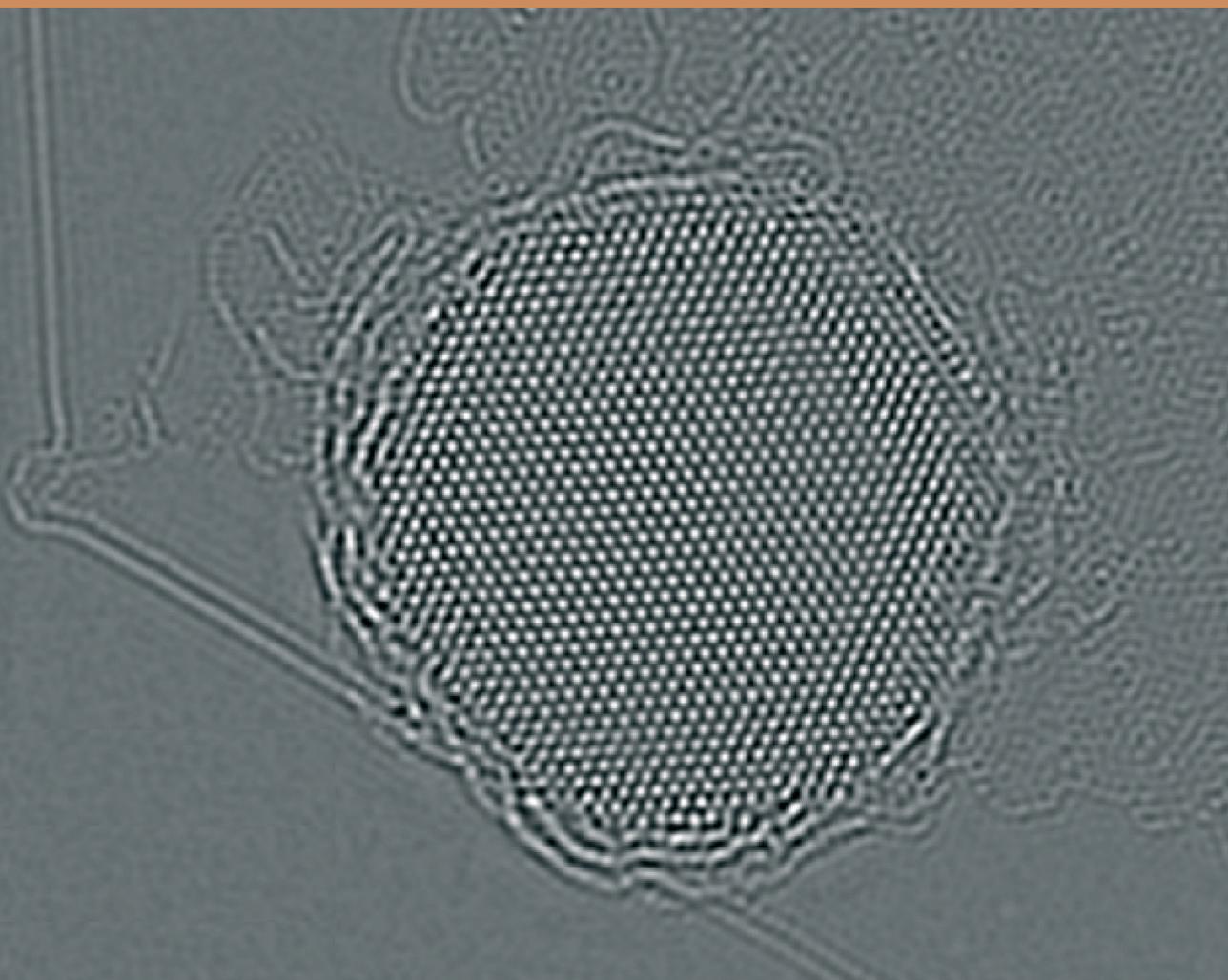


SERBIAN ACADEMY OF SCIENCES AND ARTS
СРПСКА АКАДЕМИЈА НАУКА И УМЕТНОСТИ



FASCINATING WORLD OF NANOSCIENCES
AND NANOTECHNOLOGIES
ФАСЦИНАНТНИ СВЕТ НАНОНАУКА
И НАНОТЕХНОЛОГИЈА

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AND NANOTECHNOLOGY

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FASCINATING WORLD OF NANOSCIENCE AND NANOTECHNOLOGY

Researchers whose work has led to significant discoveries, looking much further, beyond the immediate resolution of technical problems, are asking themselves important questions such as: why individual phenomena occur, how they develop, and why they work. In order to enhance our knowledge about the world around us, and to see pictures of worlds that elude the human eye, through history many experimental and theoretical methods have been developed and are still being improved, including the development of telescopes and microscopes, which enable us to see "very large" and "very small" things.

Researchers involved in the "big things" (the universe, galaxies, stars and planets) have found that a galaxy of an average size of about 100,000 light-years has, on average, around one quadrillion (10^{15}) stars. Researchers involved in the "little things" (nanostructures, molecules, clusters of atoms, individual atoms, atomic defects, etc.) have discovered that 1 cm³ of aluminum alloys also contains approximately one quadrillion (10^{15}) nanoparticles that strengthen these alloys in order to be utilized as a structural material for aircrafts, without which modern transport is unimaginable. How do we count the number of stars in a galaxy or the number of nanoparticles in an aluminum alloy? Relatively easy, because we can see the nanoparticles in aluminum alloys using electron microscopes, and stars in a galaxy using telescopes. Scientific discoveries form the basis for scientific and technological progress, and one such example are the discoveries in the fields of nanosciences and nanotechnologies.

Why is this monograph dedicated to nanosciences and nanotechnologies?

To answer this question, we must first answer the question: what are nanoscience and nanotechnology? In the inevitable *Wikipedia*, *Encyclopedia Britannica* (and any other encyclopedia), dictionaries as well as internet sources, the terms "nanoscience" and "nanotechnology" are related to the study, understanding, controlled manipulation of structures and phenomena, and the application of extremely small things, which have at least one dimension less than 100 nm. Modern aspects of nanosciences and nanotechnologies are quite new and have been developing intensively in the last twenty to thirty years, but the nanoscale substances have been used for centuries, if not millennia. Particulate pigments, for example, have been used in ancient China, Egypt, etc., several thousands of years ago. Artists have decorated windows in medieval churches using silver and gold nanoparticles of various sizes and composition, without understanding the origin of the various colors. Nanoparticles that strengthen alloys of iron, aluminum and other metals, have been used for over a hundred years, although they have not been branded with a prefix "nano", but rather called "precipitates". Scientific disci-

plines, involved in significant research activities related to nanoscience and nanotechnology, are: physical metallurgy, materials science and materials engineering, chemistry, physics, biology, electrical engineering, and so on.

Where does the prefix "nano" come from? "Nano" comes from the Greek words *vāvoç*, which means a dwarf, indicating a dimension of one nanometer (1 nm), which represents one-billionth (10^{-9}) of a meter; Similarly, "nanosecond" (ns) denotes a billionth of a second, and so on. This sounds a bit abstract to many, but to put things into context with which we are familiar, we can mention that the diameter of a human hair, for example, is on average about 100.000 nm (10^5 nm = 100 microns = 0.1 mm), which is roughly the bottom threshold of human eye detection; Thickness of newsprint on average is also about 100.000 nm = 100 μ m = 0.1 mm; Person of 2 m height is 2.000.000.000 (2×10^9) nm high. For comparison, if we assume that the diameter of a children's glass marble was 1 nm, then the diameter of the Earth would be 1 m.

When we talk about the structures of inorganic, organic and bio-nanosystems, their dimensions are as follows: Diameter of carbon atom is in the order of 0.1 nm, or one-tenth of a billionth of a meter; Single-wall carbon nanotubes have a diameter of around 2 nm, or 2 billionth of a meter; The width of the deoxyribonucleic acid (DNA) chain is also about 2 nm, or 2 billionths of a meter; Proteins, which can vary in size, depending on how many amino acids they are composed of, are in the range mainly between 2 and 10 nm, or between 2 and 10 billionths of a meter (assuming their spherical shape); Diameter of individual molecules of hemoglobin is about 5 nm, or 5 billionths of a meter.

Indeed, these are small sizes, but why should they be important, or why does size matter? When analyzing physical systems on the nanoscale, their fundamental properties change drastically. Consider the example, melting point of gold: transition temperature of solid to liquid for gold nanoparticles ~ 4 nm in size, is about 400°C, while the melting temperature of bulk (macroscopic) gold is 1063°C. The same can be said for other properties: mechanical properties, electric conductivity, magnetism, chemical reactivity, etc., also may be drastically changed, which means that nanosystems deviate from the laws of classical physics that describe the motion of the planets, the direction of movement of a rockets which carry satellites to explore space, etc. The base of this fascinating behavior of nanostructures are bonds between the atoms. As structures become smaller, more atoms are present on the surface, hence the ratio of the surface area to volume for these structures increases dramatically. It results in a dramatic change of physicochemical properties of nanostructures from the bulk, as well as possible appearance of quantum effects: nanoscale structures become stronger, less brittle, demonstrate enhanced optical and catalytic properties, and generally, are very different compared to the usual, macroscopic system dimensions to which we are accustomed to in everyday practice.

This monograph comprises a number of contributions which illustrate the sparkling and fascinating world of nanoscience and nanotechnology.

Nanoporous organometallic materials, that can mimic the properties of muscles upon outside stimuli, are ideal actuators, thereby offering a unique combination of low operating voltages, relatively large strain amplitudes, high stiffness and strength. These phenomena are discussed in the manuscript of J. Th. M. DeHosson and E. Detsi.

Drugs in nanodimension range will become much more efficient with reduced adverse effects. A typical example are drugs, carried by various types of nanoparticles which have been previously functionalized, so as to only recognize diseased cells which is a highly selective medical procedure on a molecular level. Besides drugs, functionalized nanoparticles can carry radioactive material or a magnetic structure, which in a strong magnetic field develop high temperatures, and destroy cancer cells. Some aspects of electron microscopy utilized in the study of biological nanostructures are discussed in the paper of A. E. Porter and I. G. Theodorou.

Increased production of nanomaterials raises concern about their safety, not only for humans but also for animals and the environment as well. Their toxicity depends on nanoparticle size, shape, surface area, surface chemistry, concentration, dispersion, aggregation, route of administration and many other factors. The review by M. Čolić and S. Tomić summarizes the main aspects of nano-toxicity *in vitro* and *in vivo*, points out relevant tests of demonstrating toxicity and explains the significance of reactive oxygen species, as the main mechanism of nanoparticle cytotoxicity and genotoxicity through the complex interplay between nanoparticles and cellular or genomic components.

Carbon nanomaterials are a large group of advanced materials that are in focus of extensive research, due to their interesting properties and versatile applicability, especially carbon nanostructures doped by covalently bonded heteroatoms (N, B, P, etc.) which leads to improved properties. This topic is discussed in the manuscript by G. Ćirić-Marjanović.

Combinations of optical, magnetic and photocatalytic properties of nanomaterials, especially those with large energy gaps, are of great interest for nanoscience and nanotechnology. One of such systems are TiO₂ nanostructures with different crystal lattices and shapes (spheres, nanotubes, nanorods), either pure or hybrid, in the form of nanocomposites with matrices based on conducting polymers, which is presented in the work of Z. Šaponjić and coauthors.

Design and manufacturing of multifunctional nanomaterials is one of the most important trends in materials nanoscience, where combining nanomaterials of various characteristics, such as ferroelectrics, ferromagnetics and ferroelastics can lead to achieving adequate multifunctionality, a good example of which are multiferroic nanomaterials, presented in the work of V. Srdić and coauthors.

Materials containing crystal grains of nanodimensions can demonstrate dramatically improved properties. Theoretically as well as experimentally, it has been shown that metallic nanostructures can attain a high percentage of theoretical strength, which questions the classical definition of material strength, stated

until recently by textbooks that does not depend on size of a tested sample. Some aspects of mechanisms of formation, growth and shrinking of crystal grains are discussed in the paper of T. Radetić.

Computational methods, including first principal calculations, have been proven to be a powerful tool in allowing investigations of systems of various complexities, spatial and temporal scales. This allows for screening of a large number of systems, which is not experimentally feasible, and also the understanding of general trends which is of great importance for both theoreticians and experimentalists. The use of this concept in applications of metallic and oxide nanoparticles is described in manuscript of I. A. Pašti and coauthors.

Being aware of the importance of nanosciences and nanotechnologies and their global impact on humanity, in the autumn of 2017, Serbian Academy of Sciences and Arts launched a series of lectures dedicated to these topics from which this monograph arose. We hope that this monograph will be of interest to the reader and can serve as a motivation for creating opportunity for research to those who want to find out more about these fascinating fields of sciences and technologies.

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ФАСЦИНАНТНИ СВЕТ НАНОНАУКА И НАНОТЕХНОЛОГИЈА

Истраживачи чији је рад довео до значајних открића гледају много даље, изван непосредног решавања техничких проблема, постављају себи важна питања, као што су: зашто се дешавају одређене појаве, како се оне развијају и на који начин функционишу? Кроз историју је развијен велики број експерименталних и теоријских метода, које се и дан-данас унапређују, како бисмо обогатили знање о свету који нас окружује и могли да видимо слике светова који измичу људском оку, укључујући ту и проналазак телескопа и микроскопа, који нам омогућавају да видимо „веома велике” и „веома мале” ствари.

Истраживачи који се баве „великим стварима” (универзумом, галаксијама, звездама и планетама) установили су да једна галаксија, око 100.000 светлосних година, у просеку садржи око једну билијарду (10^{15}) звезда. Истраживачи који се баве „малим стварима” (наноструктурама, молекулима, кластерима атома, појединачним атомима, атомским дефектима итд.) установили су да 1 cm^3 легуре алуминијума садржи око једну билијарду (10^{15}) наночестица које ојачавају ту легуру, како би могла да се користи као материјал за израду ваздухоплова, без којих је савремени транспорт незамислив. Како можемо пребројати звезде у једној галаксији или наночестице у једној легури алуминијума? Релативно лако, зато што уз помоћ електронских микроскопа можемо видети наночестице у легурама алуминијума, а звезде у галаксијама уз помоћ телескопа. Научна открића представљају основу научног и технолошког напретка, а један такав пример су открића у области нанонаука и нанотехнологија.

Зашто је ова монографија посвећена нанонаукама и нанотехнологијама?

Да бисмо одговорили на ово питање најпре морамо да установимо шта су то нанонауке и нанотехнологије? Према неизбежној Википедији, Енциклопедији Британици (или било којој другој енциклопедији), речницима, као и изворима са интернета, појмови „нанонаука” и „нанотехнологија” се односе на проучавање, разумевање, контролисано манипулисање структурама и појавама, као и на примену изузетно малих честица, чија је најмање једна димензија у опсегу до 100 nm. Иако су савремени аспекти нанонаука и нанотехнологија сасвим нови и интензивно се развијају у последњих двадесет до тридесет година, облици материје на нано скали користе се већ вековима, ако не и миленијумима. На пример, одређени пигменти коришћени су још у древној Кини и Египту, пре неколико хиљада година. Уметници су украшавали прозоре на средњовековним црквама користећи сребрне и златне наночестице различите величине и састава, при чему нису знали одакле потичу разне боје. Наночестице којима се ојачавају легуре гвожђа, алуминијума и других метала, користе се већ више од сто година,

иако у њиховом називу није садржан префикс „нано”, већ се обично називају „талози”. Научне дисциплине које су укључене у значајне истраживачке активности у области нанонауке и нанотехнологије су: физичка металургија, наука о материјалима и инжењерство материјала, хемија, физика, биологија, електротехника, и тако даље.

Одакле потиче префикс „нано”? Префикс „нано” потиче од грчке речи *νᾶνος*, што значи патуљак, указујући тако на димензију од једног нанометра (1 nm) која представља милијардити део метра (10^{-9} m). Слично томе, „нано-секунда” (ns) означава милијардити део секунде. Ово многим може звучати помало апстрактно, међутим, ствари можемо да поставимо у контекст који је нама познат, и да поменемо, на пример, да пречник власи људске косе у просеку износи 100.000 nm (10^5 nm = 100 микрона = 0.1 mm), што отприлике представља праг онога што може да се опази голим оком. Дебљина новинског папира у просеку такође износи око 100.000 nm = 100 μ m = 0.1 mm. Особа висине 2 m висока је 2.000.000.000 (2×10^9) nm. Поређења ради, ако претпоставимо да је пречник дечијег кликера 1 nm, онда би пречник планете Земље износио 1 m.

Када говоримо о структурама неорганских, органских и природних наносистема, њихове димензије су следеће: пречник атома угљеника је реда величине 0.1 nm, а то је једна десетина милијардитог дела метра; једнозидне угљеничне наноцеви имају пречник од око 2 nm, а то су два милијардита дела метра; ширина ланца дезоксирибонуклеинске киселине (ДНК) такође износи око 2 nm, а то су два милијардита дела метра; пречник протеина, чија величина често варира у зависности од тога од колико се аминокиселина састоје, реда је величине 2–10 nm, или између два и десет милијардитих делова метра (под претпоставком да су сферног облика); пречник појединачних молекула хемоглобина износи око 5 nm, или 5 милијардитих делова метра.

Уистину, ово су све мале димензије, али зашто би оне уопште требало да буду важне, или зашто је величина битна? Када се анализирају физички системи на нано скали, њихова основна својства се драстично мењају. Размотримо, на пример, тачку топљења злата: температура на којој наночестице злата реда величине ~ 4 nm прелазе из чврстог у течно стање износи око 400°C , док је температура топљења макроскопских узорака злата 1063°C . На исти начин мењају се и неке друге особине: механичке особине, електрична проводљивост, магнетизам, хемијска реактивност итд. могу драстично да се промене, што значи да наносистеми одступају од закона класичне физике који описују кретање планета, правац кретања ракета које носе сателите за истраживање свемира итд. Ово фасцинантно понашање наноструктура потиче од веза између атома. Што су структуре мање, то је више атома присутно на површини, услед чега се однос површине и запремине ових структура драстично повећава. Као последица јавља се драматична промена физичко-хемијских својстава наноструктура у односу на структуре макроскопских димензија, као и могућа појава квантних ефеката: структуре на нано скали

постају чвршће, мање крте, показују боља оптичка и каталитичка својства, и, уопштено, веома се разликују од структура уобичајених, макроскопских димензија, које сусрећемо у свакодневној пракси.

Ова монографија садржи низ радова који илуструју фасцинантан свет нанонаука и нанотехнологија.

Нанопорозни органометални материјали, који могу да опонашају особине мишића изложених спољашњим подстицајима, идеални су покретачи, који нуде јединствену комбинацију малих радних напона, релативно велике амплитуде напрезања, велику крутост и снагу. Ове појаве су описане у раду чији су аутори Џ. Т. М. ДеХосон и Е. Детси.

Лекови у области нанодимензија ће постати много ефикаснији и са смањеним штетним ефектима. Типичан пример су лекови које преносе различити типови наночестица, а које су претходно функционализоване тако да препознају само оболеле ћелије, што представља високо селективан поступак на молекуларном нивоу. Поред лекова, функционализоване наночестице могу да буду носачи радиоактивног материјала или магнетних структура, који у јаком магнетном пољу развијају високе температуре и тако уништавају ћелије рака. Одређени аспекти електронске микроскопије који се користе у проучавању биолошких наноструктура описани су у радовима чији су аутори А. Е. Портер и И. Г. Теодору.

Повећана производња наноматеријала изазива забринутост везану за њихову безбедност, не само по здравље људи, већ и за животиње и животну средину. Њихова токсичност зависи од величине наночестица, њиховог облика, величине и хемије површине, концентрације, дисперзије, склоности ка стварању агломерата, начина примене, као и многих других фактора. Рад чији су аутори М. Чолић и С. Томић даје преглед главних аспеката нанотоксичности ин витро и ин vivo, указује на релевантне тестове за утврђивање токсичности, појашњава значај реактивности молекула кисеоника, као главног механизма цитотоксичности и генотоксичности наночестица кроз сложено међудејство наночестица и ћелијских или генских компоненти.

Угњенични наноматеријали представљају велику групу напредних материјала, који због својих занимљивих својстава и широке примењивости заузимају централно место у опсежним истраживањима, нарочито када су у питању угњеничне наноструктуре допиране разнородним атомима, повезаних ковалентним везама (N, B, P итд.), што доводи до побољшања њихових својстава. Ову тему обрађује рад чији је аутор Г. Ћирић-Марјановић.

Комбинације оптичких, магнетских и фотокаталитичких својстава наноматеријала, нарочито оних са великим енергијским процепом, од велике су важности за нанонауке и нанотехнологије. Један од таквих система су TiO_2 наноструктуре са различитим кристалним решеткама и облицима (наносфере, наноцеви, наноштапићи), у чистом или хибридном облику, у облику нанокompозита са основама које су на бази проводних полимера, што је представљено у раду З. Шапоњића и сарадника.

Пројектовање и производња мултифункционалних наноматеријала представљају један од најважнијих трендова у наноуци о материјалима, где комбиновање наноматеријала који поседују различита својства, попут фероелектричности, феромагнетизма и фероеластичности, може довести до постизања одговарајуће мултифункционалности, чији су добар пример мултифероични наноматеријали, који су представљени у раду В. Срдића и сарадника.

Материјали који садрже кристална зрна нанодимензија показују знатно побољшане особине. Теоријски и експериментално је показано да металне наноструктуре могу да достигну висок проценат теоријске чврстоће, што доводи у питање класичну дефиницију чврстоће материјала, којом се, до скоро, у уџбеницима наводило да не зависи од величине испитиваног узорка. У раду Т. Радетић разматрани су неки аспекти механизма формирања, раста и смањивања кристалних зрна.

Показало се да рачунарске методе, укључујући ту и прорачуне на бази првог принципа, представљају моћну алатку која омогућава истраживање система различитих комплексности, како на димензионој тако и на временској скали. Оне омогућавају и преглед великог броја система, што експериментално није изводљиво, као и разумевање општих трендова који су од великог значаја, како за теоретичаре тако и за експериментаторе. Коришћење овог концепта у примени металних и оксидних наночестица описане су у раду чији су аутори И. А. Пашти и сарадници.

Свесна значаја наноука и нанотехнологија, као и њиховог глобалног утицаја на човечанство, Српска академија наука и уметности је у јесен 2017. године покренула серију предавања посвећену овим темама, на основу којих је настала и ова монографија. Надамо се да ће ова монографија бити занимљива читаоцу и да ће моћи да послужи као мотивација за стварање прилика за истраживања онима који желе да сазнају нешто више о овим фасцинантним областима наука и технологија.

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MULTIFERROIC $\text{BaTaO}_3\text{-NaFe}_2\text{O}_4$ COMPOSITES: FROM BULK TO MULTILAYER THIN FILMS

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Abstract. – Over the past decade, magnetoelectric multiferroic materials have been one of the highest priority research topics as they represent new generation of novel multifunctional materials. Multiferroics are characterized by the coexistence of at least two ferroic orders and the presence of ferroelectricity and ferromagnetism, as well as a strong coupling interaction between them (defined as magnetoelectric effect). These properties are essential for new applications in multifunctional devices. This article focuses on various fabrication techniques used for preparation of multiferroic composite ceramics and thin films. The main goals are comparing obtained composite and thin film structures and their properties and acquiring a better understanding of the coupling between magnetic and ferroelectric orders that could surely be very helpful in the design of novel multiferroic materials and hence elucidating their new applications.

Keywords: multiferroics, $\text{BaTaO}_3\text{-NaFe}_2\text{O}_4$, processing, ceramic composites, thin films, nanodevices

INTRODUCTION

New discoveries in science have promoted interest in the development of new and advanced materials and their investigations on the nanoscale. In addition, the possibility of tailoring material properties by changing its structure and composition have brought us into the position to specifically design and fabricate a material for the desired application. A very attractive way to create novel structures is to combine materials with different physical properties in one single structure, thus, improving its final functionality. One group of such novel materials are multiferroics, characterized with the coexistence of at least two ferroic orders (ferroelectric, ferromagnetic and ferroelastic). The coexistence of ferroelectricity

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and ferromagnetism and a strong coupling interaction between two ferroic orders (defined as magnetoelectric effect) is the most important factor for new applications in multifunctional devices. The magnetoelectric effect might be simply described as induction of electric polarization in a material by application of a magnetic field, or the change of magnetization by application of an electric field.

Research in the field of multiferroic materials started with single-phase multiferroics, primarily BiFeO_3 and BiMnO_3 , although only relatively weak magnetoelectric coupling (i.e. small magnetoelectric coefficient) was obtained. In recent years, since most of the examined single-phase multiferroic materials did not meet the expectations and requirements for certain applications, research focus has been largely transferred to composite multiferroics. These materials are characterized with a higher magnetoelectric effect, which arises from interaction between ferroelectric and magnetic phases. This interaction can be explained by transfer of stress, induced in piezoelectric (electrostrictive) phase, by application of an electric field to a magnetostrictive phase through shared interface, followed by a change of magnetization.

The main goals of this research are elucidating the difference between the structure and hence the properties of coupling effect between magnetic and ferroelectric orders which can lead to discover of new multiferroic materials and can help in finding their use in novel applications.

FUNCTIONAL/MULTIFUNCTIONAL MATERIALS

One of the goals of engineers has always been the design of components that will satisfy the desired application. Those components were processed in a way that they could bear various loads, conditions, temperatures, vibrations, etc. Accordingly, the process was focusing more on assembling all components into a proper device. Presently, there is a different perspective: we can think about a material (*functional material*) which is able to directly perform some actions and not just be a passive component. A functional material can respond to a stimulus (temperature, electric field changes, etc.) and therefore substitute an entire complex device composed of several components. Functional materials are often called *smart* materials. However, some authors are of the assumption that a smart material is a material able to respond to various external influences and to adapt its response accordingly [1–3]. A *multifunctional* material integrally combines two (or possibly more) properties, e.g. optical, electrical, magnetic, thermal or mechanical and the integration of those properties in such a material has become a special area of interest in recent years [3, 4]. A multifunctional material could consist of two or more phases/structures/materials. Because each phase/structure/material performs a distinctive function, multifunctional materials promise a more weight- and volume-efficient performance flexibility and require potentially less maintenance than traditional multicomponent systems. In addition, when they

act synergistically, they create new properties that cannot be achieved by each of the material used alone, Fig. 1. Composite materials can be considered multifunctional, since they can achieve multifunctionality through the proper selection of different materials combined together. Biological materials are unique natural multifunctional materials where structural capabilities are fully integrated with sensing, actuation, and healing functions [5].

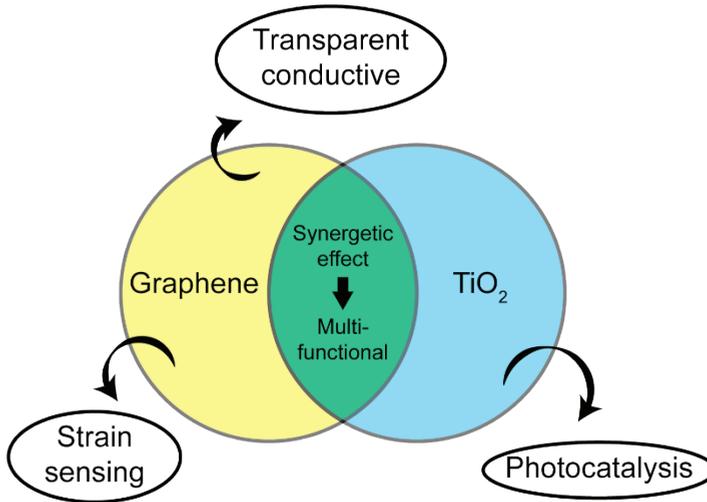


Figure 1. Example of the synergetic effect in multifunctional materials (scheme based on [6])

The evolution of multifunctional materials has been oriented towards the creation of smart systems which have functions and capabilities far beyond the traditional structural materials, driven by the important concept of “environmental awareness” [1]. *Smart* or *intelligent* materials, respond to environmental influences with particular changes in some of their variables. There are many examples of responding materials in nature, e.g. octopuses or chameleons have the ability to rapidly change color as a reaction to a threat. The materials and structures involved in natural systems have the capability to sense their environment, process the data and respond accordingly [2]. By mimicking nature, this *sense capability* could be acquired by embedding sensors into a material, activating particular chemical reactions or triggering specific components whose properties will be activated at a particular load or as a response to particular environmental changes [1]. In such a way, depending on the type of external influences, smart materials could change their structure, properties or even composition.

Multifunctionality of a material could be achieved through control of dimensionality (at nano-, micro-, meso-, and macroscale) and composition (phase structure, morphology, defects). This is where *nanotechnology* plays a significant

role. Nanotechnology is the direct control of materials and devices on a molecular and atomic scale [2] and involves manipulation of matter with at least one dimension sized below 100 nanometers, known as *nanomaterials*. Nanomaterials could be classified based on several aspects like chemical nature, dimensionality, morphology, etc. Dimensionality classification is based on the number of dimensions, which are not confined to the nanoscale range, where $d \leq 100$ nm. The value of d does not have a certain meaning because it is dictated by a critical characteristic of some physical phenomena (free path length of electrons, phonons, length of de Broglie wave, length of external electromagnetic and acoustical waves, correlation length, penetration length, diffusion length, etc.) giving rise to the size effects [7]. According to this classification we could distinguish four groups of nanomaterials: i) zero dimensional, 0D (e.g. nanoparticles, quantum dots), ii) one dimensional, 1D (e.g. nanowires, nanorods, nanotubes, nanobelts, nanoribbons), iii) two dimensional, 2D (e.g. nanolayers, nanoplates, nanosheets, nanowalls, nanodiscs) and iv) three dimensional, 3D (nanoballs dendritic nanostructures, nanocoils, nanocoons, nanopillars, nanoflowers). On the other hand, morphological diversity among nanomaterials is vast and includes all kinds of shapes, such as nanoflowers, hollow nanospheres, branched nanostructures, porous nanomaterials, core/shell nanostructures etc. (Fig. 2). Regarding the chemical nature, nanomaterials could be classified into organic, inorganic and hybrid nanostructures. If we talk about their properties, we can distinguish magnetic nanomaterials, photonics, photocatalytic nanomaterials and so on.

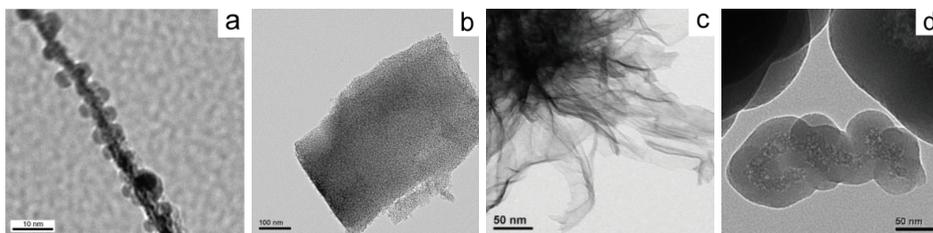


Figure 2. Some interesting examples of nanostructures: a) titanate 1D nanostructure with crystalline nanometer-sized particles attached to it [8], b) mesoporous alumina [9], c) one step in formation of titanate nanotubes [10] and d) ferrite@SiO₂ core/shell particles [11]

Producing nanoscale materials whose functionality can easily be tailored, while using fewer resources and creating less waste and pollution, is the current trend. The finer and more distributed the integration scale in the material, the faster and more autonomous the reaction times of multifunctional material will be [4]. Some authors suggest three types of integration with increasing interconnectivity between phases [2, 3, 12]. Type I: sandwich structure with coated or laminated phases that are not integrated. Type II: integrated materials, but with distinct phases. Type III: materials interconnected at the molecular level with no

physical distinctions between them. According to this classification, we could distinguish between multifunctional structures (MFS), multifunctional composites (MFC) and multifunctional materials (MFM) as shown in Fig. 3 [11].

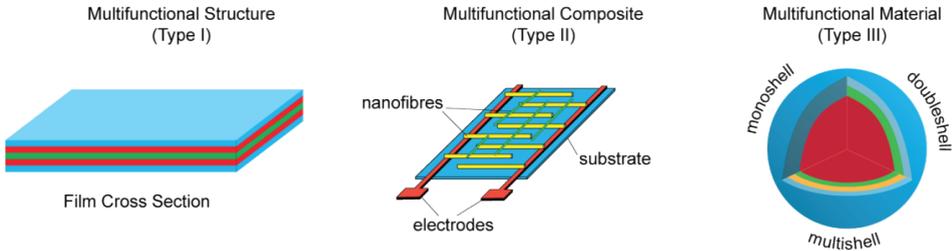


Figure 3. Classification of materials based on levels of integration between phases: multifunctional structure, multifunctional composite and multifunctional material (image in the middle based on [13]; image on the right based on [14])

These multifunctional materials systems can be processed as layered structures, as matrix-reinforced nanocomposites, where matrix can be polymeric, metallic or ceramic material, with the reinforcing phase commonly at the nanoscale, or as a system where all phases are combined in one unique designed structure, Fig. 4.

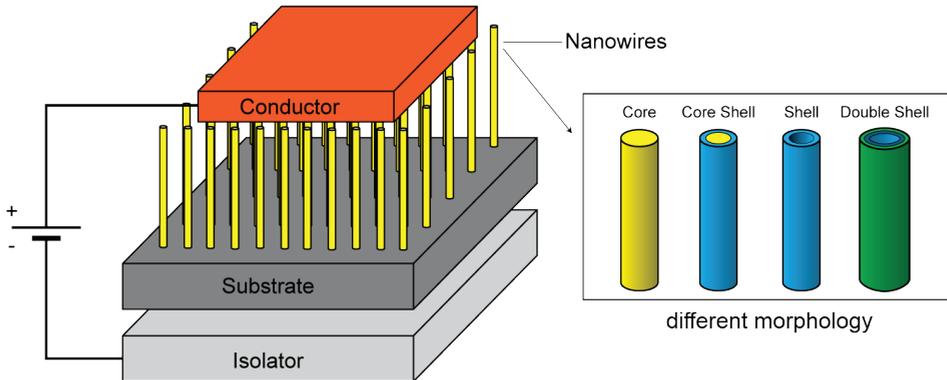


Figure 4. Complex design structure of multifunctional material (image based on [15])

Unique and interesting properties of nanostructured materials, due to the quantum confinement of charge carriers in small dimensions, have given rise to significant desirable properties, such as improved electrical, chemical, as well as mechanical properties compared to their bulk counterpart. Intensive research in the field of nanotechnology, by studying nanostructures and their interfacial interaction, has helped in developing nanomaterials with multifunctional applications. Owing to those properties, multifunctional nanomaterials have a variety of applications in bioengineering, catalysis, nanoelectronics, sensors, renewable

energy systems, etc. Good examples of interplay between the electric and magnetic properties could be found in materials such as multiferroics, spintronics, piezoelectrics (piezotronics), magnetostrictors, thermoelectrics, chemoelectrics etc. Among them, the study of multiferroic materials has driven considerable research over the past decade.

MULTIFERROIC MATERIALS

During recent years, labeled by the integration and miniaturization of electronic components, the study of new materials and their functionalities has become widespread, and one of the main goals has been integration within the existing technologies, processing and devices [16]. Due to unique combination of properties, the research has been focusing on magnetic and ferroelectric materials ranging from giant devices like electrical transformers to tiny devices like sensors, used in integrated circuits or as storage devices. Presently, interest is dedicated to multiferroic materials because of their promising properties and applications. Furthermore, the properties of these materials are likely to offer new kinds devices and functionality, which have motivated a lot of current research activity in the area of ferroelectric, magnetic and multiferroic materials [17]. The evaluation of passive magnetoelectronic components opens the field for the next generation of devices, which combine memory and logic functions and promise to set new standards in future information technology and nanoelectronics [18]. These perspectives require a new class of multifunctional materials and structures whose properties can be manipulated by several independent stimuli by affecting physical degrees of freedom set by the order parameters. The field of *multiferroic* (MF) and *magnetoelectric* (ME) materials has recently received a great deal of attention [16]. Researchers have been looking for ways to couple magnetic and ferroelectric ordering within a material for decades [19].

The development of MF and ME materials possessing coupled magnetic and electrical order parameters started with pioneer work in Russia in the late 1950s and continued intensively in the 1960s [20]. The first multiferroic material discovered was nickel iodine boracite ($\text{Ni}_3\text{B}_2\text{O}_{13}\text{I}$) which was followed by the synthesis of several multiferroic boracite compounds, all of which have complex structures with many atoms per formula unit and more than one formula unit per unit cell. However, the phenomena of ME/MF materials have mostly remained in the theoretical domain owing to the fact that, in single-phase materials, such couplings are rare and weak [21]. From the end of the 1990s, significant progress has been made in synthesizing and characterizing various oxides, which exhibit multiferroic properties at high temperatures, for example Bi-based compounds, namely BiMnO_3 and BiFeO_3 [22]. Recently, the situation has changed dramatically since advances in materials fabrication have made it possible to manufacture these materials in structures of lower dimensionality, such as thin films or nanowires,

or in composite structures such as laminates, epitaxial-layered heterostructures or complex composites including flexible structures [19]. In short, one of the most dynamic fields in the beginning of twenty-first century in material science research is related to multiferroic materials.

Multiferroic (MF) materials exhibit two or more ferroic orders: magnetic (ferromagnetic (FM), antiferromagnetic (AFM) or ferrimagnetic), ferroelectric (FE), ferroelastic or ferrotoroidic (Fig. 5) [23]. Magnetoelectric (ME) materials, on the other hand, exhibit coupling between the electric and magnetic degrees of freedom, so an electric (magnetic) polarization can be induced by a magnetic (electric) field. There are MF materials that are not ME and vice versa, for fundamental reasons, and ME coupling in composite multiferroics is larger than in single-phase MF materials. As MEs and MFs allow the possibility of switching the magnetization with electric field, they possess the opportunity for information storage applications offering the miniaturization of magnetic random-access memory (MRAM), where the write operation requires magnetic fields or large currents [24]. Another possibility is the development of memory bits with multiple stable states [25], or mixed memory and logic functions [26].

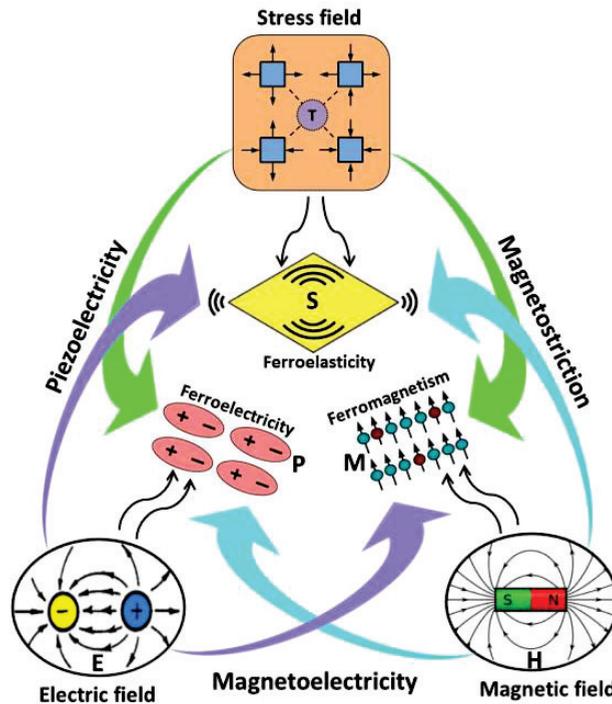


Figure 5. Schematic illustrating magnetic-elastic-electric couplings in multiferroic materials. M is magnetization, S is mechanical strain, and P is dielectric polarization (adopted from [19]).

The magnetoelectric effect appears when electric polarization occurs under the influence of an external magnetic field and magnetization occurs under the influence of an electric field. Macroscopically, the interaction of the electric (E) and magnetic (H) fields and the stress tensor (s) with the material can be described within the Landau theory of phase transitions [16]. This allows an electric field to be used to control the magnetic properties of a material and a magnetic field to be used to control the electric properties. Traditionally, one distinguishes linear, quadratic, and higher order magnetoelectric effects, but more recently the term “magnetoelectric effect” has been often used to describe any form of cross-correlation between magnetic and (di)electric properties. It is important to point out that not all magnetic ferroelectrics exhibit a linear magnetoelectric effect (in the true sense of the word) and that not all materials which exhibit a linear magnetoelectric effect are simultaneously multiferroic (Fig. 6). A multiferroic which is ferromagnetic and ferroelectric is liable to display large linear magnetoelectric effects and the magnetoelectric effect in a single-phase crystal is traditionally described in Landau theory by expressing the free energy, F , of the system in terms of an applied magnetic field H .

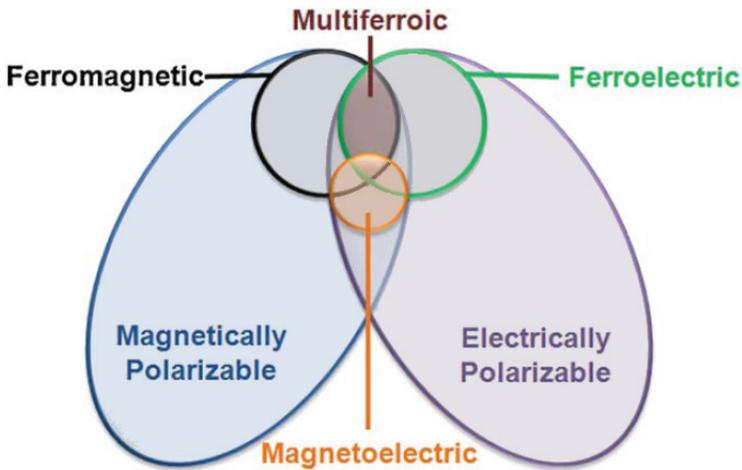


Figure 6. Magnetoelectric (ME) and multiferroic (MF) behavior

Nanostructured multiferroic materials

Even though multiferroic materials have a relatively long history of application, advancements in new techniques of synthesis supported by new theoretical approaches led to substantial progress in achieving the new applications and novel devices. New phenomena were found in ferroics and multiferroics when reduced to the nanoscale. Emergent properties in small structures with unusual geometries

(nanoislands, tubes, wires, rings, ribbons, plates, toroids for films and nanostructured powders) are recently of high interest [27]. Tybell *et al.* [28] showed that ferroelectricity in perovskite Pb(Zr_{0.2}Ti_{0.8})O₃ thin films grown by RF magnetron sputtering could exist down to thicknesses of 40 Å. First-principle calculations for PbTiO₃ thin films suggested the limit could be pushed even further [29] or that there might not be a critical size in some materials [30]. The predicted size effect was also confirmed experimentally in BaTiO₃ (Fig. 7) by Buscaglia *et al.* [31]. In magnetic systems, there are similar size effects including diminished magnetization in ultrathin films, decreased magnetocrystalline anisotropy, etc. [30]. Additionally, it has been observed that thin film strain (tensile or compressive) can change the easy magnetization direction in materials such as manganites.

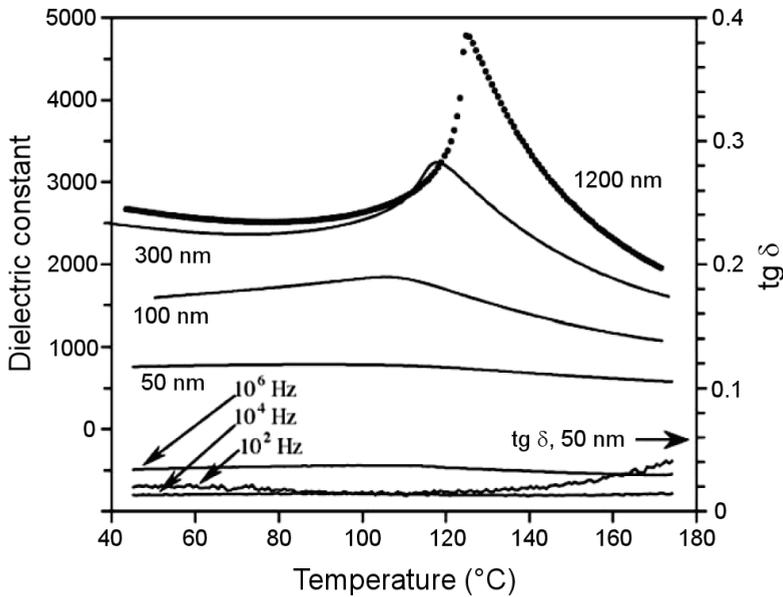


Figure 7. Relative dielectric constant at 10 kHz and loss tangent of BaTiO₃ ceramics with various grain sizes as a function of temperature [31]

Innovative methods for preparing nanosized and nanostructured multiferroics (both single-phase and composite MF) are of a particular importance, as achieving a nanosized material is usually very difficult. Currently, there is much interest in studying multiferroics and understanding controversial aspects of traditional systems like BiFeO₃ [32-34]. Although expected to produce an applications breakthrough, single-phase multiferroics show poor properties at room temperature, even when prepared at nanoscale dimensions.

However, composite multiferroics (bulk and film) which represent a combination of dissimilar materials can possess novel functionalities driven by nanoscale

interface coupling. Examples of such couplings are strain-induced ferroelectricity in quantum paraelectric heterostructures, giant permittivity in magnetic-ferroelectric nanocomposites, enhanced polarization in ferroelectric superlattices, interface spin-orbit or stress-induced magnetoelectric effect in composites [35, 36]. Their functional properties can be tailored through epitaxial strain, local chemistry engineering (inducing interface reactions) or via interface coupling. Preparing heterostructures with atomic-level-growth control and *in situ* synthesis of magnetic-ferroelectric core/shell morphology with various interconnectivities presents a great challenge. Ab initio design of new combinations of dissimilar oxides in order to obtain nanostructured multiferroics, *in situ* innovative synthesis of nanopowders and anisotropic multiferroic composites with various interconnectivities and production of ferroic-based composites multiferroics with emergent electromagnetic properties (metamaterials) are definitely a big challenge in the nanostructured multiferroic materials field [37]. However, the complexity and fast growing know-how requires a more integrated and synergic multidisciplinary approach which is common to various disciplines, but often addressed in divergent ways.

The most challenging aspects in the field of nanostructured multiferroics pertain to multiferric nanopowders, single-phase multiferroics with low dimensionality and unusual geometry, thin and ultrathin films and supported nanostructured ceramics.

SINGLE-PHASE MULTIFERRIOCS

Multiferroic, i.e. magnetoelectric materials can be single-phase or multiphase (di-phase). In *single-phase multiferroics* two ferroic properties are joined in one phase, while in *composite multiferroics* two materials of different properties (e.g. ferroelectric and ferromagnetic) are combined together.

Research into single-phase magnetoelectrics and multiferroics took off during the latter half of the twentieth century. The work on Cr_2O_3 and other antiferromagnetic crystals, such as Gd_2CuO_4 , Sm_2CuO_4 , KNiPO_4 , LiCoPO_4 and BiFeO_3 , was well summarized by Lee *et al.* [38]. As magnetoelectric coupling is determined by the structure and magnetic symmetry of a crystal, small modifications might alter, eliminate or allow magnetoelectric effects. Source of magnetically induced ferroelectricity might be spiral spin ordering, or collinear spin ordering where ferroelectricity is induced with competing FM and AFM interactions [39]. Magnetoelectric switching has been observed in orthorhombic manganites, REMnO_3 or REMn_2O_5 , where RE is a rare-earth element. These are antiferromagnets that display improper (weak) ferroelectricity. The most notable single-phase multiferroic is BiFeO_3 , which is a commensurate ferroelectric and an incommensurate antiferromagnet at room temperature. Promising multiferroic behavior was reported in thin epitaxial BiFeO_3 films, but large magnetization only appeared in the deoxygenated films

followed with high electrical conductivity [32, 34]. Bulk BiFeO₃ exhibits G-type AFM order, where the magnetic moment of each Fe cation is antiparallel to that of its nearest neighbors. A small canting of Fe magnetic moments leads to a net magnetic moment of about 0.05 μ_B per Fe atom. This weak ferromagnetism raises the question of whether small magnetization is coupled with the electric polarization so that it can be manipulated by applied electric fields [33].

Single-phase multiferroics, where magnetic and ferroelectric orders coexist due to mutual polarization and magnetization mechanisms, such as BiMnO₃, BiFeO₃, Pb(Fe_{2/3}W_{1/3})O₃, YMnO₃, EuTiO₃, RMn₂O₅ (R=Tb, Y, Eu, Gd) based solid solutions, (Sr,Mn)TiO₃, LuFe₂O₄, Fe₃O₄, etc. [32] can be produced by alternative methods in various structures whereby stabilizing the oxidation state of the magnetic ion and controlling the oxygen stoichiometry are of great interest for nanostructured systems. However, a significant materials development will be required to generate single-phase multiferroics that could make a real contribution even at nanoscale.

COMPOSITE MULTIFERRIOCS

Composite structures offer an attractive way to combine phases with different physical properties in one structure in order to take advantage of coupling between the individual phases and thus improving its final functionality. Composite magnetoelectric multiferroics consist of two separate phases, ferroelectric and ferromagnetic, and are characterized with much higher magnetoelectric coefficients than the intrinsic single-phase materials. High magnetoelectric response arises from interaction between the phases and various strategies for achievement of magnetoelectric coupling have been investigated [40, 41].

Strategies for achieving magnetoelectric coupling

The most popular approach for achievement of ME effect in composite MF is based on cross coupling between two phases, i.e. piezoelectric (electrostrictive) and magnetostrictive phases, indirectly via strain [40, 42–44]. Precisely, electric field induces change of the dimensions of ferroelectric phase and the induced stress can be transmitted to the magnetostrictive phase through the shared interface leading to a change in its magnetization (Fig. 8).

Similarly, the application of a magnetic field causes the deformation of the magnetostrictive phase which can be transferred to the piezoelectric constituent and induces electric polarization (Fig. 9). Thus, cross interaction between phases is very important and it can produce a strong magnetoelectric effect. Several material combinations geometries have been explored.

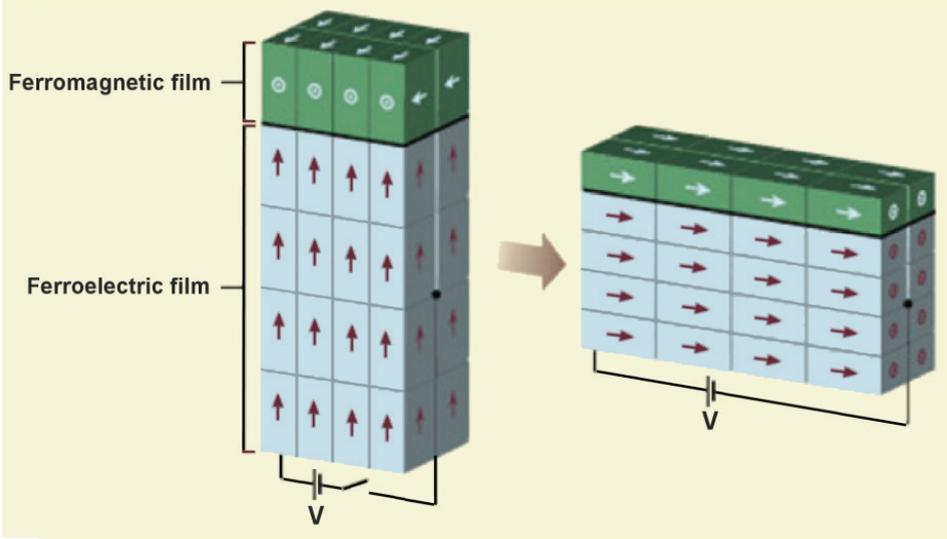


Figure 8. Schematic illustration of strain-mediated ME effect in composites when an external electric field, applied to FE phase, causes change of the preferred orientations of the magnetic dipoles and magnetization (adopted from [45]).

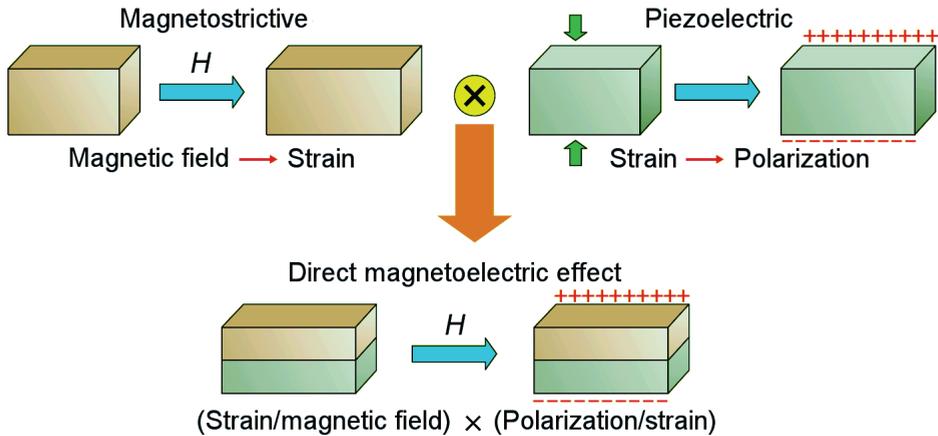


Figure 9. Schematic illustration of strain-mediated ME effect in composites when an external magnetic field induces strain in FM phase, which is mechanically transferred to FE phase and change its polarization (adopted from [46]).

An alternative approach is based on fact that modifications in the antiferromagnetic order, of multiferroics or magnetoelectrics layer, via electric fields can lead to changes in the exchange bias and in properties of the magnetic layer. It is well known that the exchange interaction that gives rise to magnetic order in ox-

ides is often mediated through adjacent oxygen atoms and causes an antiferromagnetic alignment of the spins [40]. Therefore, the magnetoelectric coupling in many multiferroics ordered antiferromagnetically occurs between the electric order and the antiferromagnetic spin configuration. This coupling offers the possibility of controlling the magnetic properties of an adjacent ferromagnetic layer through the exchange anisotropy effect, which can potentially result in a much larger magnetoelectric coupling effect [40]. Such behavior was observed in bilayer structures consisting of multiferroics (BiFeO₃, YMnO₃) and ferromagnetic layers [47] and is based on exchange coupling between the uncompensated interfacial spins of the antiferromagnetic layer and the spins of the ferromagnetic layer (Fig. 10) [40, 47].

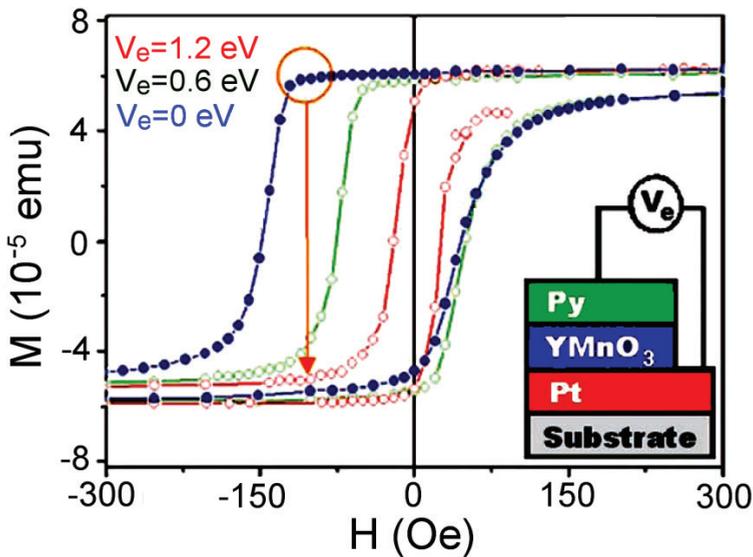


Figure 10. Electric field control of the exchange bias effect in NiFe/YMnO₃/Pt heterostructures (large increase in the exchange bias is observed as the system is cooled under an increasing electric field amplitude) (adopted from [46]).

Other multiferroic structures have also been investigated. Considerable interest has been attracted by multiferroic tunnel junctions with a ferroelectric barrier sandwiched between two ferromagnetic electrodes and the existence of ferroelectric controlled spin polarization. This concept is based on a combination of a magnetic tunnel junction, which has two ferromagnetic electrodes and ferroelectric tunneling, which utilizes a ferroelectric tunneling barrier instead of a dielectric barrier [21, 49, 50] (Fig. 11). As a magnetic tunnel junction, the spin dependent tunneling current depends on the relative orientation of the magnetizations of two ferromagnetic electrodes, creating a tunneling magnetoresistance effect [50].

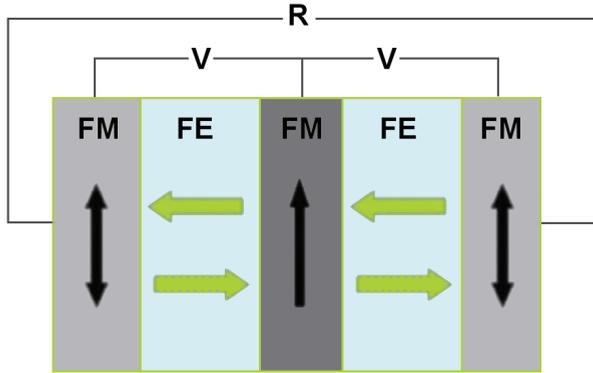


Figure 11. Schematic diagram of FM/FE/FM/FE/FM double-barrier tunnel junction with sixteen resistive states (adopted from [51]).

Composite structures

It is well known that strong magnetoelectric coupling is closely related to composite structure, and connectivity between phases and interface bonding plays an important role in determining magnetoelectric behavior. In this respect, two different approaches were developed: i) bulk composite multiferroics and ii) multiferroic thin films. In both cases, there are three common connectivity types (Fig. 12): i) bulk composite where grains of piezoelectric and magnetic phases are homogeneously mixed, or particles of one phase are embedded in a matrix of different phase (i.e. 3-3 or 0-3 type of connectivity), ii) laminate ceramic composites consisting of the piezoelectric and magnetic oxide layers (i.e. 2-2 type of connectivity) and iii) 1D fibers of one phase embedded in the matrix of another phase (i.e. 1-3 type of connectivity) [40, 44, 52].

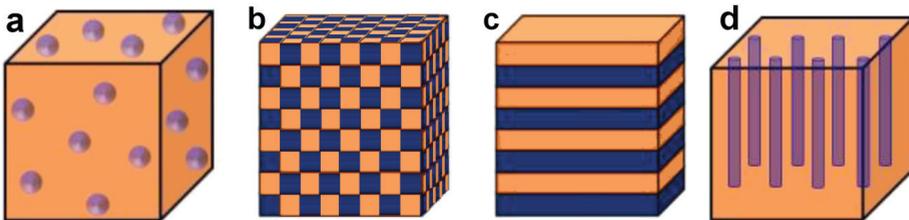


Figure 12. Different types of connectivity: a) 0-3, b) 3-3, c) 2-2 and d) 1-3 between constituent phases in magnetoelectric multiferroic composites

Boomgaard and Born [53] defined some requirements of good ME effect in composites, summarized as follows: i) two phases should be in equilibrium and no chemical reactions should occur between the constituent phases, ii) mag-

netostriction coefficient of ferromagnetic phase and piezoelectric coefficient of ferroelectric phase should be high, iii) resistivity of the constituent phases should be high in order to avoid the leakage of the charges developed in ferroelectric phase and iv) proper poling strategy should be adopted to acquire higher ME signal. Poling is a processing technique used to increase the net polarization which brings out piezoelectricity in polycrystals. In ferroelectric materials, domains are formed spontaneously upon cooling from above the Curie temperature. The direction of polarization among domains is random, so the ceramic has very small net polarization or no polarization at all (Fig. 13a). However, during poling, the domains become aligned by exposing the material to a strong DC field. Through this polarizing (poling) treatment, material becomes elongated in the direction of the field, Fig. 13b. When the field is removed, the orientation of domains is largely retained (Fig. 13c). At this time, the material has a permanent polarization (the remanent polarization) and is permanently elongated. Poling is therefore an important process for enhancing the ferroelectric and piezoelectric properties in ferroelectric materials [54]. Analogously to polarization, the magnetic field is used to increase the net magnetization in ferromagnetic materials.

The selection of ferroelectric and ferromagnetic materials for the preparation of multiferroic materials depends on the various factors required for a certain application. Ferroelectric materials used as a component in multiferroic composites usually possess a perovskite structure with a general formula ABO₃, where A (larger cation) is a monovalent, divalent or trivalent metal and B (smaller cation) a pentavalent, tetravalent or trivalent element, and O is an oxygen [56]. The most crucial and desired properties of one ferroelectric material as a constituent of multiferroic composite are high dielectric constant, low dielectric and piezoelectric losses, and high piezoelectric coefficients. Further substantial properties of ferroelectrics that should be considered are the Curie temperature (T_C), remanent polarization (P_R), coercive field (E_C) etc.

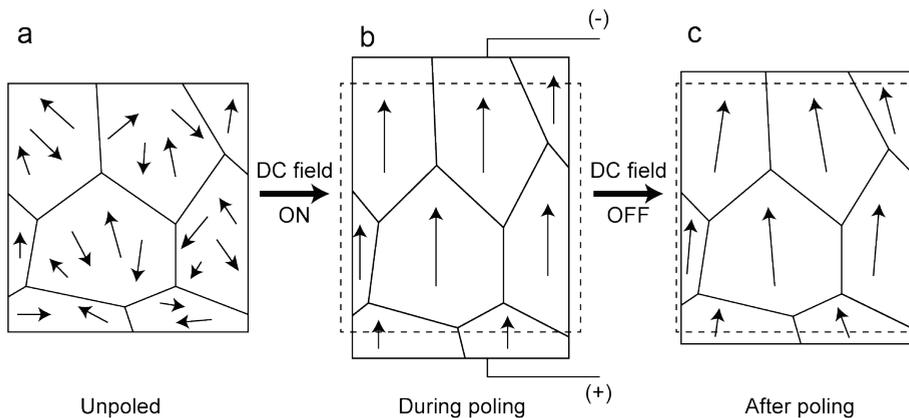


Figure 13. Schematic illustration of the poling process (scheme based on [55])

On the other hand, ferrites are mostly used as a magnetic component of multiferroic composite. Ferrites are mixed metal oxides with iron(III) oxide as a main component, with general formula MFe_2O_4 (where M is a divalent cation like Ni, Zn, Co, Mn, Mg). Additionally, some of the trivalent cations such as Nd, Cr, Y, In etc. can be incorporated into the structure influencing the structural, electrical and magnetic properties of the nanocrystalline ferrites [57], either as spinels (cubic crystal structure), garnets (cubic crystal structure) or magnetoplumbites (hexagonal crystal structure) [58]. The relevant properties of one magnetic material in composites are magnetic permeability (μ), remanent magnetization (M_R), coercive magnetic field (H_C), magnetostriction (λ_{ij}), piezomagnetic coefficient (q_{ij}) and the Curie and Neel temperatures (T_C and T_N , respectively).

BULK COMPOSITE MULTIFERRIOCS

Structure and fabrication of composite multiferroics

Bulk composite multiferroics with indirect coupling between two phases via strain have relatively high magnetoelectric coefficients, usually in the range of $1\text{--}1000\text{ mV cm}^{-1}\text{ Oe}^{-1}$, which is much higher than those typical of intrinsic single-phase multiferroics [44]. Besides composite structure (i.e. type of connectivity), selected materials and fabrication methods are also important factors which affect magnetoelectric coupling in composites [19]. Magnetoelectric coefficients of various bulk and film-based composites having 0-3, 1-3, and 2-2 connectivity are given in Fig. 14. Special attention was dedicated to composites containing the rare-earth-iron alloy $Tb_{1-x}Dy_xFe_2$ (Terfenol-D) with giant magnetostriction [59] or Metglas [60] with very high magnetoelectric coupling coefficients (Fig. 14). However, besides the alloy-based composites, particularly attractive, from a fabrication point of view and for potential technological applications, are ceramic based composites.

Magnetoelectric multiferroic bulk ceramic composites are usually prepared by sintering of corresponding oxide powders at high temperatures. This fabrication technique has the advantage of being relatively simple and cheap, and the properties of the obtained composite can be designed by selecting the constituent phases, their mass ratio, grain sizes and grain arrangement. However, there are a lot of other variables involved in the process, such as quality of the starting powders, homogenizing and shaping technique, sintering temperature and time, subsequent annealing treatments, oxygen pressure, etc. All of them can strongly affect the composite structure i.e. influence residual porosity, defects in the crystalline structure of each phase (including vacancies and dislocations), interdiffusion and/or chemical reactions between the two phases, appearance of undesirable secondary phases, variations in grain sizes and shapes, thermal expansion mismatch, etc. [44, 61, 62]. Thus, it is not surprising to find a wide array of properties of the

same multiferroics prepared by different researchers [40]. However, it should also be underlined that magnetoelectric coupling of bulk composites are lower than theoretically predicted, mainly due to the mentioned inherent fabrication problems [19, 52].

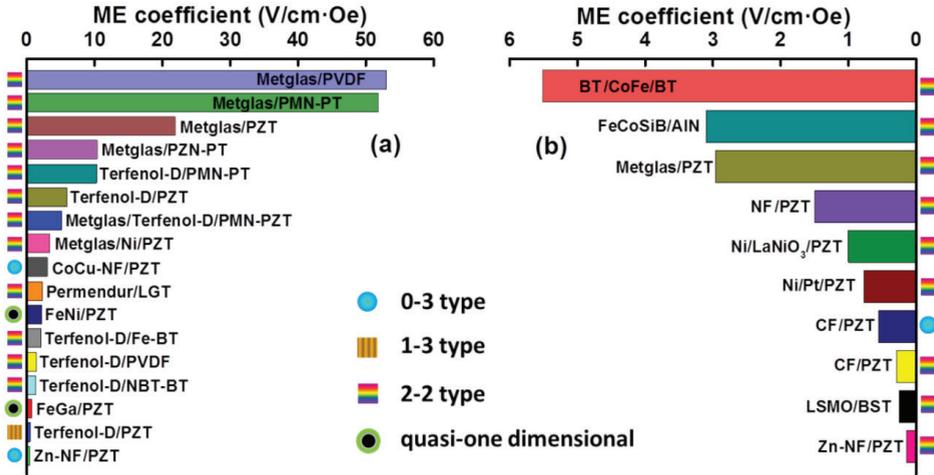


Figure 14. Reported values of off-resonance ME voltage coefficients for various material systems: (a) bulk and (b) film-based ME composites (adopted from [19])

BaTiO₃-NiFe₂O₄ composites

Multiferroic magnetoelectric bulk ceramic composites are usually fabricated by combining magnetic spinel ferrites and ferroelectric perovskites. Ferrites have large resistances (relative to other magnetic materials), but small magnetostriction and, as previously mentioned, the Ni, Mn and Co ferrites have been mostly studied, usually with Cu, Zn and Cr substitutions that aim to increase electrical resistivity [40]. Among ferrites, nickel ferrite is mostly used since it has the largest magnetostriction of any ferrite, good mechanical properties and it can be easily densified. For the ferroelectric phase, perovskite titanates are the most often employed, including BaTiO₃, PbTiO₃, Pb(Zr,Ti)O₃, Ba(Zr,Ti)O₃, Pb(Mg_{1/3}Nb_{2/3})TiO₃-PbTiO₃, and corresponding solid solutions obtained by doping with various cations [40]. BaTiO₃ has a transverse piezoelectric constant of $d_{31} = -90$ pC/N and an electromechanical coupling coefficient of $k_{33} = 0.63$. Both are lower than the corresponding values for Pb(Zr,Ti)O₃ ($d_{31} = -175$ pC/N, $k_{33} = 0.72$) and Pb(Mn_{1/3}Nb_{2/3})O₃-PbTiO₃ ($d_{33} \sim 2000$ pC/N and $k_{33} = 0.94$) [63], but BaTiO₃ has higher Curie temperatures and better mechanical properties [64].

The first results in this field appeared in 1970s when Van Run *et al.* [65] confirmed a magnetoelectric effect due to the mechanical coupling of the magnetic spinel CoFe₂O₄ and the piezoelectric BaTiO₃ perovskite phases. Moving

on from there, Boomgaard and Born [66] fabricated $\text{BaTiO}_3\text{-Ni}(\text{Co},\text{Mn})\text{Fe}_2\text{O}_4$ composites by sintering a mixture of piezoelectric and magnetic phases and investigated the influence of the cooling rate after sintering, the mole ratio of both phases and grain size on composite properties. After these pioneer works, it was recognized that designing new combinations of dissimilar oxides in order to obtain nanostructured multiferroics, *in situ* innovative synthesis of nanopowders and fabrication of anisotropic multiferroic composites with various interconnectivities are definitely big challenges in the field of nanostructured multiferroic materials. It was obvious that more integrated and synergetic multidisciplinary approaches, common to different disciplines but often addressed in divergent ways, are required. Thus, various approaches were used to tailor desired $\text{BaTiO}_3\text{-NiFe}_2\text{O}_4$ (BT–NF) composite structure and solve fabrication problems such as: i) application of novel synthesis techniques, ii) improvement of structure homogeneity, iii) control of annealing and sintering processes, iv) optimization of perovskite–ferrite phase ration, etc.

A p p l i c a t i o n o f n o v e l s y n t h e s i s t e c h n i q u e s . – Synthesis methods of BT and NF powders are being developed from conventional solid state through chemical synthesis, such as sol-gel method, co-precipitation, auto-combustion, polymeric precursor method, hydrothermal method, etc. [67-70]. The solid state method requires barium titanate and nickel ferrite powders with similar particle sizes and morphology in order to enable the proper packing of the phases in multiferroic composite ceramics. It is a very convenient method due to its simplicity and low cost, but it has disadvantages such as the introduction of mechanical defects in the structure and low percolation threshold in the randomly mixed ferrite grains [71]. An additional problem is high sintering temperatures, necessary for required density of the composite ceramics. On the other hand, chemical methods have been proven to give much smaller particle sizes, uniform morphology and a more homogeneous microstructure of the ceramics, which is a very important factor in the synthesis-structure-properties relations triad.

Modifications of powder synthesis methods have been focused on employment of novel techniques and structures. Thus, core/shell composite powders have been synthesized in order to obtain better phase distribution and avoid connectivity of the conductive ferrite particles (Fig. 15). Only a few studies on processing and characterization of multiferroic composite ceramics from core/shell powders [71-75] have been reported in literature. It was shown that both, the preparation of the powder and its subsequent densification have a big impact on magnetic, ferroelectric and magnetoelectric properties of prepared ceramics. In general, preservation of core/shell structures in fabricated ceramics is often the issue and perfect core/shell structure does not necessarily lead to desirable ceramic composite structure, due to agglomeration, lattice mismatch, difference in sinterability, interfacial diffusion or phase reaction [76]. In other words, many factors, beside the morphology of the powder, determine whether the desired characteristics of the final product will be achieved.

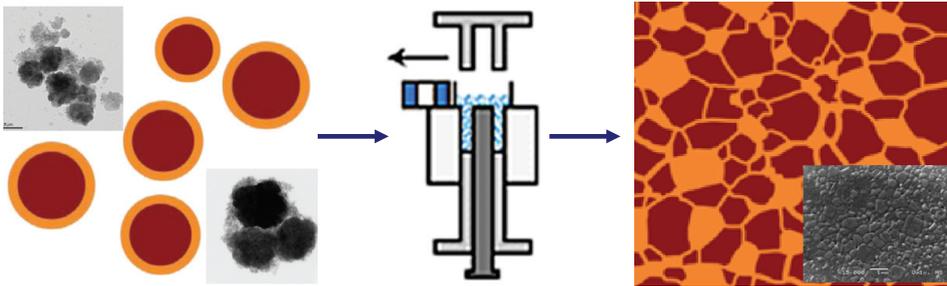


Figure 15. Fabrication steps in preparation of multiferroic bulk composites from core/shell powders [76]

Improvement of structure homogeneity. – A lot of effort has been made in obtaining homogeneous dispersion of the magnetostrictive phase into a piezoelectric matrix. Ortega *et al.* [52] prepared a series of BT–NF ceramics with various contents of ferrite phase by solid-state reaction, mechanical dry mixing and conventional sintering. The formed microstructure was quite inhomogeneous, with an extreme difference in size between the small barium titanate grains and large grains of the nickel ferrite, surrounded by BT phase. Due to conductive nickel ferrite phase, dielectric properties of the barium titanate in the composite were being diluted and dependent on the concentration of NF phase. Grigalaitis *et al.* [77] prepared barium titanate and nickel ferrite particles by chemical methods and used dry mixing method for homogenization. After sintering, very uniform and homogeneous microstructures were obtained. Dielectric permittivity vs. temperature dependence has shown similar values of dielectric permittivity, but lower losses compare to previously published data [52]. Although the dry mixing method can improve homogeneity, introduction of mechanical defects into the structure by dry mixing might present a problem [71]. Thus, other solutions were explored, such as dispersing of previously synthesized BT particles into a solution containing nickel nitrate, iron nitrate and citric acid using a so called “wet mixing route” [78, 79].

Control of annealing and sintering processes. – Sintering temperatures usually used for the preparation of BaTiO₃-NiFe₂O₄ ceramics range from 1050 to 1200 °C, depending on the mass ratio between the phases, quality of the starting powders, green density of the compacts, etc. The formation of microstructure with low density and poor contacts between the ferroelectric and ferromagnetic phases results in a low magnetoelectric effect. Thus, high sintering temperature is required (Fig. 16), although it can usually lead to the formation of secondary phases (such as BaFe₁₂O₁₉), which can collect space charges at the grain boundaries thereby increasing the dielectric permittivity, but also the dielectric losses [37]. Various heat treatment strategies have been used to improve the composite structure. Therefore, the introduction of multiple step sintering, hot pressing or spark plasma sintering can enable high density of the

ceramics and produce much better magnetoelectric properties of the composites. PZT–Ni_{1-x}Zn_{0.2}Fe_xO₄ ceramics, with various phase ratios, were processed by hot pressing in order to achieve high density while avoiding possible reactions between the constituent phases [61]. Jiang *et al.* [80] fabricated dense composites consisting of magnetic (nickel ferrite) and ferroelectric (PZT–Pb(Zr_xTi_{1-x}))O₃ with $0 \leq x \leq 1$) phases by spark plasma sintering of mechanically mixed precursor powders. They confirmed that the feasibility of retarding possible reactions occurring between the ferrite and PZT was approved by applying such a dynamic spark plasma sintering process. On the other hand, fast densification without interfacial interactions at low temperatures was obtained by combination of spark plasma and conventional sintering of SrTiO₃–NiFe₂O₄ composites [75].

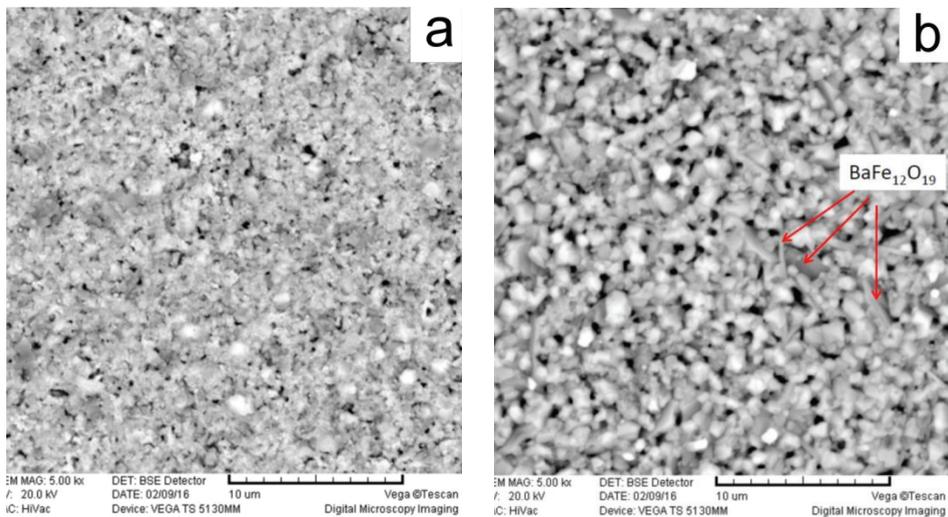


Figure 16. SEM images of BT–NF composites sintered at 1170 °C/4h where BT is doped with: a) 0.3 and b) 0.5 mol% Sb [81]

Optimization of perovskite – ferrite phase ratios. – Ratio between the perovskite and ferrite phase within the multiferroic is very important. It was shown that the ME effect can disappear when the content of the magnetic phase is below 20–30 wt.% [40]. Thus, Zhou *et al.* [71] prepared BT–NF composites from the shell particles (200–300 nm) obtained by the hydrothermal method. In ceramics with a lower concentration of NF phase (sintered at 1100 °C) mostly uniform and homogeneous microstructure was obtained. However, in the ceramics with a higher concentration of NF phase, exaggerated grain growth of nickel ferrite phase was detected causing degradation of ferroelectric and magnetic properties. Experimental studies of several ferrite–BaTiO₃ composites [82–85] also confirmed that the maximum magnetoelectric coupling coefficient is found for the content of perovskite phase in the range between 70–85 wt.%. In addition,

Srinivasan *et al.* [61] showed that in PZT-Ni_{1-xZn0.2}Fe_{xO4} ceramic system, the sample with ~40 vol.% PZT has maximal magnetoelectric coefficient (Fig. 17), but also that magnetoelectric coupling is sensitive to the composition of ferrite phase.

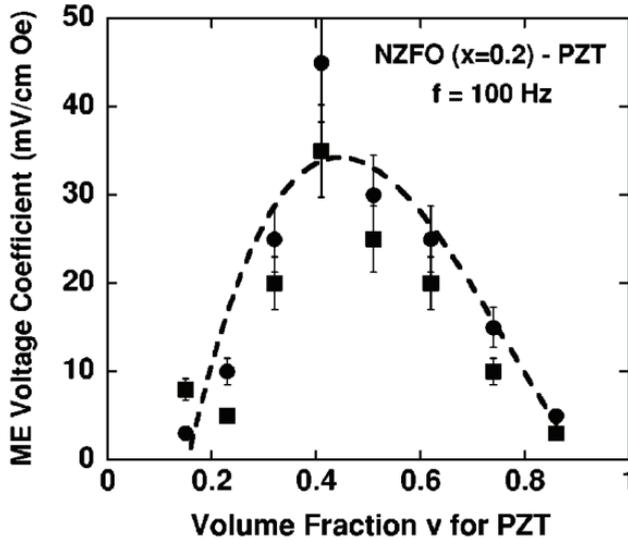


Figure 17. Magnetoelectric coefficient versus amount of PZT phase in PZT-ferrite composite [61].

Mojic *et al.* [75] confirmed that, with the increase of NiFe₂O₄ content in BT-NF composites, there is a decrease of dielectric constant and increase of dielectric loss (Fig. 18). The reasons are much lower dielectric constant and higher conductivity of NiFe₂O₄ in comparison with BaTiO₃. The sharp dielectric peak at the Curie temperature (~125 °C) for the pure BaTiO₃ becomes broader in the composite ceramics and slowly disappears with the increase of NiFe₂O₄ content (Fig. 18). This kind of temperature dependence of dielectric properties was also found in composites obtained by dry mixing method [77]. Similar behavior was observed from ferroelectric measurements and characteristic ferroelectric hysteresis curve was observed only for pure BaTiO₃ and composite with the lowest amount of ferrite phase (Fig. 18d). However, the so-called “banana” shape of hysteresis curve is clear for the composites with higher amounts of ferrite phase (Fig. 18d), due to higher conductivity of NiFe₂O₄ phase.

Magnetic behavior of composites fabricated from core/shell powders [75] and by dry mixing method [77] was also analyzed. The symmetric ferromagnetic hysteresis loops (Fig. 19) with narrow coercive field (insets in Fig. 19) show the presence of ordered magnetic structures, originating from uncompensated antiparallel oriented spins of Fe³⁺ ions at tetrahedral and octahedral sites, and Ni²⁺ ions at octahedral sites of NiFe₂O₄.

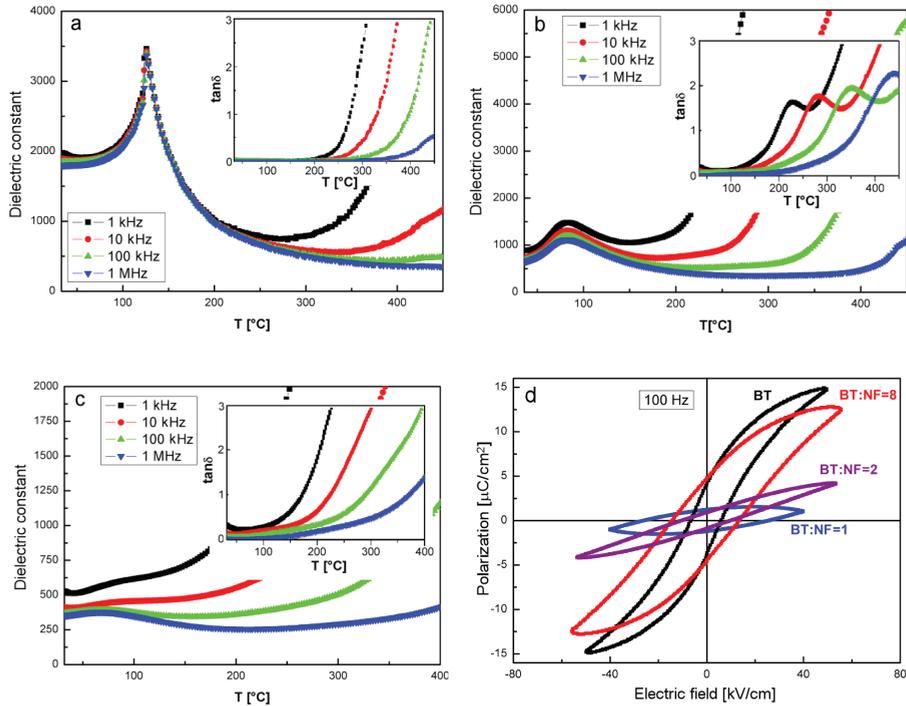


Figure 18. Temperature dependence of dielectric constant and dielectric loss of composite $\text{BaTiO}_3\text{-NiFe}_2\text{O}_4$ ceramics prepared from core/shell powders [75] with various BT/NF mass ratios: a) pure BaTiO_3 , b) BT:NF = 8:1 and c) BT:NF = 2:1.

Room temperature hysteresis P - E loops of pure BaTiO_3 and composite $\text{BaTiO}_3\text{-NiFe}_2\text{O}_4$ ceramics with 3 different BT/NF mass ratios (d).

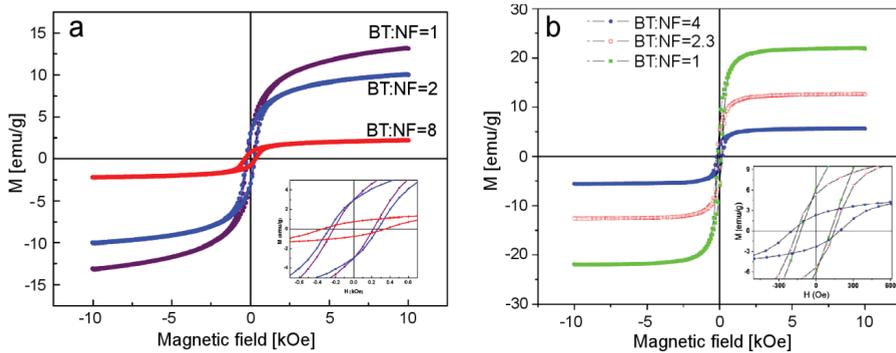


Figure 19. Room temperature hysteresis M - H loops of $\text{BaTiO}_3\text{-NiFe}_2\text{O}_4$ composite ceramics with various BT-NF mass ratios, prepared: a) from core/shell powders [75] and b) by dry mixing method [77].

It is obvious from Fig. 19 that all magnetic parameters decrease with increase of amount of BaTiO₃ content since the non-magnetic phase in the composite can act as pores and break the magnetic circuit when a magnetic field is applied [81].

MULTIFERRIOC THIN FILMS

Recent developments in nanoelectronics have been mostly based on nanostructuring and application of high quality thin films. In the 1990s theoretical calculations showed possible strong magnetoelectric coupling in a multilayer (2-2) configuration [86] after which this field continued to develop rapidly. Thus, advanced growth techniques made it possible to fabricate ultra-thin films, either single-phase multiferroic or with various FE and FM phases and design novel devices based on magnetoelectric coupling. However, retaining their multiferroic properties is very challenging. Compared with bulk ME composites, multiferroic composite thin films have unique advantages. Various phases could be combined at atomic-level, and by precise control of the lattice matching, epitaxial or superlattice composite films can be designed, facilitating the understanding of ME coupling at atomic scale [44]. It is also important to underline that multiferroic films have much higher magnetoelectric coefficients and much larger anisotropy than typical bulk composite multiferroics [52].

From the fabrication point of view, the easiest way is to prepare single-phase multiferroic films. Research interest in magnetoelectric multiferroic films has been focused on hexagonal manganites such as YMnO₃, bismuth-based perovskites (mostly pure or doped BiFeO₃) and lead-based solid solution perovskites [52, 87–91]. These single-phase films were deposited by various techniques, such as pulsed laser deposition (PLD), metal-organic chemical vapor deposition (MOCVD), sputtering, spin coating, spin-spray techniques, molecular beam epitaxy (MBE), etc. [19, 44]. General problem with single-phase multiferroic films is low magnetoelectric coupling (similar to single-phase bulk materials).

Structure and fabrication of multiferroic films

With regards to thin film geometry, there are three common configurations (Fig. 20) similar to bulk multiferroic composites: 0-3, 2-2 and 1-3 type of connectivity. The most commonly studied multiferroic magnetoelectric 2D structures are bilayer and multilayer films of the 2-2 type, and only a few publications can be found for the structures with 0-3 type of connectivity. The popularity of the 2-2 configuration is due to their ease of synthesis along with a reduced leakage problem due to the blocking of the current flow by resistive ferroelectric layers [52]. Despite the nature of multiferroics, indirect ME coupling has been observed in various ways in the 2-2 structures, while evidence of direct coupling ME has been absent in most of them.

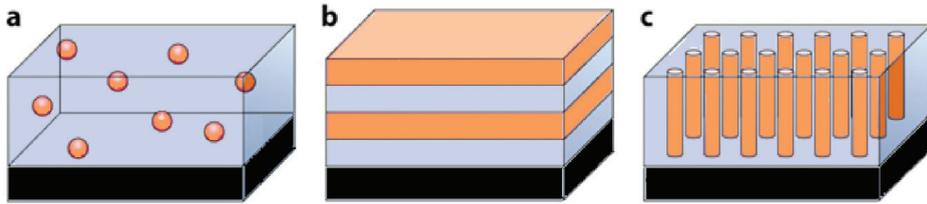


Figure 20. Different types of connectivity: a) 0-3, b) 2-2 and c) 1-3 between constituent phases in magnetoelectric multiferroic films [44]

There are various factors that affect the magnetoelectric coupling in thin film heterostructures, such as: i) types of FE and FM phases, ii) heterostructure configuration (i.e. geometry), iii) constrain from the substrate, iv) microstructural features, etc. Thus, researchers are still trying to understand the main reasons for the differences in the magnitude of ME coupling coefficients reported in literature [52].

Influence of substrate on magnetoelectric coupling of multiferroic thin films seems extremely important. It has been shown that most ME composite films reported in the literature exhibit very weak ME properties due to reduced electromechanical parameters as a consequence of substrate clamping [19]. In the 2-2 configuration, consisting of alternating layers of ferroelectric perovskites and magnetic spinels, usually only weak ME effects are present due to large in-plane constraint from the substrate (i.e. the strain generated in the magnetostrictive phase cannot be effectively transmitted to the piezoelectric phase) [52]. There are a few results which directly confirm this effect. Thus, Li *et al* [92] studied the effect of substrates on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ -BT bilayers and found a higher magnetoelectric coefficient ($263 \text{ mV cm}^{-1}\text{Oe}^{-1}$) at 1 kHz on SrTiO_3 substrate compared with $(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$ and LaAlO_3 ($169 \text{ mV cm}^{-1}\text{Oe}^{-1}$). This result is due to the strain induced by the lattice mismatch between BT and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films and larger interface coupling in the bilayer films deposited on the SrTiO_3 . In addition, Wang *et al.* [93] investigated the effect of geometry (0-3 and 2-2 type) on the magnetic properties of CoFe_2O_4 - PbTiO_3 heterostructures. They observed a reduction in magnetic moments of the 2-2 type compared to the 0-3 type and attributed this result to the formation of anti-phase boundaries due to compressive strain in CoFe_2O_4 , which was larger in the 2-2 structure. Another confirmation was reported by Lorenz *et al.* [94] who showed that the substrate clamping is smaller in vertical 1-3 configurations than in 2-2 structures. Thus, a maximum value of magnetoelectric coefficient, obtained for the 1-3 structures of BT- CoFe_2O_4 fabricated using pulsed laser deposition, was three times higher than in the case of the multilayer 2-2 film.

Various multiferroic magnetoelectric composite films were fabricated in recent investigations and the main goal was selecting compositions with phases that spontaneously separate due to their immiscibility. Thus, considerable attention was given to quasi-2-2 structures such as terfenol-D-polymer (PVDF) and PZT-polymer (PVDF) due to extremely high magnetoelectric coupling [59]. These

“soft” composites with relatively thick layers were fabricated using a hot molding press. Bilayer and multilayer thick films prepared by tape casting (for example NF-PZT [95]) and electrophoretic deposition (for example BT-CoFe₂O₄ bilayer films on Al₂O₃/Pt substrate [96]) were also investigated. However, the focus of this paper will be towards more attractive composite thin films composed of perovskite (BaTiO₃) ferroelectric and (NiFe₂O₄) magnetic phases.

Multilayer BaTiO₃-NiFe₂O₄ films

In order to achieve their full potential, preparation of ME composite thin films with high quality is desired. This has been done with a wide variety of deposition techniques, such as PLD, MBE, sputtering, spin coating, MOCVD, etc. Among them, spin coating (solution deposition by spin coating) is a convenient and inexpensive chemical method for fabricating polycrystalline films or textured films with preferential orientation, and provide flexibility in obtaining large area thick films [44].

S p i n c o a t i n g t e c h n i q u e. – This technique consists of four steps: i) synthesis of the precursor solution, ii) deposition of solution on substrate, iii) low-temperature heat treatment for drying and/or pyrolysis of organics and iv) densification by sintering. Bajac *et al.* [97, 98] used the spin coating technique for fabrication of multilayer thin films by alternate deposition of BaTiO₃ and NiFe₂O₄ layers. Up to twelve layers were deposited on ultrasonically cleaned commercially available Pt/TiO₂/SiO₂/Si substrate starting with the BaTiO₃ layer. Immediately after every deposited layer, the system was calcined at 500 °C in order to completely evaporate traces of residual solvents, which can cause surface defects in the prepared films [97]. The obtained films had a well-defined layered structure with an overall thickness of around 500 nm, and individual thicknesses of around 60 nm and 40 nm for BaTiO₃ and NiFe₂O₄ layers, respectively (Fig. 21) [99]. The films exhibited ferroelectric and ferromagnetic behavior and coupling between the ferrite and titanate phases and the influence of layer geometry on the mentioned behavior and coupling.

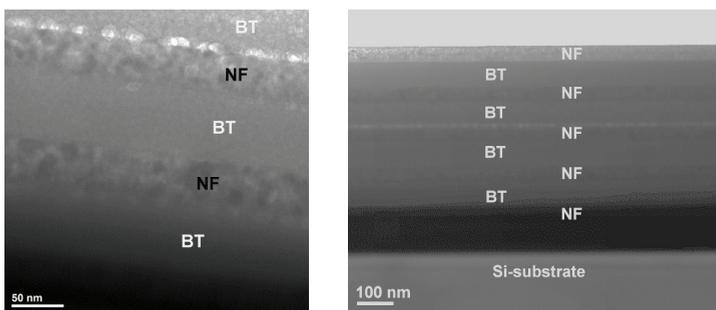


Figure 21. TEM images of multilayer BT-NF films prepared by solution deposition technique [99]

Dai *et al.* [100] also used chemical solution deposition for preparation of $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ multilayer thin films on the Pt/Ti/SiO₂/Si (100) substrate (Fig. 22) with various thicknesses (obtained using precursor solutions with various concentrations). The thickness effect on film microstructure as well as ferroelectric, leakage, dielectric, magnetic and magnetoelectric properties was investigated. The results show that the grain size, ferroelectric and dielectric response were increased with the increasing thickness. A decrease in saturation magnetization of the thickest film was also observed and attributed to the pinning effect of the microcracks to the domain wall movement.

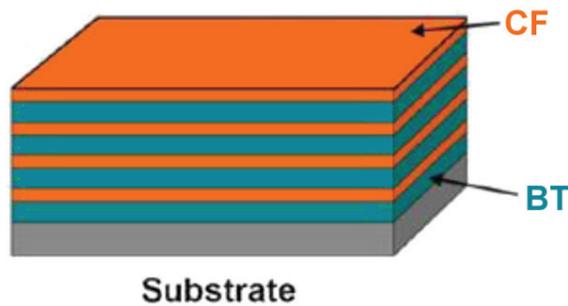


Figure 22. Schematic presentation of multilayer $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ films prepared by solution deposition technique [100]

Vapor deposition techniques. – When the growth of oxide thin films with high structural perfection and the ability of customizing oxide layering down to the atomic layer level are demanded, traditional chemical deposition methods are not applicable. Alternatively, vapor deposition techniques (e.g. PLD, MBE, and sputtering) have the ability of yielding excellent epitaxial growth of thin films with atomic scale thickness control and coherent interfaces [44].

In physical vapor deposition techniques, numerous factors need to be carefully controlled. First of all, the choice of substrate plays the most important role in controlling the orientation and strain state of the epitaxial films. Orientation control is vital for the preparation of films suitable for establishing the intrinsic properties of multiferroic materials, as it influences the crystallization and morphology of a multi-component nanostructure [44]. PLD system consists of a vacuum chamber equipped with pumps, a target holder and rotator, substrate heater, and is typically equipped with various pressure gauges, controllers, and other instruments which control the deposition environment of the system. The deposition is achieved by vaporization of materials by an external energy source and growth can be carried out in reactive environments.

Aguesse *et al.* [101] deposited various multilayer films, consisting of highly magnetostrictive CoFe_2O_4 and piezoelectric BaTiO_3 , by PLD method on a SrRuO_3 buffered SrTiO_3 (001) single crystal substrate, at 700 °C in an oxygen atmosphere.

Dense BaTiO₃ and CoFe₂O₄ targets were struck by a KrF excimer laser. In order to prevent the formation of oxygen vacancies, an annealing step in an oxygen atmosphere was performed. The thickness of each layer was controlled by the number of laser pulses ranging from 6 to 60 nm (Fig. 23). It is important to underline that in the epitaxial CoFe₂O₄-BaTiO₃ multilayer thin films a significant reduction in magnetization of ferrite layers was observed. It was also shown that there is a strong correlation between the number of interfaces and the reduction in magnetization.

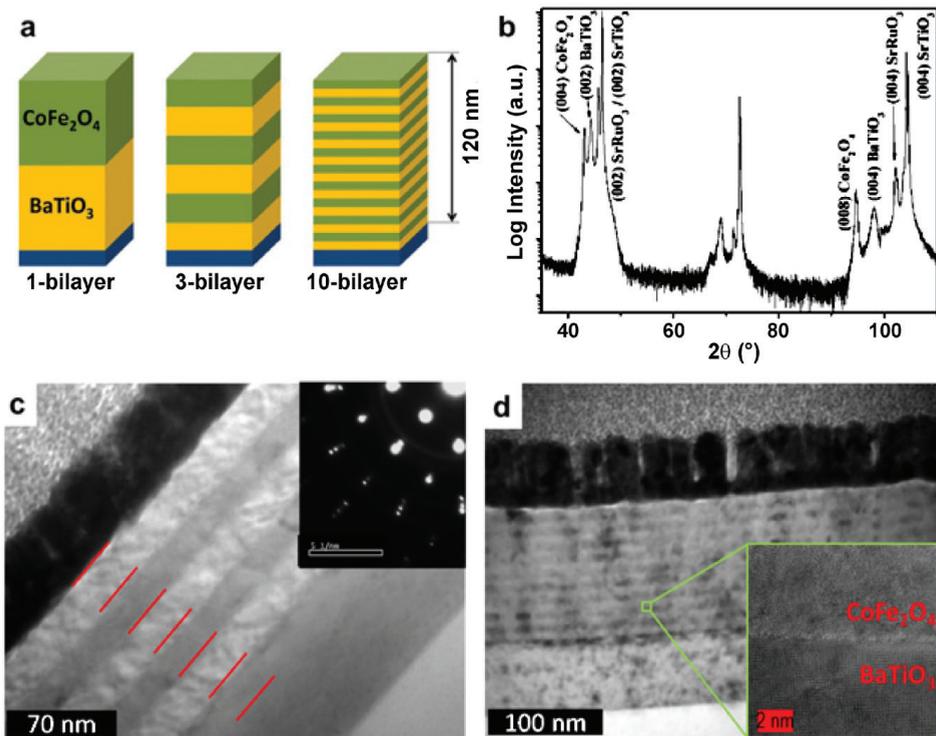


Figure 23. Schematic presentation of CoFe₂O₄ and BaTiO₃ multilayer structures (a), XRD pattern of CoFe₂O₄ and BaTiO₃ multilayer structure (b) and TEM images of multilayer films (c) and (d) (adopted from [101])

Lin *et al.* [102] deposited (001)-oriented PZT/CoFe₂O₄ multilayer thin films on LaNiO₃-coated Si substrate by a dual-cathode RF sputtering method (Fig. 24). The total thickness of PZT and CoFe₂O₄ sublayers were from 80 to 280 nm. The multilayer films showed both FE and FM characteristics. The highly (001)-oriented PZT-CoFe₂O₄ thin films on LaNiO₃ ensured the alignment of electric polarization and magnetic moment. However, the FE and FM properties as well as ME-coupling were reduced with increasing the number of layers suggesting the presence of a passive layer at the PZT-CoFe₂O₄ interface.

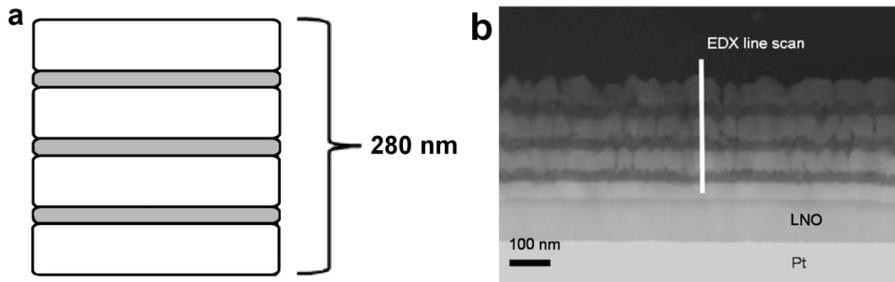


Figure 24. Schematic picture (a) and TEM image (b) of PZT/CoFe₂O₄ multilayer thin film (adopted from [102])

Bilayer multiferroic thin films

Advanced growth techniques make it possible to fabricate ultra-thin films with various FM and FE phases, together with atomic level connections between them. In addition, recent findings have suggested that ferroelectricity persists in ultra-thin films (~ 3 nm) [28, 29], which enables further miniaturization and fabrication of new devices based on ferroelectric materials. One example of this additional multifunctionality was demonstrated in the work of Binek and Doudin [103] on the transport properties of multiferroic heterostructures, where tunnel junction devices employing ME and MF materials as tunnel barriers were designed. Such spintronic devices, having architectures obtained by combining a giant-magnetoresistance or tunnel-magnetoresistance unit with ME/MFs systems, have already found successful application in nanoelectronics. Thus, thin film bilayer heterostructures have opened a new field of research.

Bilayer (or trilayer) heterostructured thin films composed of manganite magnetic (La_{1-x}Sr_xMnO₃ or LSMO) and perovskite (BT, PZT, PMN-PT and PZN-PT) layers have been of special interest and various fabrication approaches have been investigated, the simplest of which is growth of a magnetic thin film on a ferroelectric substrate (Fig. 25) [44]. In such a manner, Wang *et al.* [46] deposited an epitaxial ferroelectric PZT film on LSMO single crystal, and conversely, an epitaxial magnetic LaCa(Sr)MnO₃ (LCMO) film on a ferroelectric single crystal (*e.g.* BT and Pb(Mg,Nb)O₃-PbTiO₃). Magnetoelectric coupling in such multiferroic thin film structure was analyzed and magnetization changes were observed by electric field induced strain of FE phase.

The standard technology in fabrication of bilayer heterostructured thin films utilizes epitaxial growth on a single crystal substrate by pulsed laser deposition, such in the case of La_{0.7}Sr_{0.3}MnO₃/BaTiO₃ bilayer film deposited on (001) oriented SrTiO₃ single-crystal [90], or Pb(Zr_{0.53}Ti_{0.47})O₃ and La_{2/3}Sr_{1/3}MnO₃ bilayer thin films on (100) oriented LaAlO₃ single-crystal [52]. From the application point of view, various approaches have also been explored by introducing a phase transition layer at the interface or by using an electrode material close to the phase

transition boundary. Thus, a greatly enhanced tunneling electroresistance was observed in LSMO/BT/LCMO/LSMO multiferroic tunnel junctions by inserting an ultra-thin La_{0.5}Ca_{0.5}MnO₃ (LCMO) layer between the BaTiO₃ ferroelectric barrier and the La_{0.7}Sr_{0.3}MnO₃ electrode (Fig. 25a) [104]. For the ferroelectric polarization pointing to the La_{0.5}Ca_{0.5}MnO₃ side (Fig. 25b), the screening electron accumulation (hole depletion) will effectively reduce the doping level x of La_{1-x}Ca_xMnO₃ to $x < 0.5$ side, which is in the ferromagnetic metallic phase. On the other hand, for the ferroelectric polarization pointing away from the La_{0.5}Ca_{0.5}MnO₃ layer (Fig. 25c), the electron depletion (hole accumulation) will change the La_{1-x}Ca_xMnO₃ to $x > 0.5$ side, pushing it into the antiferromagnetic insulating phase [105, 106].

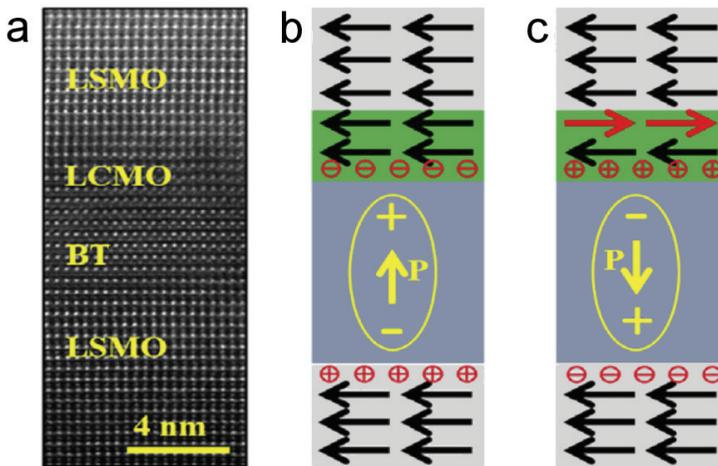


Figure 25. HRSTEM image of LSMO/BT/LCMO/LSMO multilayer structure (a) and schematic demonstration of the screening charge accumulation in the electrodes for the multiferroic tunnel junctions with ferroelectric polarization upwards (b) and downwards (c) [106].

SUMMARY

Labeled by the integration and miniaturization of electronic components, the study of new materials and their functionalities became very widespread, with the main goal being the integration within the current technologies i.e. processing and devices. Due to their unique combination of properties, research has been focused on magnetic and ferroelectric materials, with a special interest dedicated to multiferroics/magnetoelectrics. The multiferroic materials are well known for a very long time, but due to advances in materials fabrication and processing of complex structures with lower dimensionality (such as nanostructured thin films, nanowires, core/shell nanoparticles, etc.) offering some unexpected properties, this field become increasingly important.

Magnetoelectric multiferroic ceramics can be single-phase or composites. The main difference between those two are the combination of two ferroic properties in one material (i.e. single-phase) or joining together two materials of different properties (e.g. ferroelectric and ferromagnetic phase) in composite. Single-phase multiferroics, produced by various methods, exhibit poor properties at room temperature even when prepared at nanoscale dimension. Magnetoelectric coupling is closely related to composite structure rather than single-phase structure, and connectivity between phases and interface bonding play an important role in determining the magnetoelectric behavior. Having this in mind, two distinguished approaches were developed: i) bulk composite multiferroics and ii) multiferroic thin films.

Magnetoelectric multiferroic bulk ceramic composites are usually prepared by sintering process which is relatively simple and cheap technique. There are a lot of parameters involved in the process, such quality of the starting powders, homogenizing and shaping technique, sintering temperature and time, subsequent annealing treatments, oxygen pressure, etc. However, by proper selection of variables influencing in this way the type of the constituent phases, their mass ratio and distribution, grain size and size distribution it is possible to tailor the properties of such materials.

Recently, special attention was given to the preparation of multiferroic thin films. Fabrication methods for preparation of ultra-thin films and design of novel complex nanodevices based on magnetoelectric coupling are developed nowadays. Compared to bulk magnetoelectric composites, multiferroic composite thin films have unique advantages. Different phases could be combined at atomic-level, and by precise control of the lattice matching, epitaxial or superlattice composite films can be designed, facilitating understanding of magnetoelectric coupling at atomic scale. Spin coating is a convenient and inexpensive chemical method for fabrication of polycrystalline films or textured films with preferential orientation. However, when the growth of multiferroic thin films with high structural perfection and the ability to customize oxide layering down to the atomic layer level are demanded, the traditional chemical methods are not applicable. Alternatively, vapor deposition techniques (e.g. PLD, MBE, and sputtering) offer excellent epitaxial growth of thin films with atomic scale thickness control and coherent interfaces.

Multiferroic materials have many interesting properties that can help to achieve the ambitious goals set for nanotechnology in general. Some future applications can greatly benefit the use of these materials, including electrical engineering, medicine, transportation, energy conversion, etc.

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МУЛТИФЕРОИЧНИ BaTaO₃-NaFe₂O₄ КОМПОЗИТИ: ОД КЕРАМИКЕ ДО ВИШЕСЛОЈНИХ ТАНКИХ ФИЛМОВА

Резиме

Током протекле деценије магнетоелектрични мултифероици су били један од приоритетних истраживачких праваца у науци о материјалима, јер представљају нову генерацију мултифункционалних материјала. Мултифероике карактерише истовремено постојање бар два феро-уређења и присуства фероелектрицитета и феромагнетизма, као и снажна интеракција између њих (дефинисана као магнетоелектрични ефекат). Та својства су веома битна за примене у различитим мултифункционалним уређајима. У овом раду дат је преглед различитих техника добијања мултифероичних керамичких композита и танких филмова на бази BaTiO₃-NiFe₂O₄. Главни циљеви су били поређење композитних и танкослојних структура и њихових својстава и стицање бољег разумевања повезаности интеракције између магнетних и фероелектричних уређења, које би засигурно могле бити од велике користи у дизајнирању нових мултиферонских материјала, а тиме и сагледавању њихових нових примена.