book. Among them are Prof. V.V. Skorokhod, drs. O.O. Vasilkiv, V.V. Laguta and E.A. Eliseev (Ukraine). We are also grateful to Profs. Yu. D. Tretyakov (Russia), R. Newnman and C. Randall (USA), R. Blinc (Slovenia) for collaboration and fruitful discussions of physics, chemistry and technology of nanoferroics.

We are also grateful to Ms. L. Yurchenko for her invaluable help with the manuscript preparation.

Kiev, Ukraine M.D. Glinchuk
Kiev, Ukraine A.V. Ragulya
Opole, Poland V.A. Stephanovich

Contents